# ALTA 1997

# URANIUM ORE TO YELLOWCAKE SEMINAR

## FEBRUARY 20, 1997
## CARLTON CREST HOTEL, MELBOURNE, AUSTRALIA

ALTA Metallurgical Services
Melbourne, Australia
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AIA

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# PROCESS SELECTION, PLANT DESIGN AND EQUIPMENT SELECTION

by
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# 1. HISTORICAL PERSPECTIVE

There have been two intense periods of activity in uranium ore treatment. The first stretched from the late nineteen forties to the early sixties. It was encouraged by the availability of government supply contracts and by government sponsored process development programs in a number of countries. During this period, most of the basic steps in uranium ore treatment were developed and applied in numerous operations. The second era lasted from the mid nineteen seventies to the early eighties. Processing technology was further refined and improved equipment designs were introduced such as high rate thickeners and belt filters. Since then, activity has slowed considerably due to the stagnant uranium market. The bullish current forecast will undoubtedly spawn another round of technical developments, which are already emerging.

## 2. MINERALOLGY AND TREATMENT IMPLICATIONS

A list of common uranium minerals is given in Table 1. The key point to note is variety, and this is reflected in the diversity of process flowsheets adopted by the industry. The situation is further complicated by the fact that some operations have been designed as toll facilities, treating ores from a number of different deposits in the surrounding region.

The presence of other elements has some profound effects on ore treatment. Adverse effects include rendering the minerals more refractory, hindering solid-liquid separation, complicating recovery from solution and imposing environmental challenges. On the positive side there may be a by-product opportunity, such as vanadium.

The generally oxidised nature of uranium minerals has led to the dominance of hydrometallurgy for uranium extraction, though in some cases a preroasting step is included to improve recovery of uranium or vanadium, or to eliminate troublesome carbonaceous materials. Some uranium deposits, such as those in Wyoming, USA, contain significant amounts of carbonaceous matter which can cause major problems in the operation of leach, CCD and solvent extraction circuits.

The nature of the uranium and associated gangue minerals makes it difficult to apply preconcentration methods which have been successful for other metals. Flotation has found limited application such as for the removal of sulphide minerals ahead of carbonate leaching, and the scavenging of uranium/gold concentrates from pyritic gold plant slimes in South Africa. Gravity treatment has found only occasional use for splitting off a high grade portion of the feed. The most effective upgrading method has been radiometric ore sorting. For example, ore sorting was used at the former Mary Kathleen operation in North Queensland to increase the head grade from 0.17 to 0.24% $U_3O_8$. Currently, it is under consideration for the Kintyre project in Western Australia. It is particularly applicable when the mineralisation is concentrated in veins.

Although uranium minerals themselves are oxidised, they are at times closely associated with sulphide minerals such as pyrite and heavy metal sulphides. In some cases the sulphides and the uranium are closely intertwined rendering uranium extraction more difficult. More aggressive treatment conditions are required which can result in solution purification problems and environmental issues. As mentioned above, flotation is sometimes effective in removing the sulphides, and the resulting concentrate may be treated separately to recover any contained uranium.

Uranium minerals commonly occur with other commercially valuable materials such as gold, copper sulphides and phosphate. Typical examples of co-production include the South Africa gold/uranium deposits, the Olympic Dam copper/uranium deposit in South Australia, and the uranium from phosphoric acid plants operated in Florida some years ago.

**TABLE 1 COMMON URANIUM MINERALS**

| Type | Name | Composition |
|---|---|---|
| Oxides | Uraninite | $(U^{+4}_{1-x}, U_x^{+6})O_{2+x}$ |
| | Pitchblende | Variety of uraninite |
| Hydrated oxides | Becquerelite | $7UO_2.11H_2O$ |
| | Gummite | Alteration product of uraninite |
| Nb-Ta-Ti complex oxides | Brannerite | $(U,Ca,Fe,Th,Y)(Ti,Fe)_2O_6$ |
| | Davidite | Ideally $FeTi_3O_7$ |
| Silicates | Coffinite | $U(SiO_4)_{1-x}(OH)_{4x}$ |
| | Uranophane | $Ca(UO_2)_2(SiO_3)_2(OH)_2.5H_2O$ |
| | Uranothorite | Uranoan variety of thorite, $ThSiO_4$ |
| | Zircon | Uraniferous $ZrSiO_4$ |
| Phosphates | Autunite | $Ca(UO_2)_2(PO_4)_2.10\text{-}12H_2O$ |
| | Torbernite | $Cu(UO_2)_2(PO_4)_2.12HO_2O$ |
| Vanadates | Carnotite | $K_2(UO_2)_2(VO_4)_2.1\text{-}3H_2O$ |
| | Tyuyamunite | $Ca(UO_2)_2(VO_4)_2.5\text{-}8H_2O$ |
| Hydrocarbons | Thucholite | Uraninite complex with hydrocarbons |
| | Asphaltite | Many varieties containing U-organic complexes |

(Merritt, 1971)

# 3. KEY PROCESS ISSUES

The key step in the hydrometallurgical treatment of uranium ores is leaching. Without an efficient and economic method of solubilising the uranium, there can be no project. Leaching methods employed commercially include:

- agitated leaching of ground ore with sulphuric acid at atmospheric pressure
- agitated leaching of ground ore with sodium carbonate solution at atmospheric pressure
- pressure oxidation of ground ore in autoclaves
- pressure carbonate leaching of ground ore in autoclaves
- pugging (or curing) of dry ground ore with strong sulphuric acid followed by water leaching
- vat leaching of crushed ore with sulphuric acid at atmospheric pressure
- heap leaching of run-of-mine or crushed ore with dilute sulphuric acid, including the use of bio-leaching conditions
- In-situ leaching with sulphuric acid or alkaline solutions
- bacterial leaching in mined out areas

Roasting processes have been used ahead of leaching using both multihearth and rotary kiln equipment. These include:

- salt roasting with sodium chloride to improve the co-recovery of vanadium from carnotite type ores
- oxidising roast to improve uranium recovery from tetravalent minerals
- roasting of clayey ore to improve solid-liquid separation characteristics after leaching (rarely used now due to availability of effective flocculants)
- roasting to remove troublesome carbonaceous materials

The second key issue is the separation of the pregnant leach solution from the leach residue solids. The most common techniques are counter-current decantation (CCD) using thickeners or multiple stage filtration. In both cases, barren solution and/or water is utilised as a final wash to minimize the loss of soluble uranium. Percolation type process such as vat, heap and in-situ leaching have the major advantage of eliminating the need for solid-liquid, separation, thus saving significant capital and operating costs and avoiding potential operating headaches.

Methods used to extract the uranium from the usually impure and dilute leach solutions include:

- ion exchange using resins
- solvent extraction using liquid organic reagents
- chemical precipitation

The optimum method depends on a number of interrelated factors including leach solution composition, solution strength, solid-liquid separation characteristics and the type of leaching process used. As a general rule, ion exchange has been used for more dilute solutions and is applicable to both acid and alkaline leach solutions. It can also be used in turbid or even fine slurries which can be useful for difficult solid-liquid separation systems. Various types of equipment are available including the forerunner of the CIP tanks now common for gold recovery. Solvent extraction is applicable to acidic solutions and generally requires clarified solutions, though solvent-in-pulp operation has been investigated. A variety of equipment has been utilised, the most common being mixer-settlers. In some cases a combination of ion exchange and solvent extraction (eluex) has been successfully applied to utilise the best features of both techniques. Chemical precipitation has generally been practised in alkaline leach circuits, though precipitation from high strength acid solution with peroxide has been proposed.

The final product recovery step depends on the leach and extraction processes employed, and on whether vanadium is a co-product. Precipitants used include ammonia, caustic soda, magnesia and peroxide. The requirement for a purer product has favoured ammonia, and releaching and ammonia reprecipitation is used for refining precipitates produced by caustic or magnesia. Peroxide has also found increasing favour with environmental advantages over ammonia in some locations.

Most plants include a product drying or calcination step, though in some cases a product slurry has been transported to the refinery or to a central drying facility where a relatively short distance is involved. A variety of equipment has been used including belt and screw type dryers and multi-hearth roasters. The latter is generally favoured for calcining of ammonium diruranate which involves driving off the ammonia.

Handling and packaging of the dried product is the most critical area for operators' safety, and is generally designed for remote operation and restricted personnel access.

# 4. COMMERCIAL PROCESSES

## 4.1 AGITATED SULPHURIC ACID LEACHING

This is undoubtedly the most widely used process with high recoveries possible from a wide range of feedstocks. Operating costs are highly dependent on the acid consumption, and the process becomes uneconomic when the ore contains a significant proportion of acid consuming materials such as limestone, calcite and dolomite. The cut-off point for acid leaching is obviously affected by the cost of sulphuric acid, which may be purchased or produced on site from elemental sulphur or pyrite. A typical flowsheet is shown in Figure 1.

The conditions required for successful acid leaching depend on the uranium minerals, the rock types, and the style of mineralisation. Hexavalent uranium minerals are generally readily soluble in dilute sulphuric acid solutions at low to moderate temperatures. Typical examples include carnotite, uranophane and torbernite. Oxidants are generally only needed to counteract the presence of reductants including iron from the grinding operation. Minerals containing tetravalent uranium such as uraninite, pitch blend and coffinite require the presence of an oxidant such as pyrolusite, sodium chlorate or Caro's acid. The oxidant converts ferrous iron to the ferric form which in turn oxidises the uranium to the acid soluble hexavalent form. Alternatively, the ferric may be generated externally to the leach circuit using bacterial oxidation as in the Bacfox Process in South Africa, or using oxygen as recently proposed by Atomaer in Australia. Iron must obviously be present in solution when treating tetravalent uranium minerals and generally originates from the gangue minerals or the grinding circuit. Complex oxides such as brannerite and davidite are more difficult to leach and require more aggressive leaching conditions with higher temperature (up to 80°C), longer duration, and stronger acid concentration, as well as the use of an oxidant. Finer grinding may also be necessary to achieve high extraction. More aggressive conditions may also be needed to maximise vanadium recovery if present. Leaching is generally carried out in a series of agitated tanks equipped with mechanical or air agitation. The duration can vary from 6-48 hours. Most acid leaching operations incorporate a CCD or filtration step for solid-liquid separation, followed by solvent extraction using a tertiary amine. Mixer-settlers are still the most popular equipment though pulse columns are currently receiving renewed attention. The solvent extraction system frequently includes one or more scrub stages to deal with particular impurities. The ammonium sulphate stripping process has been widely applied, followed by ammonia precipitation and calcining in a multi-hearth furnace. The alternative of strong sulphuric acid stripping and precipitation with peroxide can have process and environmental advantages.

The acid leaching-CCD-solvent extraction route has generally been followed for plants in Australia including the currently operating Ranger and Olympic Dam facilities.

An example of a low grade operation using ion exchange is the Rossing plant in Namibia. Here, coarse material is split off from the leached pulp and washed. The pregnant leach solution containing fines is treated in a multi-stage ion exchange circuit followed by solvent extraction.

## 4.2 AGITATED ALKALINE LEACHING

Although less common than acid leaching, alkaline leaching has been applied at a significant number of operations, particularly in North America. It is generally used for ores containing high acid consuming gangue minerals. The lixiviant is a sodium carbonate-bicarbonate solution, though the equivalent ammonium salts have been tested up to pilot plant stage without showing any additional benefits. A typical flowsheet is presented in Figure 2. Carbonate leaching often requires a finer grind than acid which may be due to the less aggressive nature of the lixiviant, but also can be influenced by the style of mineralisation. Hexavalent uranium minerals react with sodium carbonate and sodium bicarbonate to form uranyl tricarbonate. Without the presence of bicarbonate, a portion of the uranium tends to reprecipitate. Tetravalent uranium minerals are oxidised with air to render than soluble. Occasionally, chemical oxidants have been added to improve leach kinetics. Leach times tend to be long and can be in excess of 48 hours, despite temperatures of 60-80°C. For difficult to leach brannerite at Beaverlodge in Canada, 96 hours were needed at 95°C. Leach times can be shortened by using autoclaves, which will be addressed later. Because of the need for aeration, air agitated pachucas are commonly employed. Depending on the particular flowsheet and water balance, carbonate solution may be recycled to the grinding circuit. A flotation circuit is sometimes included to remove sulphide minerals which can cause excessive reagent consumption. Carbonate leaching has the advantage of being more selective than acid, though some impurities do go into solution.

The leach discharge slurry is cooled in heat exchangers using either leach feed slurry or precipitation feed solution, depending on the temperature profile and overall energy balance. Shell and tube exchangers can be used if the coolant is precipitation feed solution. However, for leach feed slurry, concentric pipe exchanges are more suitable. Solid-liquid separation is generally carried out by filters in order to minimise reagent losses, though a combination of thickeners and filters is sometimes used.

Sodium diuranate is precipitated from the clarified pregnant solution by reacting with excess caustic soda at 60 - 80°C in a series of agitated tanks. The resulting slurry is generally thickened and filtered to recover and recycle the solution. The recycle solution is contacted with carbon dioxide to reform sufficient sodium bicarbonate for leaching. This can be achieved utilising flue gas if available.

The sodium diuranate can be sold as product, but is usually refined to improve purity. This can be achieved by redisolution in sulphuric acid and reprecipitation with ammonia or peroxide, followed by calcination or drying.

For leach pulps with difficult to filter slimes, a sand-slime separation and resin-in-pulp system can be employed instead of caustic precipitation. An example of this was the Atlas Minerals operation in Utah. (In this case pressure alkaline leaching was employed.)

## 4.3 ACID PRESSURE LEACHING

Pressure acid leaching has been commercially applied in South Africa, USA and Canada. By reacting sulphides such as pyrite with oxygen at 130 - 180°C, sulphuric acid and ferric sulphate can be generated, which in turn oxidise and leach the uranium minerals. In some cases, the oxidation of the sulphide may liberate further uranium and other valuable by-products (or co-products) such as gold which otherwise would not be recovered. Potential advantages include faster leach kinetics, higher extraction, lower operating cost, lower impurity levels and better solid-liquid separation characteristics. Liquid oxygen is generally used but compressed air has been employed for lower temperature operation. The process has commonly been carried out in horizontal pressure autoclaves, though a pressurised pipe reactor was utilised at Randfontein in South Africa. At Key Lake in Canada a two-stage leaching arrangement is used with the second stage carried out in pressure autoclaves with oxygen at 60°C. The ore is complex and contains significant nickel-arsenic minerals which make processing difficult. Chemical oxidants such as manganese dioxide and sodium chlorate are unsuitable. The remaining steps in pressure acid leaching circuits are similar to agitated acid leaching. A typical flowsheet is presented in Fig. 3.

## 4.4 ALKALINE PRESSURE LEACHING

In some alkaline leach applications, it is necessary to employ elevated temperatures in the range of 110 - 140°C in order to achieve adequate uranium recovery in a reasonable time. In such cases, leaching is carried out in pressure autoclaves. For some operations, a combination of atmospheric leaching in pachucas and pressure leaching in autoclaves has been included. Both vertical and horizontal autoclaves have been used. Oxidation is generally by compressed air or oxygen. Chemical oxidants have occasionally been added. Because of the higher leach temperature, heat recovery is even more important than for the atmospheric pressure leach, and the leach discharge is passed through heat exchangers. The recovery circuit is similar to the atmospheric process flowsheet. A typical flowsheet is given in Fig 4.

Pressure alkaline leaching circuits have been operated in the USA, Canada and France. It was proposed for WMC's Yeelirrie project in Western Australia for the treatment of carnotite ore, and an integrated pilot plant was run in Kalgoorlie in 1981.

## 4.5 STRONG ACID PUGGING

This process consists of blending (or pugging) coarsely ground dry ore with concentrated sulphuric acid and allowing it to cure. The ore is crushed and dry ground to about 0.8-1.0 mm. Concentrated acid and a small amount of water are added to obtain a moisture content of about 10%. Curing is carried out for several hours at 75-100°C.

Plants have been operated in Niger (Arlit) and the USA. The process can achieve higher uranium recoveries from some refractory ores, and can enhance the recovery of by-products such as vanadium. The UK Atomic Energy Authority did extensive research in the seventies and claimed that reduced capital and operating costs are achievable for some ores. The UKAEA process could be also classified under vat leaching, as some vat leaching operations have utilized strong acid curing. However, alternative washing/leaching techniques were considered, which bring it closer to the Arlit type of operation. Disadvantages of the technology include high maintenance cost and increased acid consumption in some applications.

The circuits applied and proposed have varied considerably. The Arlit plant in Niger includes separate ore heating, curing and water washing steps, all carried out in rotary equipment. The UKAEA system utilized a combined rotary heater/cure step followed by percolation washing/leaching. Product recovery steps are similar to agitated acid leaching circuits. The Arlit flowsheet is illustrated in Fig. 5. Sodium carbonate stripping was used in the solvent extraction circuit and the product was sodium diuranate with a 68-71% uranium content.

## 4.6 VAT LEACHING

Vat leaching has occasionally been applied to ores which exhibit good percolation characteristics. The main attractions are the considerable circuit simplification and cost saving due to the elimination of unit operations such as grinding and thickening. Also, disposal of "dry" coarse tailings can be advantageous. The ore is first crushed to adequately expose the uranium minerals, and is loaded into vats fitted with false bottoms to provide for upward or downward percolation. Loading and unloading can be accomplished by a variety of means including loaders or traveling gantries. Leaching and washing can be done "counter-currently" to maximise the pregnant solution strength. Final recovery can be via ion exchange and/or solvent extraction as for agitated acid leaching plants.

At the Spook operation in Wyoming, the ore was crushed to 85% passing ¼ inch, then agglomerated with concentrated acid to assist percolation. After a curing period of 14 hours, 90% recovery was achieved in 72 hours in a 3m deep bed. Ranchers employed an innovative vat leaching system for tailings at Naturita, New Mexico, in which the tailings were acid cured then loaded into plastic lined earthen vats using a mobile conveying system. The vats were buried after completion. In-ground vat leaching of crushed ore was evaluated for operations such as Key Lake in Canada and Copper Mountain, USA. Vat leaching can also be carried out in covered vessels which is useful in cold climates. Such a system was studied for treating shales at Ranstad, Sweden.

The UKAEA in the nineteen seventies piloted a vat leaching process using hot ferric sulphate solution at 50°C. The ferric content was regenerated in an external bio-oxidation reactor.

A typical vat leach flowsheet is illustrated in Fig. 6.

## 4.7 HEAP LEACHING

Most uranium heap leaching operations have been satellites to conventional agitated acid leaching plants. Typically, solution from the conventional circuit containing some ferric iron is fortified with acid then applied to the heaps. The resulting solution is processed through the main plant. However, stand alone heap leaching has been practised, for example, in Salamanca, Spain. Here the pregnant solution is treated by solvent extraction.

Bacterial heap leaching of pyritic uranium ores was first applied at the Urgeirica plant in Portugal after leaching of the stockpiles by rain water was observed. With this system, acid is generated in the heaps, thus reducing or eliminating acid make-up. Ores may be crushed or run-of-mine. Pad construction, heap building methods and solution management are comparable to other heap leaching applications.

Recovery method depends on solution concentration with solvent extraction being used for higher grade solutions and ion exchange for more dilute. Generally, heap leaching has been limited to low grade ores, below 0.1% $U_3O_8$. Recoveries have been in the 50-80% range. A typical flowsheet is given in Fig. 7.

## 4.8 IN-SITU LEACHING

From the mid nineteen seventies, a significant number of commercial in-situ leaching operations were established in southern Texas and Wyoming. These were applied to sandstone orebodies which were sufficiently permeable to allow passage of the leaching solutions and sufficient contact with the uranium minerals. The deposits were horizontal, underlain by impermeable rock for containment, and located in aquifers below the water table to facilitate flow of the solution.

In a typical installation the leaching solution is introduced via an injection well surrounded by several recovery wells containing submersible pumps. The wells are fitted with plastic casing (PVC or FRP) which is perforated in the ore layer. The system is held in hydraulic balance with a slight inflow of water from the aquifer into the recovery wells to ensure that the leach solutions do not spread.

Both sulphuric acid and alkaline leaching solutions can be used. Alkaline solutions can contain either sodium or ammonium carbonate. Oxidants include sodium chlorate, hydrogen peroxide and liquid oxygen. The choice of lixiviant depends on mineralogy, rock types and trace element issues. Alkaline solution is generally used if significant acid consumers are present, to avoid plugging the system with precipitates.

The pregnant solutions are generally dilute, and ion exchange is commonly used followed by precipitation with ammonia or hydrogen peroxide. Testwork was carried out for the Honeymoon deposit in South Australia using sulphuric acid solution with recovery by solvent extraction.

Decommissioning involves cleaning up the aquifer to its original state. The aquifer must be also monitored during operation.

In-situ leaching is seen to be suitable for small, low grade, deep deposits, or for deposits where conventional mining is environmentally or socially unacceptable. A typical flowsheet is given in Fig. 8.

"Natural" in-situ leaching systems have been established in some mines by ground water draining down into the mining areas. In such cases, ion exchange recovery equipment has been used.

## 4.9 BACTERIAL LEACHING IN MINED OUT AREAS

Mine waters from mined out areas in operations in the Elliot Lake region of Canada contain uranium extracted by bacterially assisted leaching of the residual pyritic ore. This encouraged programs to increase the output by spraying or flooding the mined out areas. Denison Mines went further and blasted residual low grade ore to form in-place leaching areas.

In such cases, in would be normal to recover the uranium in the adjoining main plant. However, after closure, an ion exchange system could be employed. The system is depicted in Fig. 9.

It is conceivable that this technique could be applied to new deposits, as has been considered in the copper industry.

## 4.10 BY-PRODUCT RECOVERY PROCESSES

Two processes have been commercially significant:

- recovery of uranium from phosphoric acid, particularly in Florida. Solvent extraction processes have been developed using special reagents.

- recovery from copper leach solutions containing very low uranium levels. Here, the recovery method is ion exchange or a combination of ion exchange and solvent extraction. Examples were the dump leaching operation at Bingham Canyon, Utah, and the former oxide agitated leaching plant at Twin Buttes, Arizona.

# 5. PROCESS SELECTION AND PROJECT DEVELOPMENT

## 5.1 PROCESS SELECTION

The selection of the optimum process for any particular application will be influenced by many factors. These include:

- size, grade and structure of deposit
- type and style of mineralisation
- mineralogical composition of host rock
- opportunities for upgrading
- behaviour of potential impurities
- site location and characteristics
- environmental and social impact issues
- climatic conditions
- opportunity for by-products or co-products

The above and other issues will normally be evaluated by a series of test programs and related economic and environmental studies. The historically open nature of the industry generally makes it possible to draw on the experience of others in the treatment of similar orebodies.

## 5.2 PROJECT DEVELOPMENT

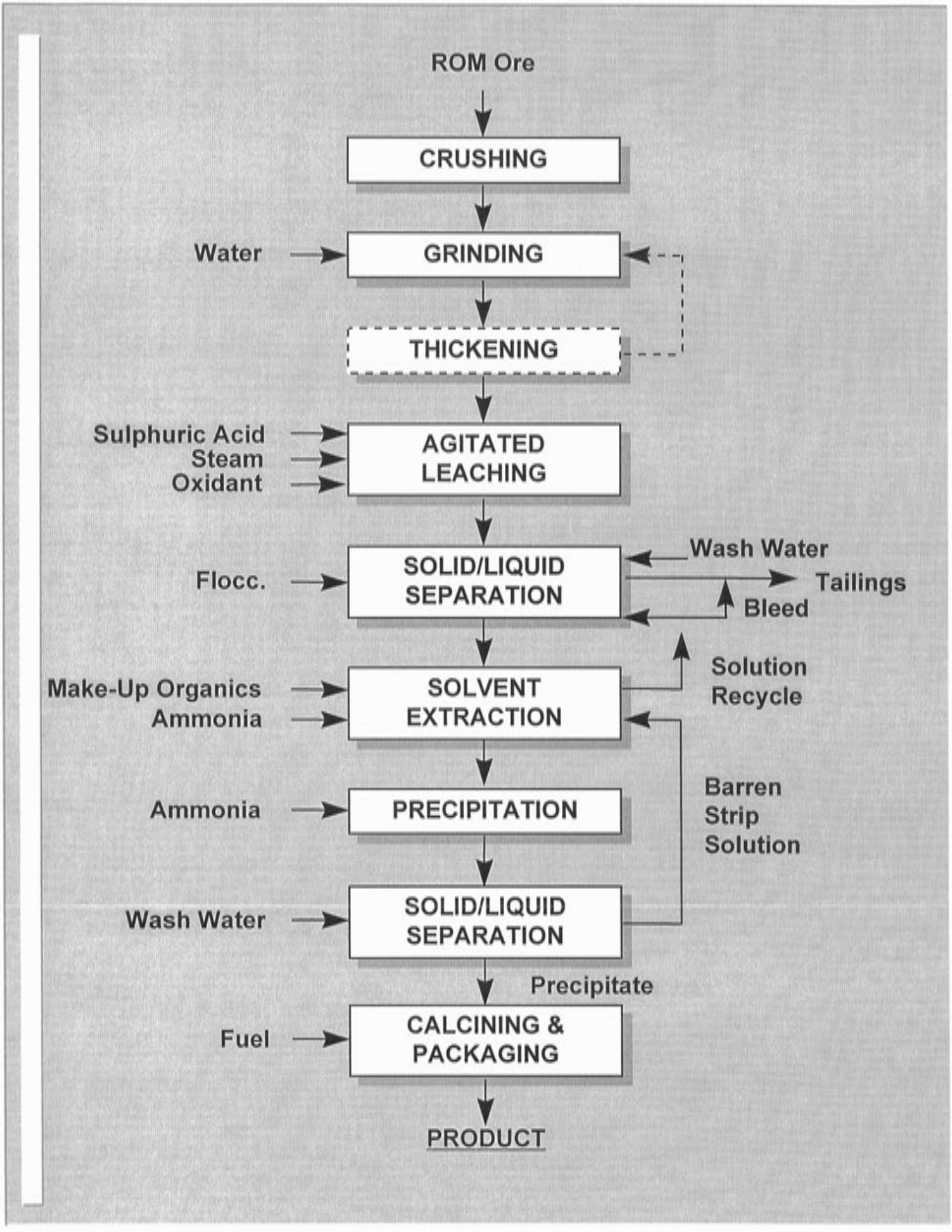
Process selection is, of course, only one element of the overall project development program which will typically include:

- geology studies and reserve estimation
- evaluation of mining methods and cost studies
- assessment of infrastructure requirements
- evaluation of tailings disposal methods

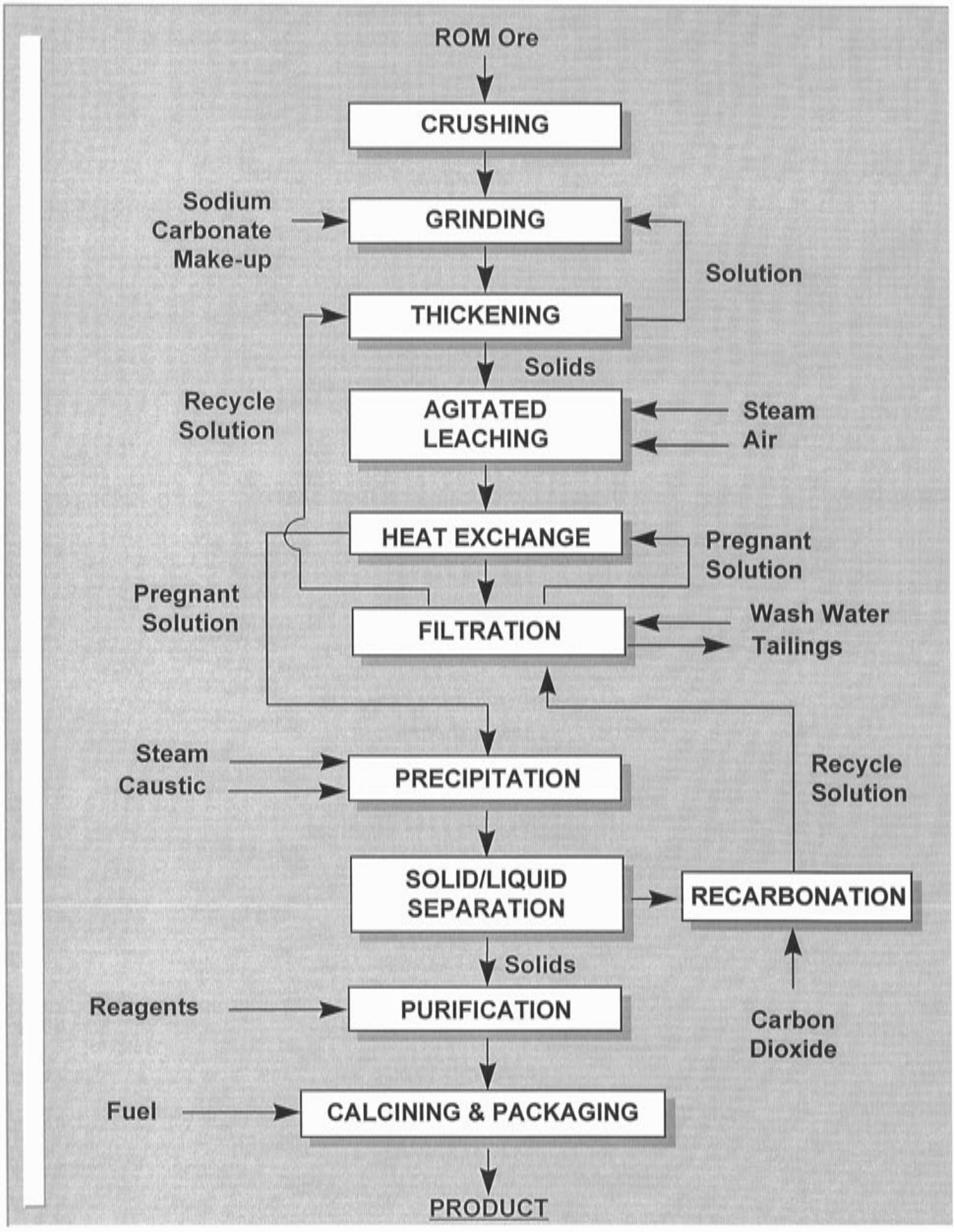
- determination of overall site water management plan
- baseline environmental studies and preparation of environmental impact statement to meet applicable government regulations
- development of personnel safety and health strategy

Many of these items interact with process selection and could have a significant bearing on the final choice.

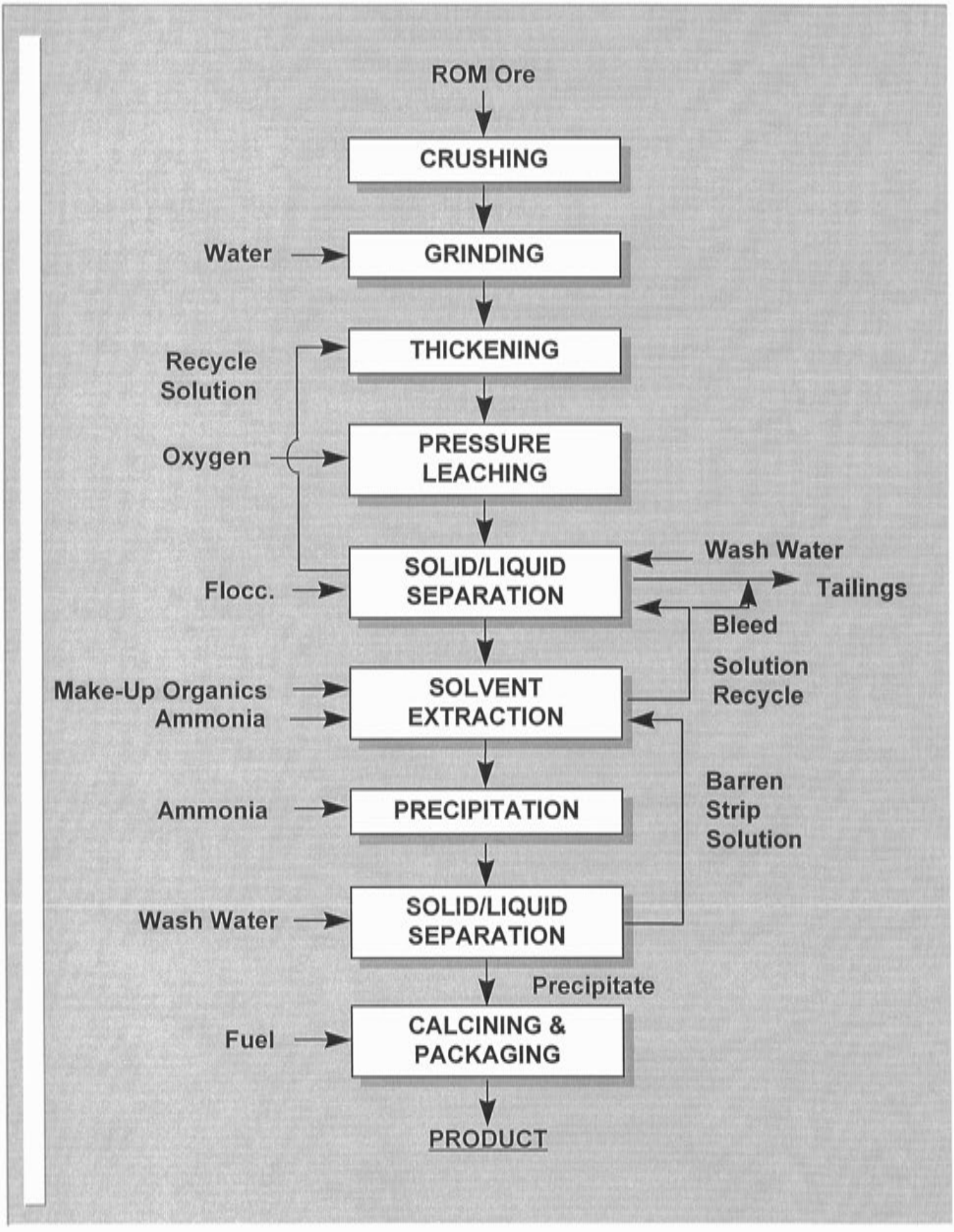
# FIGURE 1
# AGITATED ACID LEACHING FLOWSHEET



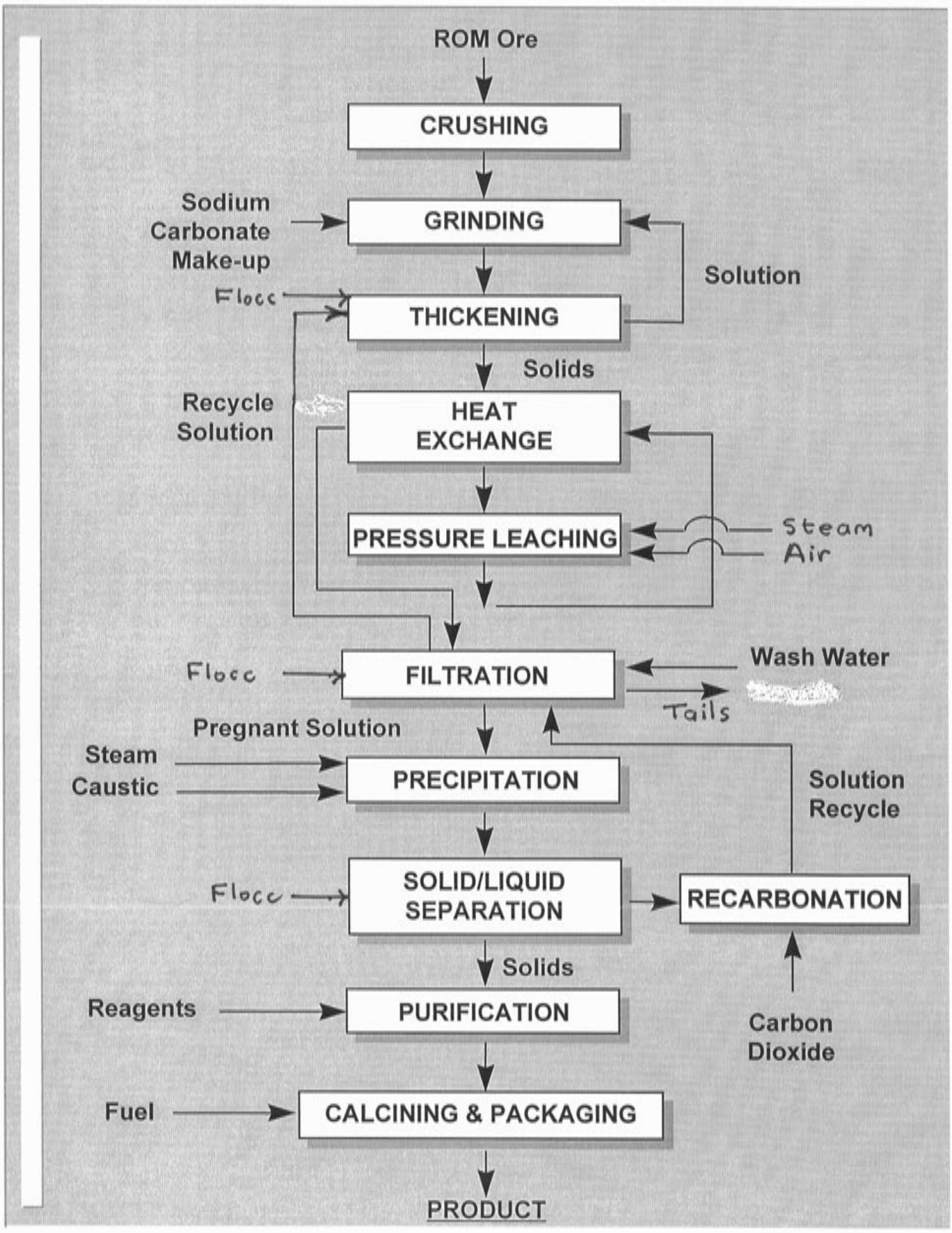
# FIGURE 2
# AGITATED ALKALINE LEACHING FLOWSHEET



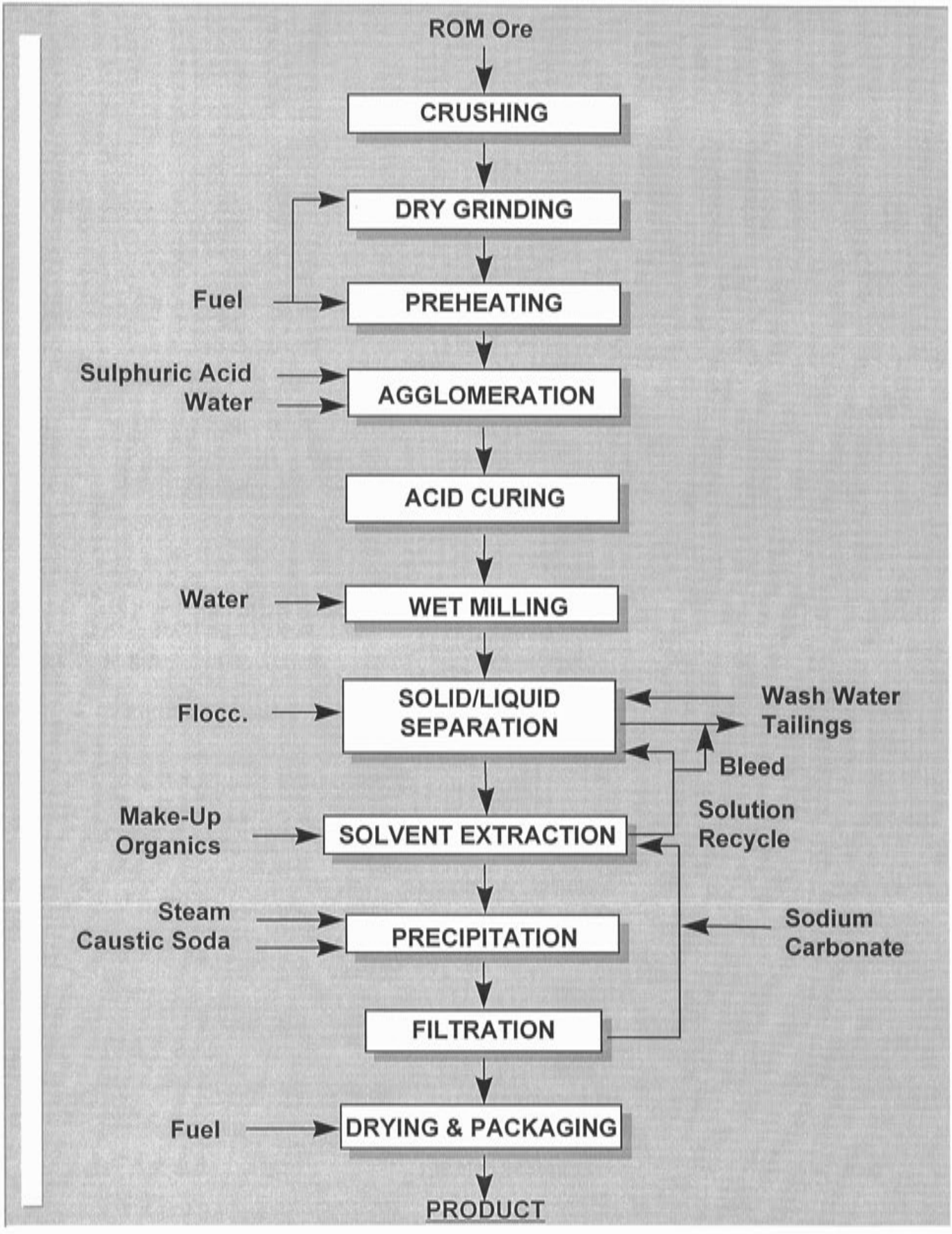
# FIGURE 3
# ACID PRESSURE LEACHING FLOWSHEET



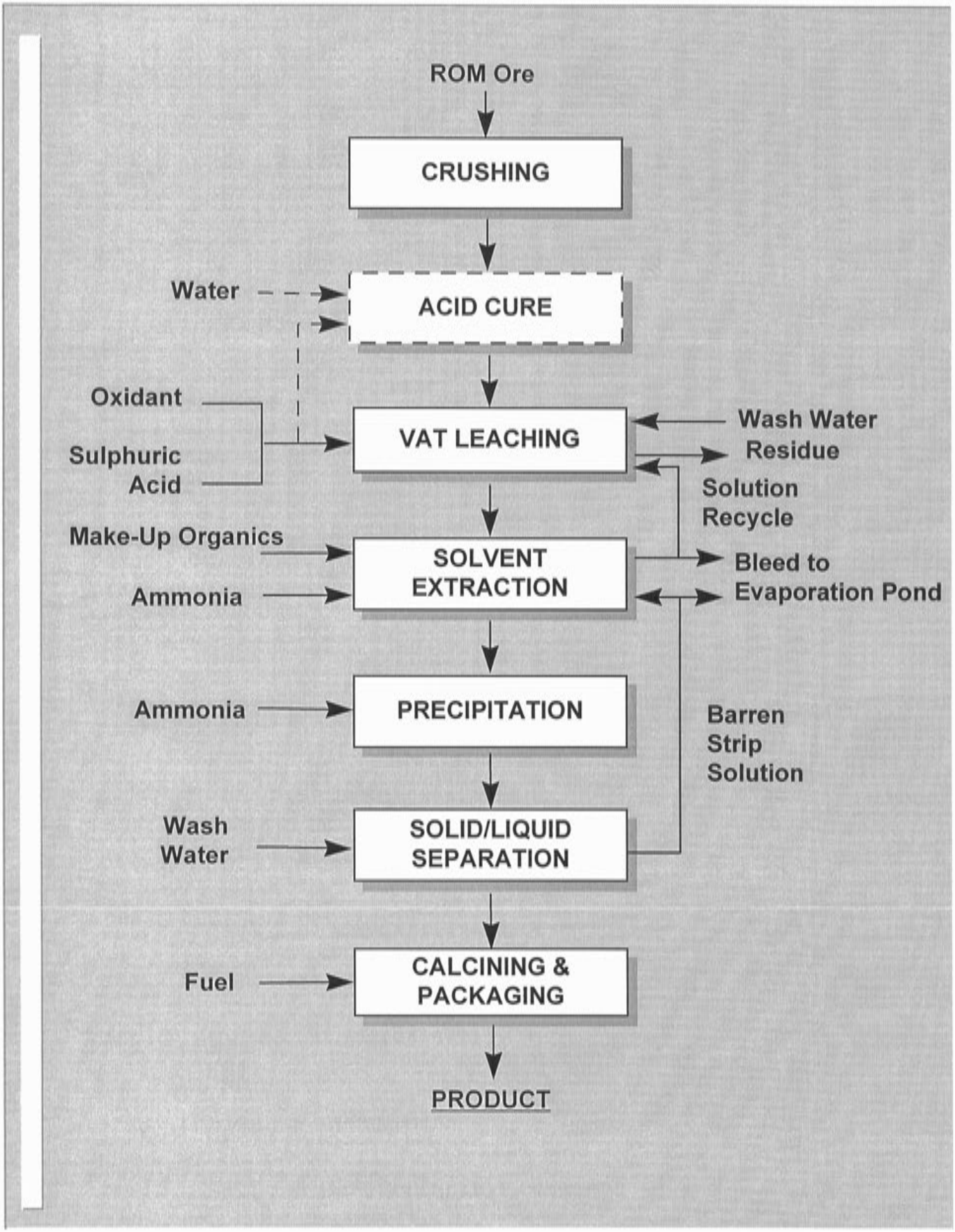
# FIGURE 4
# ALKALINE PRESSURE LEACHING FLOWSHEET



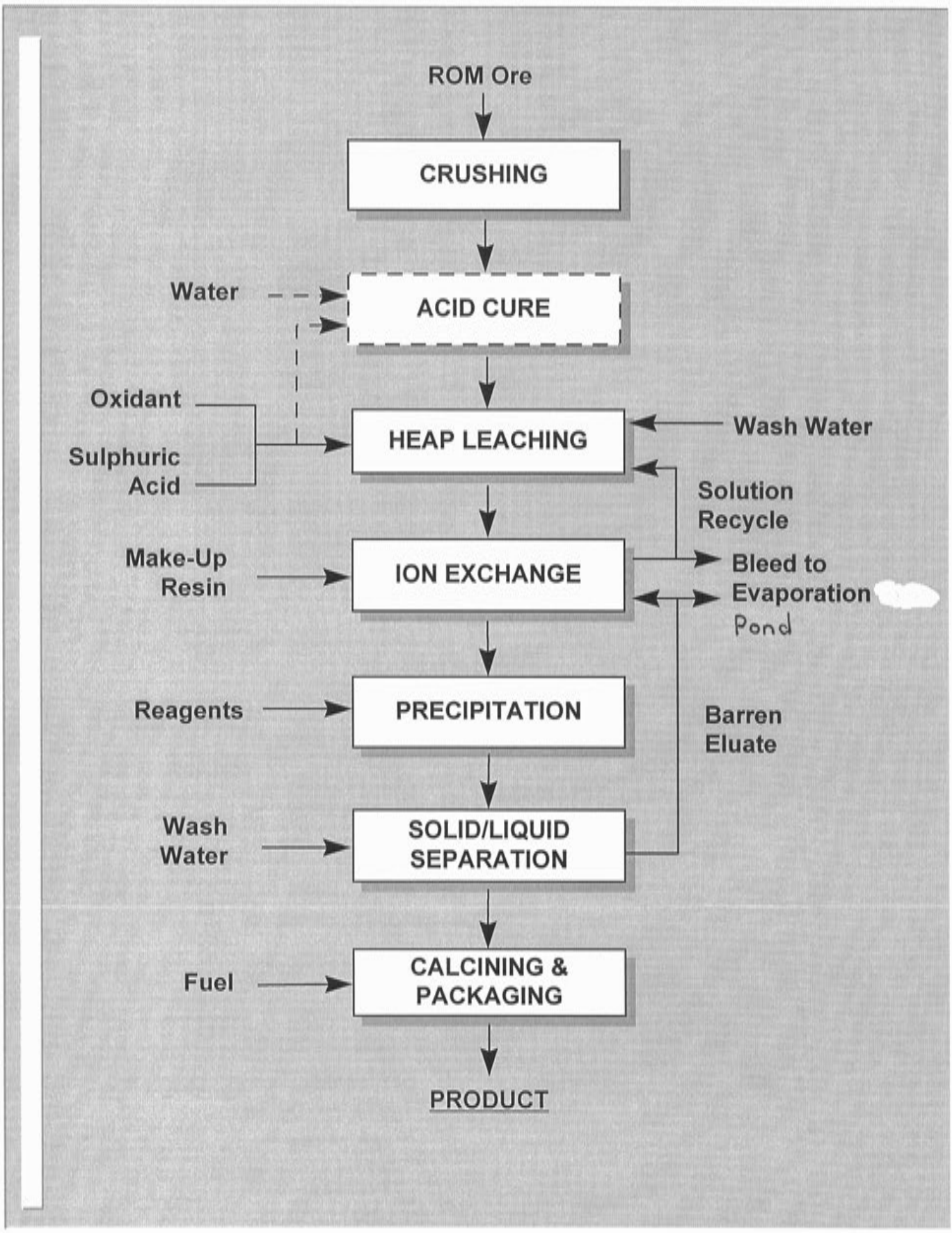
# FIGURE 5
# STRONG ACID PUGGING FLOWSHEET (ARLIT)



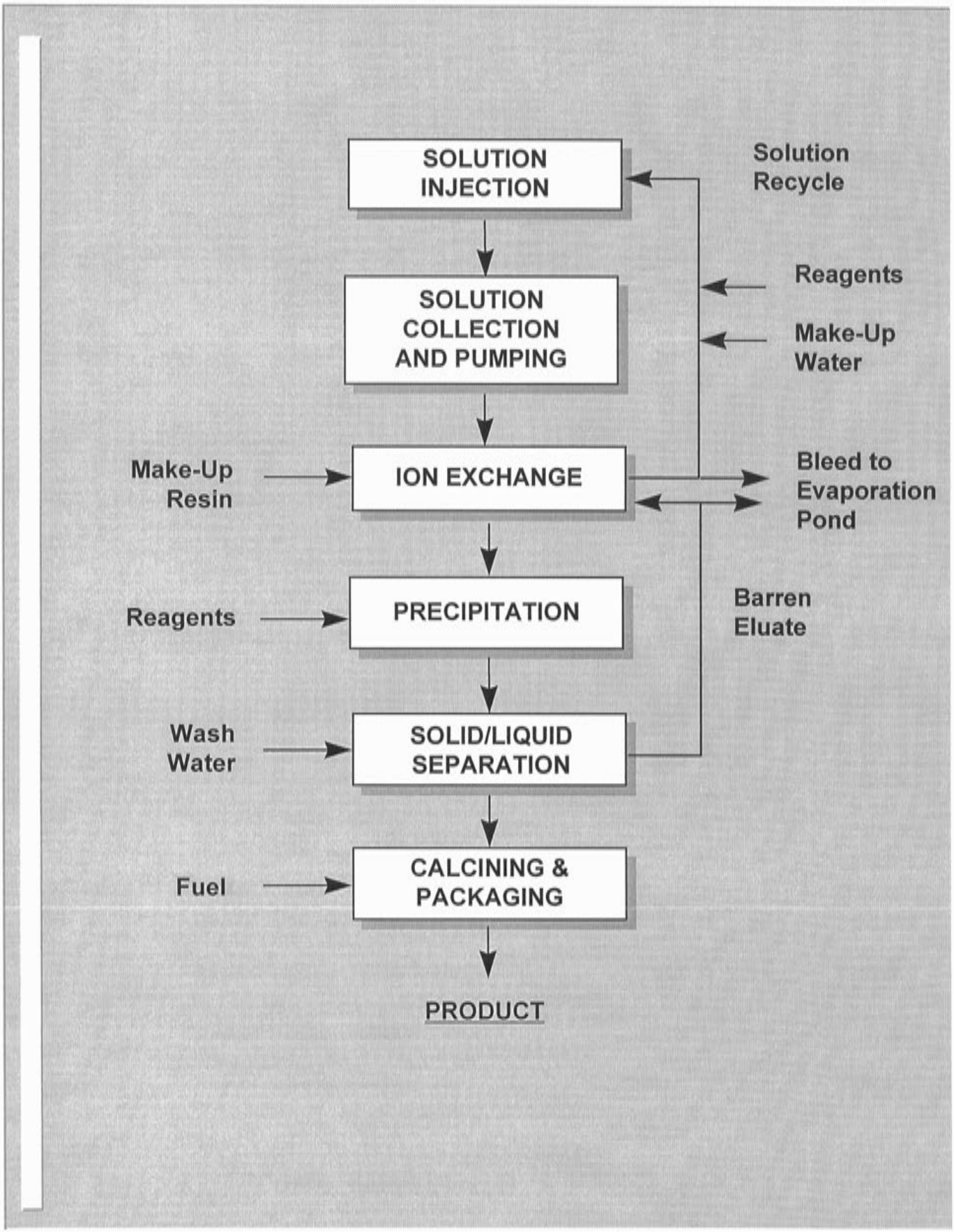
# FIGURE 6
# VAT LEACHING PROCESS FLOWSHEET



# FIGURE 7
# HEAP LEACHING PROCESS FLOWSHEET



# FIGURE 8
# IN-SITU LEACHING PROCESS FLOWSHEET



# APPLICATION OF BATEMAN PULSE COLUMNS FOR URANIUM SX

## From Pilot to Industrial Columns

by
**R.L. Movsowitz, R. Kleinberger, Dr. E.M. Buchalter**

**Bateman Projects Limited (Israel)**

# APPLICATION OF BATEMAN PULSE COLUMNS FOR URANIUM SX

From Pilot to Industrial Columns

by
R.L.Movsowitz, R.Kleinberger, Dr. E.M.Buchalter
Bateman Projects Limited (ISRAEL)

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## ABSTRACT

Bateman Projects Limited have the technology and know-how to design and supply Pulse Columns for the extraction, scrubbing and stripping of uranium. The Bateman Pulse Column is designed to overcome the difficulties in the operation of other traditional Liquid Liquid Contacting (LLC) devices such as mixer-settlers used in the uranium SX industry.

The Bateman Pulse Column consists of upper and lower settlers and a cylindrical contacting section. The contacting section is alternately filled with discs and doughnuts. The aqueous phase enters the column from the upper settler and the organic phase from the lower settler. Energy for dispersion is provided by pulsing the column either pneumatically or mechanically.

Recently pilot Pulse Column studies were successfully performed at Olympic Dam (ODO) on uranium SX. Based on these results industrial columns have been supplied to run in parallel with existing mixer-settlers. The project was performed as a joint venture between Bateman Projects Israel and Bateman Kinhill Australia.

# 1. INTRODUCTION

**Bateman Projects Limited** (BPL - Israel) have been involved in the piloting, design, supply and construction of Pulse Columns in Israel for the last ten years. Traditionally Bateman Pulse Columns have been built for the fertilizer industry covering all the fields of SX, extraction, stripping, scrubbing (washing) and purification. Columns have typically been of the size of 0.5 - 3.0 m diameter and with an effective height of up to 35 m. All the columns have been constructed from FRP (GRP) using different resins as per the clients particular requirements.

Recently BPL were requested by Western Mining Corporation at their Olympic Dam Operation to investigate the use of Pulse Columns for uranium extraction. An additional stage of uranium extraction was being considered, to increase uranium recovery and a number of options were investigated. Uranium extraction in the existing plant takes place in Krebs mixer-settlers. The potential advantage of Pulse Columns include higher efficiency, which can be achieved in a single unit which is both space saving, insensitive to solids, fully automated, cost effective, maintenance free, safe and with low environmental risk.

In order to achieve their requirements as is also required for most applications of Pulse Columns, it was necessary to first perform pilot studies before an industrial plant could be designed and the necessary performance guarantees given. Trials were performed over a number of weeks on live streams in parallel to the existing mixer-settlers, using a 4 m high 100 mm diameter solid glass column. Different internals i.e. plastic and metal were tested together with different phase ratios (Aqueous : Organic) and flowrates, in order to optimize the operation of the pilot pulse column. These results are used for scale-up to industrial columns. In addition to tests on uranium extraction, the pilot column was also operated on uranium scrubbing and stripping.

Once all the parameters for the industrial columns were defined and knowing the required flowrates as defined by WMC the industrial columns could be designed, manufactured, shipped and erected. Due to the special design and fabrication requirements, it was decided to manufacture the columns in Israel where there are a number of FRP manufacturers with hands-on experience in fabricating such columns.

The Bateman Pulse Columns are offered as an integrated system including the supply of all equipment and the civil, structural, instrument, electrical and piping design. Experience gained from past projects shows that these additional items are no less important to the effective operation of the column than the scale-up itself.

# 2. DESIGN & OPERATING PRINCIPLES

The Bateman Pulse Column is a liquid liquid contacting (LLC) unit which is designed to overcome the problems and difficulties in the operation of any other type of LLC unit i.e. stage contact like mixer-settlers or continuous contact like tray columns. The comparative chart, Table 1, presents an evaluation of some of these advantages.

The column consists of two settlers (upper and lower) as shown in Figure 1. Mounted between the two settlers is a vertical cylindrical contacting section. This section is filled alternately with discs and doughnuts. The diameter of the column and the spacing between the discs and doughnuts, are all calculated from the client's required flowrates and the optimal design flux as determined experimentally during pilot tests. In addition the height of the column is also scaled-up from the experimental results and the equilibrium curve for the organic and aqueous phases. The height and diameter of the settlers are calculated to ensure sufficient residence time for separation of the particular two phase medium, with minimization of entrainment of organic in water or vice versa.

The material of construction of the discs and doughnuts is selected in order to avoid coalescence of the dispersed phase and enhance the establishment of the continuous phase. In general, the continuous phase will wet the internals and the dispersed phase will not. When the solvent phase is continuous, the interface is in the lower settler, while when aqueous continuous it is in the upper settler.

The heavy (aqueous) phase enters through a disperser at the top of the contacting section, while the light (organic) phase enters through another disperser at the lower entrance to the contacting section. The light phase overflows from a weir in the upper settler from where it flows by gravity to its destination. The heavy phase flows from the bottom settler under interface control in order to maintain the interface level in either the bottom or top settler (depending on which phase is continuous).

In large industrial columns pulsation is provided pneumatically via a pulsation leg, which enters the column through the lower settler. In smaller columns pulsation can also be provided mechanically. Pneumatic pulsation is achieved by providing air at the required frequency and amplitude. The diameter of the pulse leg is designed to provide the required amplitude (' A ') in the column. The pulsation air supplied by air blowers through three-way valves which allow the frequency (' F ') of the pulse to be controlled. The product 'AxF' is the energy which is supplied to the column. High energy means high shear of the dispersed phase and small droplets which give a large area for mass transfer and thus low HTU, but this has to be balanced with the entrainment obtained. High flux ($m^3/hr/m^2$) is required to reduce the column diameter to a minimum. At any particular flux should too little or too much energy be supplied this may result in the column flooding (see Graph 1 - Typical Flooding Curve).

# 3. PILOT PLANT STUDIES

## 3.1 PILOT PLANT

The pilot pulse column used for all the experiments at Olympic Dam (ODO) consists of four one meter glass segments and two glass settlers, as shown in Figure 2. The internals are of the disc and doughnut type. For the tests at Olympic Dam polypropylene internals were used for experiments conducted where the aqueous phase was the dispersed phase (W:O) and stainless steel internals when the organic was the dispersed phase (O:W).

The pilot plant was erected at a convenient position so that it could easily be tied in to the live streams feeding the existing mixer-settlers. From the aqueous and solvent tie-in points the respective header tanks on the pilot plant were fed and from these they flowed to measuring tanks. The measuring tanks are used to calibrate the individual rotameters for the solvent and aqueous feeds. Magnetic drive pumps were used for pumping the feeds to their respective inlet points on the column and the flowrates controlled manually with the feed rotameters. Other instruments available on the column are points for thermometers and conductivity measurement. The interface can also be controlled using a radio frequency probe and a solenoid valve on the outlet stream. The control is on-off and found to be ample for pilot plant studies.

In the pilot plant the column was mechanically pulsed using a mechanical pulsator, with variable stroke (0-30 mm) and variable frequency (16-144 cpm). The pulsator is situated on the side of the bottom settler.

Samples are taken from the inlet and outlet streams and from sample points SP1 to SP5 along the column. All streams are sampled for uranium concentration and the outlet streams for entrainment of solvent in the aqueous outlet and aqueous in the solvent outlet. Imhoff measuring cylinders are used for measuring entrainment. In addition holdup is measured along the column using sample points SP1 to SP5. Hold-up is considered an indication of mass transfer.

## 3.2 URANIUM EXTRACTION

### 3.2.1 Experiments

Experiments were performed on copper raffinate against solvent, containing Alamine 336 as the active ingredient, Dodecanol and Shellsol as the diluent, both taken from online streams. From basic chemistry it can be seen that four moles of Alamine are required for extracting one gram equivalent of uranium. As it is not possible to extract more uranium than 100% loading of the solvent and as other contaminants are also present the actual loading is much lower.

The desired phase ratio is derived directly from the concentration of uranium in the feed and the maximum possible loading of the solvent. Typical phase ratios tested ranged in the order of 5 - 7:1 (i.e. 5-7 volumes of aqueous to 1 volume of solvent). Increasing the phase ratio should not affect the extraction efficiency as long as the concentration of Alamine in the solvent is high enough. Practically a phase ratio of 10:1 could be used, but as some safety factor for deterioration due to contamination and concentration changes is required it is not advisable to use such a high phase ratio. Too high a concentration also has other side affects which could be detrimental to the downstream processes.

In Bateman Pulse Columns it is possible to disperse the major phase (i.e. the one present in excess) and keep the minor as the continuous phase. This differs from mixer-settlers where the minor phase must be the dispersed phase. For the uranium experiments performed the minor solvent phase was chosen as the continuous phase. This is not possible in mixer-settlers due to the mixing and pumping. It also has the advantage that it minimizes organic entrainment with the raffinate.

### 3.2.2 Results

Typical results for uranium extraction are shown in Table 2.

a. Entrainment

Aqueous entrainment at the top of the column was found to be below 10ppm and solvent losses at the bottom of the column around 50-70ppm. This is significantly lower than that obtained with mixer-settlers. The reasons being that:

- the range of droplet size distribution is smaller.
- there is no air mixed with the phases due to mixing and pumping.

b. Flooding Curve

The results from flooding experiments show that hydrodynamically the desired energy is less than 2.5 cm/s. In addition operating fluxes of 50-60 $m^3/hr/m^2$ were found compared to typical fluxes of 5-8 $m^3/hr/m^2$ in mixer-settlers.

c. Efficiency

It was found that under the correct operating conditions the column could achieve efficiencies of greater than 95% within 2-3 m of the pilot column. 3-4 m were required when the feed was rich in silica or the barren solvent returned with high uranium concentrations. Typically the height of a theoretical stage (HTU) would be 1-1.5 m. It is believed that silica affects the mass transfer rate (i.e. kinetics) and this is the reason that the column needs to be higher. Increasing the height of the column can be done with little additional capital cost outlay, which is not the case for mixer-settlers. In addition stable emulsions are formed which cannot easily be dealt with by the mixer-settlers for the reasons mentioned above and can in most cases be dealt with by the Pulse Column.

d. Operation

The column was continuously operated over a period of several weeks with minimal supervision. No long term effects of solids was noted on operation or efficiency.

## 3.3 URANIUM STRIPPING

### 3.3.1 Experiments

Experiments were also performed on stripping the uranium from the pregnant solvent. For optimization of the stripping process a pH profile of 3.3 - 3.9 needs to be maintained along the length of the column. pH's higher than ~4 result in precipitation of ADU "yellowcake" and a reduction in the stripping efficiency. In order to maintain a pH-profile along the column a 5% aqueous ammonia solution was injected at three points along the column. The pH was measured by taking samples from the sampling points (SP1 to SP5), separating phases and measuring the pH with a pH electrode. Ammonia was introduced by gravitational flow from a tank situated above the inlet points. The flow was adjusted manually using Hoffman clamps on flexible tubing.

All experiments were performed using a phase ratio of 1:10 (W:O), with the major phase (i.e. organic) as the dispersed phase (i.e. O:W).

### 3.3.2 Results

Due to the fact that the pH in pilot columns can only be controlled manually, it was very difficult to control the pH-profile along the column which adversely affected the experimental results. Addition of excess ammonia resulted in the precipitation of ammonium diuranate (ADU or "yellowcake"). When the "yellowcake" appeared in the column section it quickly redissolved once the pH was brought back under control.

Results obtained indicate that an energy of less than 3 cm/s is required with fluxes ranging from 50-65 $m^3/hr/m^2$ obtainable. Entrainment values were similar to those found for extraction. Efficiencies obtained were relatively low due to the nature of the pH control in the pilot column. There is nevertheless no reason that the pulse column should not give better efficiencies than mixer-settlers under the right control conditions. In addition the pulse column has other advantages:

- higher pH at the top can be used, thus saving ammonia.
- periodical higher pH, which causes the appearance of "yellowcake" does not disturb the normal operation of the column.

# 4. INDUSTRIAL PULSE COLUMNS

## 4.1 SCALE-UP

Once all the parameters from the pilot studies are known it is possible to scale-up the column. The values which are important for the scale-up are the flux which together with the desired flowrate determine the diameter of the column section. Column dimensions can range from less than one meter to a maximum of three meters. BPL has the know-how and experience to scale-up Pulse Columns from 80 mm pilot columns to 3 m industrial columns.

Another important parameter is the height as determined during the experiments. Using this height and the number of theoretical stages determined from the equilibrium curve for uranium, in the aqueous and solvent phases at the operating temperature, the HTU can be found. The actual height of the industrial column then is a function of this parameter and the cross sectional area of the industrial column.

The dimensions of the settlers are determined by the phase separation rate, which determines the residence time required, and thus the height. The diameter is a function of velocity as it is desirable to reduce the velocity so as to enhance the settling.

Another parameter which needs to be scaled-up is the pulsation air requirements which is critical for the optimal performance of the column.

## 4.2 MECHANICAL

The mechanical design of the industrial pulse column is no less important than the actual scale-up. Due to the materials of construction i.e. FRP and the physical size and weight of the columns, it is important that the column be correctly designed. Parameters which need to be considered in the design include earthquake, wind loads, hydrostatic and pulsation pressure.

The distance between the internals (i.e. doughnut) and the shell is a critical design factor as this gap can lead to channeling, which will affect the efficiency of the pulse column. As the shell (FRP) and internals (HDPE) are made from different materials it is critical to take into account the operating temperatures in the design, as each material expands at a different rate. This was a fairly critical design factor for the uranium pulse columns due to the fairly high operating temperatures (i.e. 40-50 °C).

Static electricity can also be a hazard when operating with flammable materials and here two preventative measures have been included. The first being the use of a conductive paint and the second copper conductors which are placed at predetermined distances along the column and connected via a copper strip to the earthing for the column.

## 4.3 INSTRUMENTATION

The pulse columns are designed to be fully automated with minimum operator intervention. The interface between the solvent and aqueous phases, which in both uranium extraction and stripping, in the bottom settler is controlled using a float type level measuring device. The float is so designed that it floats on the denser medium. A similar device, situated at the top of the cylindrical column section, is used for indicating hold-up. Hold-up of greater than ~60% (i.e. aqueous phase) indicates that the column is flooding or about to flood.

The only other critical instruments on the column are the three-way valves used for controlling the frequency of the pulse. By adjusting the open (i.e. to pulse leg) and close (i.e. to atmosphere) time the frequency ('F') of the pulse is determined. The amplitude ('A') is controlled by controlling the pressure in the air reservoir at the inlet to the three-way valves. Typical air pressures range from 0.4-0.6 barg. All three-way valves operate in parallel and the number is a function of the size of column and size of valve available (typically 4-7 valves are required).

# 5. CONCLUSIONS

The Bateman Pilot Pulse Column has shown that pulse columns are ideal for uranium extraction and stripping. High extraction efficiencies of greater than 95% can easily be achieved. In addition the columns are space saving, fully automated and maintenance free. Capital costs are also less than that required for mixer-settlers to obtain similar efficiencies. Pulse Columns are also safer and have less environmental risk.

Experimental results show that the Bateman Pulse Column is insensitive to solid loading and tolerant to silica contamination. Crud which may form can continuously be drained from the interface, and as such the columns should not require shutdown for cleaning and maintenance.

Fluxes obtained using Bateman Pulse Columns are ~10 times greater than those for mixer-settlers. Further pulse columns permit one to determine the continuous and dispersed phases independent of the flow ratios, by choosing the right material of construction for the internals.

# Table 1

# PULSED COLUMNS VS. MIXER SETTLERS

| FEATURE | PULSED COLUMN | MIXER SETTLER |
|---|---|---|
| 1. **PROCESS** | | |
| HETS | Low, about 1 m for many commercial applications. | Unit |
| Efficiency | Very good | High |
| Extraction Type | Continuous, excellent if many stages required | Stagewise |
| Stages | Many stages possible in one unit | Battery of M-S |
| Entrainment Separation | Very good | Good |
| Control | Very good | Poor |
| Vapor Conservation | Good | Poor |
| Safety | Very good | Poor (Fire) |
| Dispersion Control | Good | Poor |
| Continuous Phase Control | Good | Poor |
| Throughput | High | High |
| Handling Liquids containing Suspended Solids | Good | Poor |

# PULSED COLUMNS VS. MIXER SETTLERS

## cont'd;

| FEATURE | PULSED COLUMN | MIXER SETTLER |
|---|---|---|
| 2. **MECHANICAL** | | |
| Moving Parts | No internal moving parts, requires air compressors & 3-way valves | Special belt-driven axial pumps for each stage |
| Maintenance | Low operating and maintenance cost | High operating and maintenance cost |
| Construction | One piece | Many units/stages |
| Material of Construction | Metals & plastics | Metals and plastics |
| Interconnections | Few | Many and complicated (leakage) |

# PULSED COLUMNS VS. MIXER SETTLERS

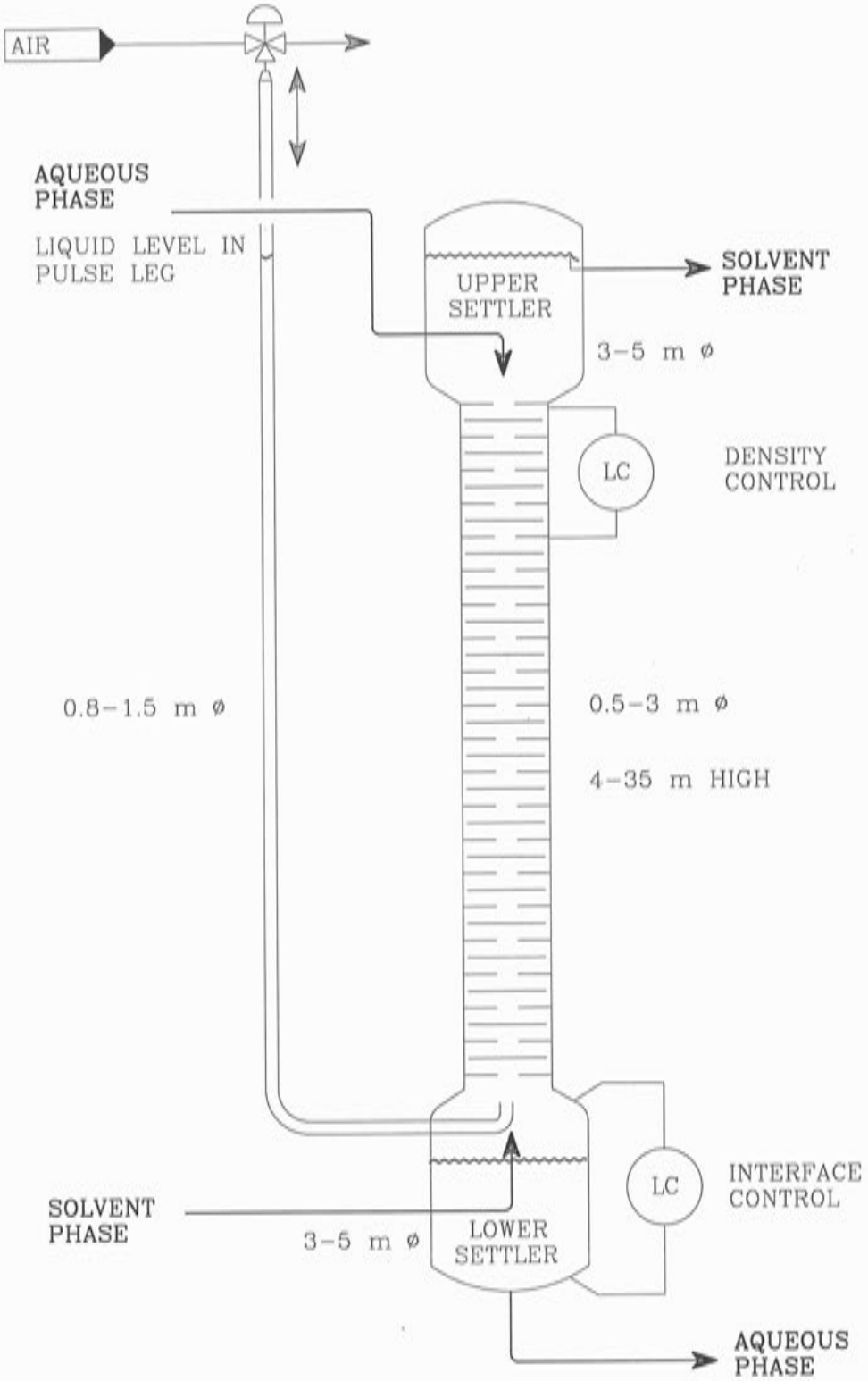
## cont'd;

| FEATURE | PULSED COLUMN | MIXER SETTLER |
|---|---|---|
| 3. **MISCELLANEOUS** | | |
| Layout | Area savings high; High structure | Large floor area one level; Low massive structure: 1 floor M-S 1 floor below for tanks |
| Delivery Time | Good | |
| Installation | One piece | Many units |
| Investment Cost | The more stages the more competitive | Expensive due to foundations, vessels, piping and pumps |
| Energy Cost | Depends on intensity of dispersion | High |
| | | |

## TABLE 2

# URANIUM EXTRACTION EXPERIMENTAL RESULTS

| Phase | Amplitude | Frequency | | | HOLD-UP (vol. %) | | | Energy | Flux | Efficiency |
|---|---|---|---|---|---|---|---|---|---|---|
| Ratio | mm | 1/min. | SP1 | SP2 | SP3 | SP4 | SP5 | cm/s | | |
| | | | | | | | | | | |
| 5:1 (A:S) | 20 | 72 | 25 | 29 | 14 | 24 | 50 | 2.4 | 51 | 98 |
| 7:1 (A:S) | 28 | 64 | 20 | - | - | 55 | - | 3 | 51 | 98 |

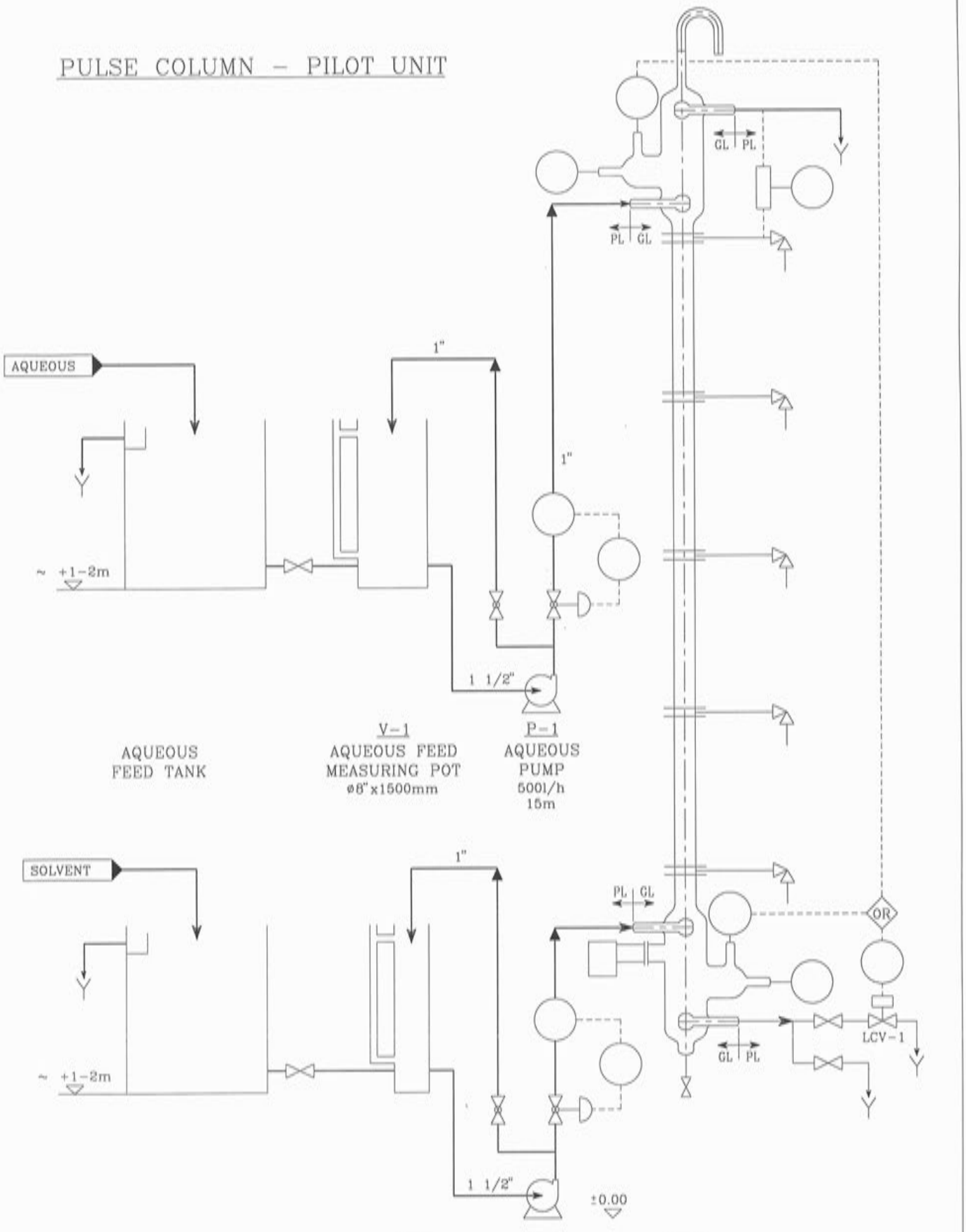



# BATEMAN PULSED COLUMN

FIGURE 1

FILE No. FIGURE1

# PULSE COLUMN – PILOT UNIT




AQUEOUS FEED TANK

V-1
AQUEOUS FEED MEASURING POT
ø8"x1500mm

P-1
AQUEOUS PUMP
500l/h
15m

SOLVENT FEED TANK

V-2
SOLVENT FEED MEASURING POT
ø4"x1500mm

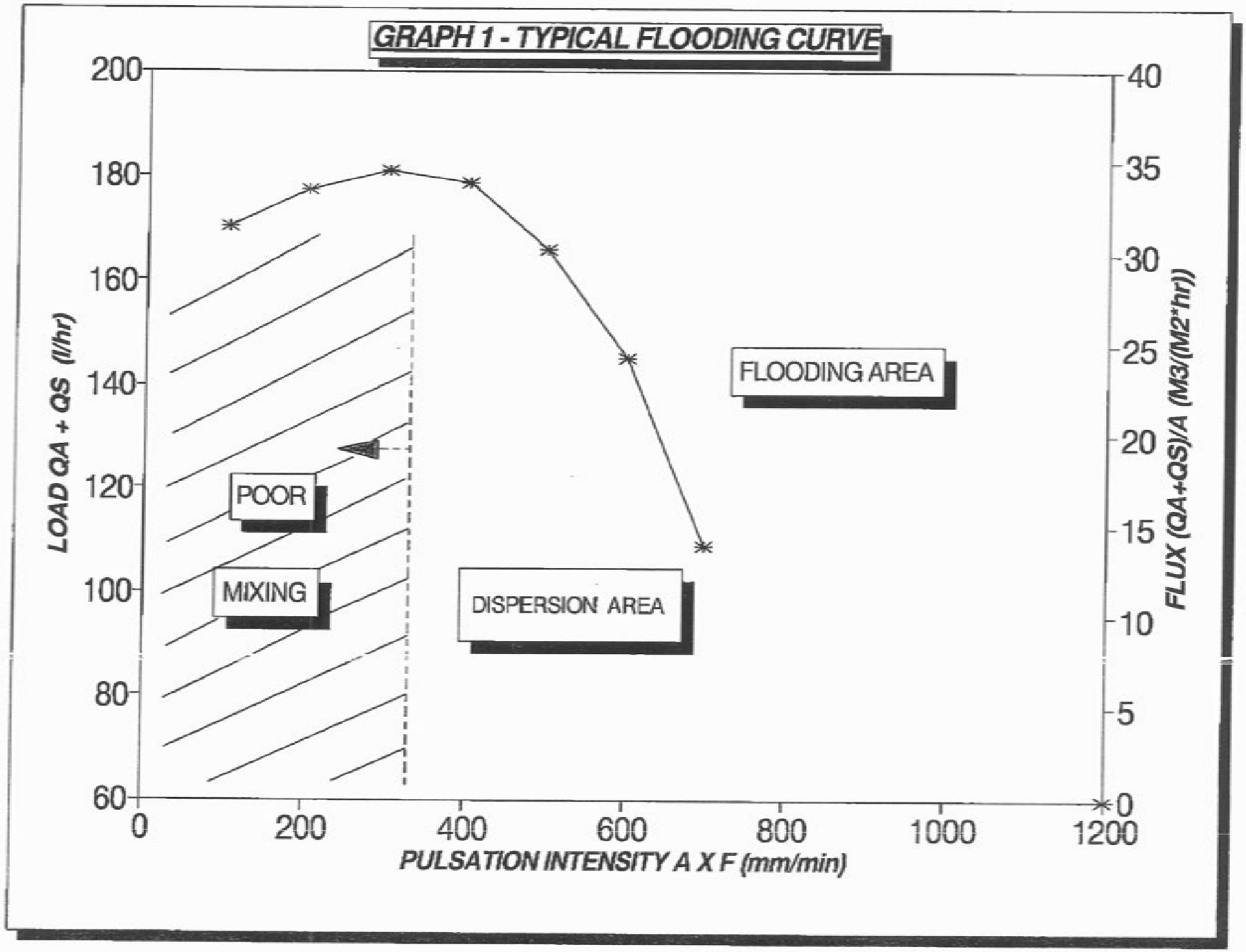
P-2
SOLVENT PUMP
500l/h
15m

PC-1
PULSED COLUMN
ø100x1000mm
(4 SECTIONS)

LEGEND:
PL - PLASTIC
GL - GLASS

FIGURE 2

FILE No. FIGURE2



# URANIUM ORE PROCESSING IN CANADA AND AUSTRALIA AND TECHNOLOGICAL DEVELOPMENTS

## PART I

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## ABSTRACT

At present there are three uranium ore processing facilities operating in Canada and two in Australia: the Cluff Lake, Key Lake and Rabbit Lake plants in Canada and the Ranger and Olympic Dam plants in Australia. Each plant utilises a different process flowsheet. These process flowsheets and the general operating experiences of the facilities are reviewed.

Three new projects are in the development stage in Canada and two in Australia. The Canadian projects are the McLean Lake, Cigar Lake and McArthur River projects. The committed Australian projects are the Ranger and Olympic Dam expansion projects. Other potential Australian projects include the Kintyre and Yeelirrie projects. The plant development programs include new facilities, expanded plant facilities and use of existing modified facilities. The process design aspects of some of these projects are discussed.

For existing operations and new development projects, the review and discussion focuses on the peculiarities of the flowsheet, equipment and technology innovations: and process design advances as well as process design disappointments.

Revisited technologies, new technologies and developing technologies for the uranium processing industry are reviewed. The potential of these technologies is assessed.

# PART I

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# 1. INTRODUCTION

As elsewhere, the uranium industry in Canada has gone through the well-known development-stagnation cycles.

At present, the cycle is in development with three new projects poised to join production with the current three operating projects.

This presentation is a review of those operating and the developing projects. It is not intended to present detailed descriptions as these are known and/or available from numerous sources. Rather, the focus will be on new processing technology and modified technology as utilised by these projects. In addition, an analysis is attempted of perceived shortcomings in process design, and the subsequent consequences and necessary remedial actions are discussed.

The questions raised with respect to the uncertainties found in process design of the new and existing projects are examined as to requirements for adaptation of modified known technology, new technology, and emerging technology.

The projects reviewed are the existing operating projects Cluff Lake, Key Lake and Rabbit Lake. The developing projects are McClean Lake, Cigar Lake and McArthur River.

# 2. DESCRIPTION OF EXISTING OPERATIONS

The current operating mills are Cluff Lake, Key Lake and Rabbit Lake. These mills treat various orebodies in the vicinity of the mills. In some cases the newer orebodies are very different from the ores for which the original mills were designed. The mill designs for the current ores being treated are discussed.

## 2.1 CLUFF LAKE

The Cluff Lake mill was initially built to process a very high-grade ore (1981). That mill was modified to a conventional mill in 1984 with the following major flowsheet parameters:

- 800 tonnes per day ore at 0.41% U low arsenic ore;
- 2,700,000 lb $U_3O_8$/year
- conventional ore crushing with jaw crusher and secondary cone crusher to minus 19 mm;
- conventional rod mill - ball mill grinding with spiral classification to P80 of 350 µm;
- neutral thickening with conventional agitation leach at 50°C with sulphuric acid and sodium chlorate oxidation;
- five-stage conventional thickener CCD;
- multi-media pressure filtration of pregnant aqueous solution;
- tertiary amine (5% amine, 4% isodeconal) solvent extraction utilising Krebs equipment with 4 stages of extraction, aftersettler, and 5 stages of stripping and one stage of sodium carbonate regeneration;
- chloride stripping (75 g/L NaCl or 1.3 M Cl-) with 30% organic regeneration with sodium carbonate;
- water wash of stripped organic to reduce chloride loading of raffinate;
- magnesia precipitation of yellowcake and drying in a Proctor-Schwartz tunnel dryer;
- washing of yellowcake (prior to drying), on a belt filter with ammonium sulphate solution to meet commercial concentrate specifications;

- tailings neutralisation to pH 7.5 with lime and effluent treatment with barium chloride and pressure sand filtration;

- paste thickening of tailings.

The Cluff Lake mill flowsheet is presented in Figure 1.

The chloride strip process was popular in the 1950s in the southwest U.S.A. prior to development of the ammonium sulphate strip process. The chloride process was also used when molybdenum concentrations were high, as this process is more tolerant of molybdenum in solvent extraction.

The reasons for selection of the chloride strip process for the Cluff Lake ores is not known. The owners are known to use this process elsewhere and probably felt comfortable with it. Also, the high carbonate scrubbing rate (30% of barren organic) suggests possible chemistry problems (Mo, others) in solvent extraction.

The chloride strip process appears to have several possible shortcomings. The need for ammonium sulphate washing of yellowcake indicates that commercial concentrate specifications can not be met with the above flowsheet. The use of ammonia adds to the operating costs and to the effluent loading (environmental considerations).

Chlorides have also been suggested of as possibly enhancing the solubility of uranium and other metals in process effluent (Figure 2). This was recognised by the Canadian uranium industry regulators in their requirements that chlorides be reduced in the project effluents by reducing or eliminating sodium chlorate use in leach. Unfortunately, the basis for these requirements was erroneous for this project, since 85% of the chloride concentration in effluent is due to chloride strip in solvent extraction ($NaClO_3$ 2.7 kg/t ore; NaCl 8.6 kg/t ore). For any project where there may be a concern for enhanced metal solubility in effluent, the chloride strip process should be avoided.

## 2.2 KEY LAKE

The Key Lake mill commenced operation in 1983. The flowsheet was designed to process a high grade ore with high variability in uranium and the nickel-arsenic-sulphide minerals.

- The flowsheet at start-up, before modifications, was as follows:

- 700 tonnes per day ore at 2.00% U, 1.5% As, 2.00% Ni, 0.03% Mo;

- 12,000,000 lb $U_2O_8$/year;

- primary gyratory crushing;

- ore blending, hammer mill secondary crushing, ball mill grinding;
- neutral thickening and ground ore storage/blending;
- two-stage leaching, atmospheric first stage (acid and emf control) and pressurised autoclave (10 vertical independent tanks) second stage with acid and oxygen addition at 65°C and 500 kPa pressure;
- eight-stage CCD circuit after pressure leach using conventional thickeners; pregnant solution recovery from the inter-stage (primary) thickener;
- reactor clarifier and pressure precoat filter for clarification of pregnant aqueous;
- tertiary amine solvent extraction using Krebs equipment with four stages of extraction, three stages of loaded organic acid water wash, four stages of stripping, one stage of barren organic water wash and one stage of sodium carbonate regeneration.;
- ammonium sulphate stripping, conventional ammonia precipitation, multi-hearth calciner for product;
- ammonium sulphate crystallisation and recovery;
- separate raffinate solution neutralisation with solid-liquid separation (thickening and filtration);
- separate leach residue neutralisation and "sub-aerial" tailings disposal.
- effluent treatment for radium removal and acidification of effluent to meet ammonia specifications.

The Key Lake process flowsheet is presented in Figure 3.

The ammonium sulphate strip process was developed for the southwestern U.S.A. ore during the 1960s.

There have been several process changes to the original Key Lake flowsheet.

The crushing circuit using a hammer mill crusher was not operable with the clayey ore and the very cold climate. This was previously experienced in areas such as Wyoming, where the conventional hammer crushing circuits were replaced by SAG mill circuits in the 1970s. A SAG mill closed circuit with a vibrating screen was installed at Key Lake to alleviate the plugging and freezing problems.

One of the leach autoclave arrangements exploded. The explosion was attributed to hydrogen gas build-up and hydrogen monitors have been installed to control concentration. This control scheme has been successful to-date.

The precoat pressure filters have not operated very satisfactorily in pregnant aqueous solution clarification. They have been replaced by standard pressure sand filters (multi-media).

Difficulty has been experienced in solvent extraction-precipitation with molybdenum. Key Lake developed a cationic solvent extraction process (using a known Mo extractant such as LIX-64 or Kelex 100, to control the molybdenum. The technology related to use of the process in the flowsheet and techniques for minimising solvent reagent cross-contamination have been patented (U.S. Patent No. 5,229,086). The molybdenum extraction flowsheet for strip solution is presented in Figure 4.

The quality of the precipitated yellowcake in terms of sulphur content has been improved by improving the precipitation conditions, including process agitation.

The directly fired multi-hearth calciners are known to produce a heavy solids load in the conventionally scrubbed discharged gases. The Key Lake unit was no exception. Packed column scrubbers have been installed to provide second stage treatment. Solids loading has been reduced but the loading is still greater than that obtained with the indirectly heated type dryers.

The filters for the precipitated raffinate solids have not been used as a satisfactory density is obtained by the recycling (seeding) process during neutralisation and thickening.

Subsequent to an effluent spill, an ion exchange plant was installed to remove radium from additional effluent introduced into tailings storage. The radium selective cation resin XFS 43230 supplied by Dow Chemical is used to reduce radium from 104 Bq/L to $<0.2$ Bq/L. The ion exchange feed is passed through a sand filter before contacting the resin.

The original tailings disposal scheme (the "sub-aerial" technique) has not operated as planned because of the obvious climatic conditions. Dewatering has not been achieved with considerable ice entrapped in the tailings. The tailings may be moved for in-pit disposal in one of the previously mined-out ore pits. The in-pit storage method is the preferred (regulators) method for tailings disposal for uranium tailings.

In conjunction with the replacement of the tailings, the recovery of nickel and cobalt (2.00% and 0.2% respectively in the ore) was revisited. It is reported that previously dissolved (and precipitated in tailings neutralisation) metals as well as host minerals would be recovered from the tailings, solubilised using pressure leach and recovered by solvent extraction using a DEHPA based system, possibly to high purity chemical compounds and/or electrowon metal. Although a significant pilot plant was run, the flowsheet selected for economic evaluation was not fully demonstrated with various circuits operating in tandem. The project as demonstrated and as evaluated did not meet economic objectives.

## 2.3 RABBIT LAKE

The original ore for the Rabbit Lake mill was depleted in 1985. The process flowsheet required extensive modification to accommodate the new ore, Collins Bay, B-Zone. The original ammonium sulphate strip process was not suitable because of excessive crud formation in solvent extraction, and tailings and effluent treatment circuits were required to cope with the arsenic and nickel in the ores.

The current flowsheet, including modifications, is as follows:

- 2200 tonnes per day ore
  0.62% U, 0.47% As, 0.35% Ni, 0.01% Mo
- 6,000,000 lb $U_3O_8$/year
- SAG mill - ball mill grinding with cyclone classification
  no neutral thickening
- conventional sulphuric acid leaching with sodium chlorate oxidation
- six-stage CCD thickening
- reactor clarifier and multi-media pressure filtration of pregnant aqueous
- tertiary amine solvent extraction with strong acid stripping using conventional mixer-settler equipment. Four stages of extraction, five stages of stripping, water wash for acid recovery, sodium carbonate regeneration
- pregnant strip solution purification (gypsum precipitation)
- hydrogen peroxide precipitation with magnesia pH control
- indirectly fired, paddle type "Porcupine" drying of yellowcake, area dust collector scrubber

- tailings neutralisation and process solution recovery

- tailings filtration for in-pit disposal with final effluent treatment.

The Rabbit Lake process flowsheet is presented in Figure 5.

The strong acid strip process was specifically developed to treat the Collins Bay B-Zone ore. The ammonium sulphate process was not operable with this ore and several of the subsequent ores. The new ore was variable in terms of uranium and impurity concentrations. The concentration ranges for uranium, arsenic and nickel were 0.28-15.0% U, 0.49-10.2% As and 0.36-8.27% Ni respectively.

The wide variations in metal grade resulted in periodic over-dosage with chemical oxidant (sodium chlorate) in maintaining oxidising conditions in leaching. The residual oxidant did cause some deterioration of amine in solvent extraction but more precise control of oxidant addition reduced this problem.

Significant amine deterioration was experienced during initial operations of the strong acid strip process. It was determined that temperatures in solvent extraction solutions approached up to 60°C when testwork had clearly shown 30°C to be a reasonable operating temperature and 35°C to be a practical limit. Subsequent reduction in operating temperature reduced the amine deterioration (losses) to generally normal levels. There was some postulation that metal concentrations were the cause. However, metal concentrations remain generally unchanged throughout all the operating temperature ranges. Figure 6 presents data on the effect of temperature on amine extraction of uranium.

The strong acid strip - hydrogen peroxide precipitation process produces a high purity yellowcake that meets all commercial concentrate specifications.

The Porcupine drier operates very well, resulting in much lower solids discharge into the site environment than experienced with multi-hearth calciners.

It is reported that the Rabbit Lake mill is now using the new Controlled Acid - Strong Acid Strip Process (U.S. Patent No.5,419,880; patent pending in Canada and Australia). Patent defence will commence upon patent issue.

The operation of the solution recovery thickener for process selection recycle was difficult because reasonable underflow densities could not be obtained. Underflow recycle to process was necessary to achieve density control. This process flowsheet change is presented in Figure 7.

The filtration of tailings for in-pit disposal was not completely successful because of the poor filtration characteristics of neutralised tailings. Tailings filtration was reduced to filtration of the neutralised raffinate to remove precipitated solids. These solids were mixed with neutralised tailings (CCD underflow) for disposal into the pit.

# 3. DESCRIPTION OF DEVELOPING PROJECTS

Three new projects are being developed in Canada, namely the McClean Lake, Cigar Lake and McArthur River projects. These projects involve new high grade orebodies. The process designs and process modifications to treat these ores are discussed.

## 3.1 MCCLEAN LAKE

The McClean Lake mill is currently under construction with start-up scheduled for mid-1997. The mill is to treat ore from McClean Lake site (JEB, Sue C, Sue A+B, McClean deposits) and one from the nearby Midwest deposit. The current major flowsheet parameters are as follows:

- 425 tonnes per day ore
  2.0% $U_3O_8$, 1.5% As
- 6,000,000 lb $U_3O_8$/year
- SAG mill - ball mill grinding cyclone classification
- ground ore storage and blending
- primary leaching, fresh pulp and pregnant solution mixing (2-stage leach process) in conventional leach equipment, interstage thickening
- conventional second stage acid leaching with chemical oxidation
- 6-stage CCD pregnant aqueous solution recovery using high rate thickeners
- high rate clarifier with integral surge
- continuous upflow sand filters for pregnant aqueous polishing
- tertiary amine solvent extraction using Krebs equipment with 4 stages of extraction, 3 stages of loaded organic acid water wash, 4 stages of stripping, 3 stages of water wash for ammonia removal, sodium carbonate regeneration
- ammonium sulphate stripping, activated carbon removal of molybdenum, conventional ammonia precipitation, multi-hearth calciner for yellowcake
- ammonium sulphate crystallisation and recovery, ion exchange removal of ammonium ion from evaporation exhaust

- tailings neutralisation for in-pit (sub-aerial) disposal

- effluent (and pit drainage) treatment for radium and metals removal and acidification of effluent to meet ammonia specifications.

The McClean Lake process flowsheet is presented in Figure 8.

The original flowsheet design for the McClean Lake mill was based on the use of the Strong Acid Strip Process for uranium recovery. With the development of the Controlled Acid - Strong Acid Strip Process, this new process was proposed for the mill. However, as with any process considered for uranium, appropriate continuous testing was required.

The owners were reluctant to do this testing and decided to change the process to the ammonium sulphate strip process based on perceived savings. Unfortunately, the selected flowsheet with ammonia sulphate stripping (sodium chlorate oxidation in leaching, ammonium sulphate crystallisation) is not known to have been operated previously at a uranium plant. Also, unfortunately, this process combination was not tested before materials of construction were selected.

Richard C. Swider Consulting Engineers Limited undertook a test program relating to conventional materials of construction and the above process combination. It was determined that chlorides tended to smear throughout the flowsheet when used in a uranium recovery process, and these chlorides were also found to contaminate the crystallisation process. The research report concluded that, "there is uncertainty as to the suitability of conventional 316L stainless steel for ammonium sulphate crystallisation equipment (which is under differential pressures) in view of the potential for pitting, stress and crevice erosion with the presence of chlorides in by-product solution".

The consequence of the use of untested technology appears to be a major process change in terms of chemical oxidant in leaching. Hydrogen peroxide will now be used in place of sodium chlorate with a significant increase in costs. The process change is now in the approvals stages.

The use of the ammonia stripping - precipitation process results in ammonia contamination of the process (and site) effluents, and this is a concern in areas where there is a positive outflow from the site (including McClean Lake).

Two process circuits have been installed in an attempt to control the ammonia contamination. The stripped organic is water washed to remove entrained ammonium sulphate and the crystallisation condensate is treated with cationic ion exchange to remove evolved ammonia.

The conventional pressure sand filters used in other plants for clarification of final effluent have been replaced by continuous upflow filters. These filters have an established operating record in water treatment. Initial reports from operating personnel are positive. However, project design personnel report problems with media cementing (common problem at uranium operations) and with the quality of the materials of construction. It is reported that these would not be used in other process applications.

The leaching circuit will be modified to include pressure leaching when the ore with higher oxygen demand (high arsenic ores, Sue A+B, Midwest, McClean) are processed. Oxygen injection would be used for oxidation.

With the treatment of Midwest ore, it is proposed to change tailings disposal to a sub-aqueous system from the sub-aerial system. The sub-aqueous (post-tailings) in pit system does not utilise the filtration envelope (graded crushed rock and sand). The fractured pit walls are used for the same purpose. This proposed disposal process is in the licensing stage.

## 3.2 CIGAR LAKE

Ore from the Cigar Lake project will be treated at an expanded McClean Lake mill facility. The process flowsheet used for treatment of Midwest ore (including pressure oxidation leaching) will be used for this ore. The major flowsheet parameters for the facility expansion are as follows:

- 190-500 tonnes per day ore;
  5-13% $U_3O_8$; 1.0-1.5% As;
- 18,000,000 lb $U_3O_8$/year;
- ground ore shipment from minesite to mill in ore shipment capsules;
- paste tailings with sub-aqueous disposal in the pit depository.

Figure 9 presents the pressure leaching flowsheet to treat Midwest and Cigar Lake ore.

Cigar Lake ore will be prepared as a pulp at the minesite and shipped to the McClean mill site as a slurry, in slurry shipping containers.

The slurry preparation facilities, the slurry container loading facilities, and slurry container hauling units will be generally similar for the Cigar Lake, McArthur River and Midwest ores.

The proposed project is currently under licensing review. More process flowsheet details will evolve once the licensing procedure has been completed.

## 3.3 MCARTHUR RIVER

Ore from the McArthur River project will be treated at the Key Lake mill. The existing mill facility will be used, although the mill may be expanded for greater production. The major flowsheet parameters for treatment of this ore at the existing mill are as follows:

- 80-700 tonnes per day ore;
  4-30% $U_3O_8$; low arsenic; highly variable ore grade;

- dilution with special waste (Key Lake) to 4% $U_3O_8$ and 0.08-0.2% As;

- 18,000,000 lb $U_3O_8$/year;

- paste tailings with sub-aqueous disposal in a pit depository.

The typical arrangements for preparing, loading and shipping the high grade ore to processing plants are presented in Figures 10, 11 and 12.

This project is also under licensing review.

# 4. TECHNOLOGICAL DEVELOPMENTS

## 4.1 GENERAL

The development cycle in the uranium industry, in addition to the ever present pressures of costs and environmental regulations, has led to technological developments. The developments include modification/adaptation of known technology, new technologies and emerging technology.

The uranium business is becoming more competitive, and this competition has permeated into the area of information availability. Much of the new technology and emerging technology is subject to confidential agreements and/or proprietary property controls. The information provided herein is presented subject to these legal and ownership constraints.

## 4.2 GRINDING

Technological development in this circuit has meant the improvement of testing techniques for design and sizing of grinding equipment.

SAG grinding is almost universally used and previously the minimum test was a batch mill evaluation requiring several tons of ore. The alternative was a SAG mill pilot plant run requiring 20-50 tons.

At present SAG mill designs are based on two small-scale tests, the MacPherson Autogenous Grindability Test and the empirical method of Barratt-Allan.

The MacPherson Test (using an 18" Aerofall dry grinding mill) is a proprietary process (Lakefield Research and Hazen Research) developed by A. R. MacPherson. Small size samples (300-400 kg) are required permitting a variety of ore types from one ore deposit to be tested at a reasonable cost. This test procedure is used for process design for a wide variety of metal ores, for a large range of feed rates.

The empirical method of Barratt-Allan is based on calculations using indices (crushing, Bond, Rod and Ball) and appropriate factors. Again the advantages of small sample size, variety of testing and low costs are provided. This approach has been successfully used for design of very large installations.

The costs related to obtaining an adequate sample, transportation to the laboratory, and pilot plant costs can not normally be justified for relatively small tonnage operations, and typically uranium plants are small tonnage operations. The significant costs of a pilot plant test are better utilised in providing assurance of successful operation by being spent on grinding plant equipment.

## 4.3 LEACHING

The more complex ores and process solution chemistry requirements have provided a need for pressure oxidation leaching. The leaching conditions are not extreme (relative to pressure oxidation of refractory gold ores) and the existing technology will continue to be used.

The recent increase in uranium price (U.S.$15.00/lb $U_3O_8$) has resulted in interest in smaller, higher grade deposits and large low-grade deposits that were not considered economical in the recent past. Revisited technologies of vat and heap leaching are being considered (or used) for these types of deposits. Vat and/or heap leaching can provide economic advantage for certain operations.

Ore leaching techniques are very specific to the ore treated. Proper consideration of all the design parameters is required to permit the leaching circuit to maximise uranium extraction while minimising problems that can originate during the leaching process and cause problems in other sections of the flowsheet.

## 4.4 THICKENING

High rate thickeners have generally become the standard for CCD service especially in colder climates where these units can easily be housed. Progress has been made in process control developments to permit more automatic operations.

Conventional type thickeners with proper component (feed well, flocculation) design can be competitive, in retrofit outdoor installations. Conventional thickeners can be refitted with feed wells that can provide throughput increases comparable to those provided by the high rate design.

The use of the so-called "paste thickener" (enhance compression zone or compression time) provides some benefits for tailings disposal. Some operating problems are being reported, but detailed information on performance is not available at this time.

## 4.5 CLARIFICATION

The integral surge clariflocculator and the pressure filter (sand or multi-media) are still considered standards for clarification.

New equipment includes the Walker Claricone and the continuous upflow sand filters.

The Walker Claricone clarifier (Figure 13) is a cone shape unit, with flocculated tangential feed and settled solids removal via a removable cone. These units have operated successfully at several smaller operations. High clarity overflow is provided.

The continuous upflow sand filter (Figure 14) has been used successfully in water treatment at many operations, for many years. The advantages are continuous solution feed, continuous backwash, open tank (unpressurised vessels) operation, and minimal instrumentation requirements.

These units have at present been installed for effluent filtration. Operating personnel find them very easy to run. The process design engineers have reported problems with bed (sand) cementing. Because of this perceived problem these units may not be used for pregnant aqueous filtration.

Proprietary treatment that minimises filter bed cementing problems (both pressure and continuous upflow filters) has been developed. Appropriate in-plant testing is required to confirm applicability. The concept has been demonstrated in the laboratory.

## 4.6 URANIUM RECOVERY

Solvent extraction with tertiary amine is the current standard for uranium recovery.

There are several stripping alternatives available including carbonate, chloride, ammonia and strong sulphuric acid.

The carbonate process, is generally now not used because of cost considerations. The chloride process limits solution recycle especially with higher grade ores. Process solution recycle is stressed by regulators. There is also the potential for increased solubility of uranium and metals in the process effluent.

The ammonia process is suitable with many ores, but can result in environmental concerns. With some ores, the ammonia process is not useable because of crud formation in stripping. Environmental restrictions on ammonia in some cases require ammonia removal (ammonia recovery, ammonium sulphate crystallisation) from process effluents. The restrictions require additional solvent extraction equipment (raffinate wash) and removal of ammonia from minor process streams (crystallisation condensate). In most cases effluent must be acidified to meet environmental specifications.

The strong acid strip process is useable with all ores in that the strong acid tends to purify the organic and maintain impurities soluble during stripping because of the high acidity used. The patented Controlled Acid - Strong Acid Strip Process provides for savings in comparison to the ammonia and conventional strong acid process. This process provides all the process advantages of the strong acid strip process with substantial savings in reagents. Table 1 presents a summary of comparative process costs. The comparative flowsheets are presented in Figure 15.

Two new operating practices have been incorporated into solvent extraction circuits. Pregnant organic washing with acidified water is being used to remove physical entrainment of raffinate solution and stripping of mildly bonded impurities (mildly bonded anions). This washing technique has not been successful in removing the more tightly held and most problematic impurities (such as $SiO_2$, Mo, Bi, Zr) that cause problems in stripping, especially ammonia stripping. A vast range of washing solution has been tested without any significant effect.

Acidified water wash is also used for removing residual ammonia from stripped organic to prevent ammonia contamination of raffinate solution. Some success has been achieved, but ammonia in raffinate still tends to be the major source of ammonia contamination of process effluents.

Acidified wash has also been used to wash chloride from stripped organic to reduce chloride concentrations in raffinate and permit mill solution recycle in process. This washing does not significantly reduce the overall chloride loading in process effluent.

A proprietary process is in development that may reduce the formation of crud in both extraction and stripping. Also in development is a process that may reduce the levels of constituents that cause crud, impurity and operating problems throughout the uranium recovery and purification circuits.

As previously mentioned various ore deposits are now being considered for uranium recovery using non-conventional processes. There is a possibility of ion exchange based processes being used. Ion exchange might offer advantages in the case of heap leaching and vat leaching projects. Ion exchange using resin-in-pulp technology might be considered as an alternative to conventional processing which includes solid-liquid separation (CCD). Resin-in-pulp ion exchange processing is suitable for both acid and alkaline leach systems. The technology has undergone significant improvement in the gold industry (CIP and RIP processes) and this developed technology is applicable to uranium.

## 4.7 PRECIPITATION AND PURIFICATION

New developments in precipitation have been improvements to existing processes.

The ammonia precipitation process has been improved such that the sulphate content of the final product has been reduced very significantly. Sufficiently low sulphate levels may be achievable to permit replacement of the multi-hearth calciner by the more environmentally desirable indirectly fired dryer. The inter-relationships of the precipitation variables need further study to permit designs for consistent product purity.

Where magnesia is used for precipitation, the "split magnesia process" has been laboratory tested. In this process approximately 80% of the uranium is precipitated as a hydrated oxide as the final product. The remaining 20% is then precipitated as a magnesium diuranate which is recycled to re-dissolution and re-precipitated as the hydrated oxide product. The resultant product is low in magnesium and other specified cations (Ca, Na). Further development is required.

In case of direct magnesia or sodium hydroxide precipitation the standard ion replacement process can be used to reduce cation contamination. The yellowcake can be washed (and/or re-pulped) with an ammonium sulphate solution. This metathesis process is used at Cluff Lake and has been used previously in alkaline circuits. However, ammonia is introduced into process effluents.

An improved hydrogen peroxide process has been developed. The conventional process requires 1.7 to 2.0 times stoichiometric quantities of peroxide for complete uranium precipitation. The relationship between percent $U_3O_8$ precipitation and peroxide addition is shown in Figure 16. The "split peroxide process" uses almost stoichiometric quantities of peroxide. Approximately 98% of the uranium is precipitated by approximately 98% of the stoichiometric peroxide. The remaining 2% is precipitated by a suitable base and recycled for re-dissolution and re-precipitation. There are no additional reagent costs where the pregnant strip solution is acidic. This process requires further development for proper definition of the inter-relationships of the variables. The flowsheet for this process development is presented in Figure 17.

Impurity control in many cases focuses on molybdenum removal. Key lake have developed and are reported to use a LIX extraction from strip solution. McClean Lake (and Cigar Lake) are reported to be designed for the use of activated carbon absorption from pregnant ammonium sulphate strip.

The strong acid strip processes allow for any of the above molybdenum control methods to be used. In addition, the gypsum precipitation process provides for removal of many other impurities (Zr, Bi, $SiO_2$), as required.

## 4.8 DRYING AND PACKAGING

The use of the indirectly heated dryer in place of the multi-hearth calciner has been significant improvement. The Porcupine dryer (Figure 18), a paddle-type unit, has been used successfully. The large drive provides for a good control basis, and the dryer has low emissions in comparison to the calciner.

Two-stage exhaust scrubbing (venturi and packed column) is now standard practice. In some plants dust collector-scrubbers are used for the drying/packaging areas to control dust loads during equipment maintenance.

Automatic (at least semi-automatic) packaging stations are now standard. Enclosed and vented sampling and lidding stations are provided.

One alternative being considered is the shipping of wet cake to a central drying plant. This is appealing for smaller operations, since significant savings in terms of capital are realised for the drying and packaging area. In addition, environmental loading can be significantly reduced, both in terms of worker exposure and discharge from the site. The conceptual designs for the hauling containers have been developed and are generally similar to the design for the ore hauling containers.

## 4.9 TAILINGS AND EFFLUENT TREATMENT AND ENVIRONMENTAL CONSIDERATIONS

Tailings and effluent treatment processes are very site specific (ore, process). Process design is directed to the specific problems at each site.

The use of reverse osmosis to treat well dewatering water is reported at Key Lake. Present performance is not known. A major disadvantage is the need for prior filtration of feed solution to protect the membrane from plugging.

Most effluent treatment processes require the use of significant quantities of several chemicals (acid, lime, ferric sulphate, barium chloride). These chemicals produce large quantities of chemical precipitates that require disposal. A new proprietary process is in development that greatly reduces the quantities of solids produced and reagents used.

With high grade ores radon concerns have led to a pressurised process building design. This is considered excessive and unnecessary. Proper equipment ventilation (especially in grinding) and air agitation of fresh pulp storage tanks should control radon from the primary source (fresh ore). Proper clean-up of spills and venting of dead air spaces reduces radon from these sources.

The removal of ammonia from process effluent requires the installation of ion exchange for removal of ammonium ion from crystallisation condensate. The process is effective only if there are no competing cations in solution.

## 4.10 BY-PRODUCT RECOVERY

By-product recovery (rare earths, thorium, nickel, cobalt) has always been a difficult economic undertaking. Experience suggests that work with a product user may be of assistance in developing a successful recovery plant.

## 4.11 TESTWORK FOR PROCESS DEVELOPMENT

Work on many projects has clearly demonstrated the need for proper testing, not only of new or developing technologies but also known technologies as they might apply to the uranium deposits under consideration.

Failure to do proper testing and evaluation may result in process failure that can be catastrophic.

## 5. REFERENCES


1. Schell, A.H., "Cluff Lake Mill Phase 2 - Expansion", presented at 17th Canadian Mineral Processors Operators Conference, Ottawa, 1985.
2. Environment House "Enhancing Environmental Performance by Technological Improvements to Uranium Mill Processes". A report to Mines Pollution control Branch, Saskatchewan Environment and Public Safety, September 1991.
3. Key Lake Project
   Environmental Impact Statement and Related Documents.
4. U.S. Patent No. 5,229,086
   "Removal of Molybdenum from Uranium Bearing Solution", July 20, 1993.
5. Milde, W.W., "Milling and Metallurgy, The Rabbit Lake Story", presented at the 90th Annual General meeting of the Canadian Institute of Mining and Metallurgy, Edmonton, Alberta, May 1988.
6. McClean Lake Project
   Environmental Impact Statement and Related Documents.
7. Cigar Lake Project
   Environmental Impact Statement and Related Documents.
8. McArthur River Project
   Environmental Impact Statement and Related Documents.
9. Barratt, D.J., and Allan, M.J., "Testing for Autogenous and Semi-Autogenous Grinding: A Designer's Point of View", Minerals and Metallurgical Processing, May 1986.
10. U.S. Patent No. 5,419,880
    "Controlled Acid - Strong Acid Strip Process", May 30, 1995.
11. Swider, R.C., "Controlled Acid - Strong Acid Strip Process: Operating and Capital Cost Comparison", October 18, 1995.
12. Files of Richard C. Swider Consulting Engineers Limited.

TABLE 1: OPERATING COST COMPARISON CONTROLLED ACID – STRONG ACID STRIP PROCESS
STRONG ACID STRIP PROCESS
AMMONIUM SULPHATE STRIP PROCESS

| Cost Item | Unit Cost $ | Usage Rate Units | Controlled Acid | | Strong Acid | | Ammonium Sulphate | |
|---|---|---|---|---|---|---|---|---|
| | | | Usage Rate | $/lbU3O8 | Usage Rate | $/lbU3O8 | Usage Rate | $/lbU3O8 |
| Sulphuric Acid | 100.00 /tonne | lb/lbU3O8 | 1.50 | 0.07 | 3.64 | 0.17 | 1.50 | 0.07 |
| Lime | 192.00 /tonne | lb/lbU3O8 | 0.86 | 0.07 | 2.22 | 0.19 | 0.51 | 0.04 |
| Magnesia | 480.00 /tonne | lb/lbU3O8 | 0.21 | 0.05 | 0.21 | 0.05 | 0.00 | 0.00 |
| Hydrogen Peroxide(70%) | 850.00 /tonne | lb/lbU3O8 | 0.19 | 0.07 | 0.19 | 0.07 | 0.00 | 0.00 |
| Sodium Carbonate | 330.00 /tonne | lb/lbU3O8 | 0.16 | 0.02 | 0.16 | 0.02 | 0.81 | 0.12 |
| Ferric Sulphate(45%) | 400.00 /tonne | lb/lbU3O8 | 0.20 | 0.04 | 0.20 | 0.04 | 0.00 | 0.00 |
| Ammonia | 320.00 /tonne | lb/lbU3O8 | 0.00 | 0.00 | 0.00 | 0.00 | 0.60 | 0.09 |
| Propane | 0.27 /L | L/lbU3O8 | 0.13 | 0.03 | 0.13 | 0.03 | 0.56 | 0.15 |
| Product Drums | 33.00 /drum | lbU3O8/drm | 500.00 | 0.07 | 500.00 | 0.07 | 900.00 | 0.04 |
| Electrical Power | 0.07 /kWh | kWh/lbU3O8 | 1.07 | 0.07 | 0.98 | 0.07 | 1.40 | 0.10 |
| Ammonium Sulphate (net credit) | 15.00 /tonne | lb/lbU3O8 | 0.00 | 0.00 | 0.00 | 0.00 | 1.78 | −0.01 |
| TOTAL COST $/lbU3O8 | | | | 0.50 | | 0.71 | | 0.59 |
| TOTAL COST $/kgU | | | | 1.29 | | 1.83 | | 1.54 |

| COST SAVINGS,$/lbU3O8 | |
|---|---|
| Controlled Acid – Strong Acid vs Strong Acid | 0.21 |
| Controlled Acid – Strong Acid vs Ammonium Sulphate | 0.10 |
| Ammonium Sulphate vs Strong Acid | 0.11 |

TABLE 2: CAPITAL COST COMPARISON CONTROLLED ACID - STRONG ACID STRIP PROCESS
STRONG ACID STRIP PROCESS
AMMONIUM SULPHATE STRIP PROCESS

| | Capital Cost, $ (in 1000's) | |
|---|---|---|
| | 6.0 x $10^6$ lb $U_3O_8$/year | 12.0 x $10^6$ lb $U_3O_8$/year |
| Controlled Acid - Strong Acid Strip Process<br>Estimate includes SX extraction, stripping, gypsum precipitation, uranium precipitation, uranium drying, reagent preparation and storage | 19,700 | 29,900 |
| Strong Acid Strip Process<br>Estimate includes SX extraction, stripping, gypsum precipitation, uranium precipitation, uranium drying, reagent preparation and storage | 17,900 | 27,200 |
| Ammonium Sulphate Strip Process<br>Estimate includes SX extraction, arsenic scrub, ammonia stripping, ammonia removal scrub, ammonia removal IX, molybdenum control, uranium precipitation, uranium calcining, ammonium sulphate crystallization, by-product screening, reagent preparation and storage. | 24,300 | 36,900 |

## FIGURE 1: CLUFF LAKE MILL FLOWSHEET

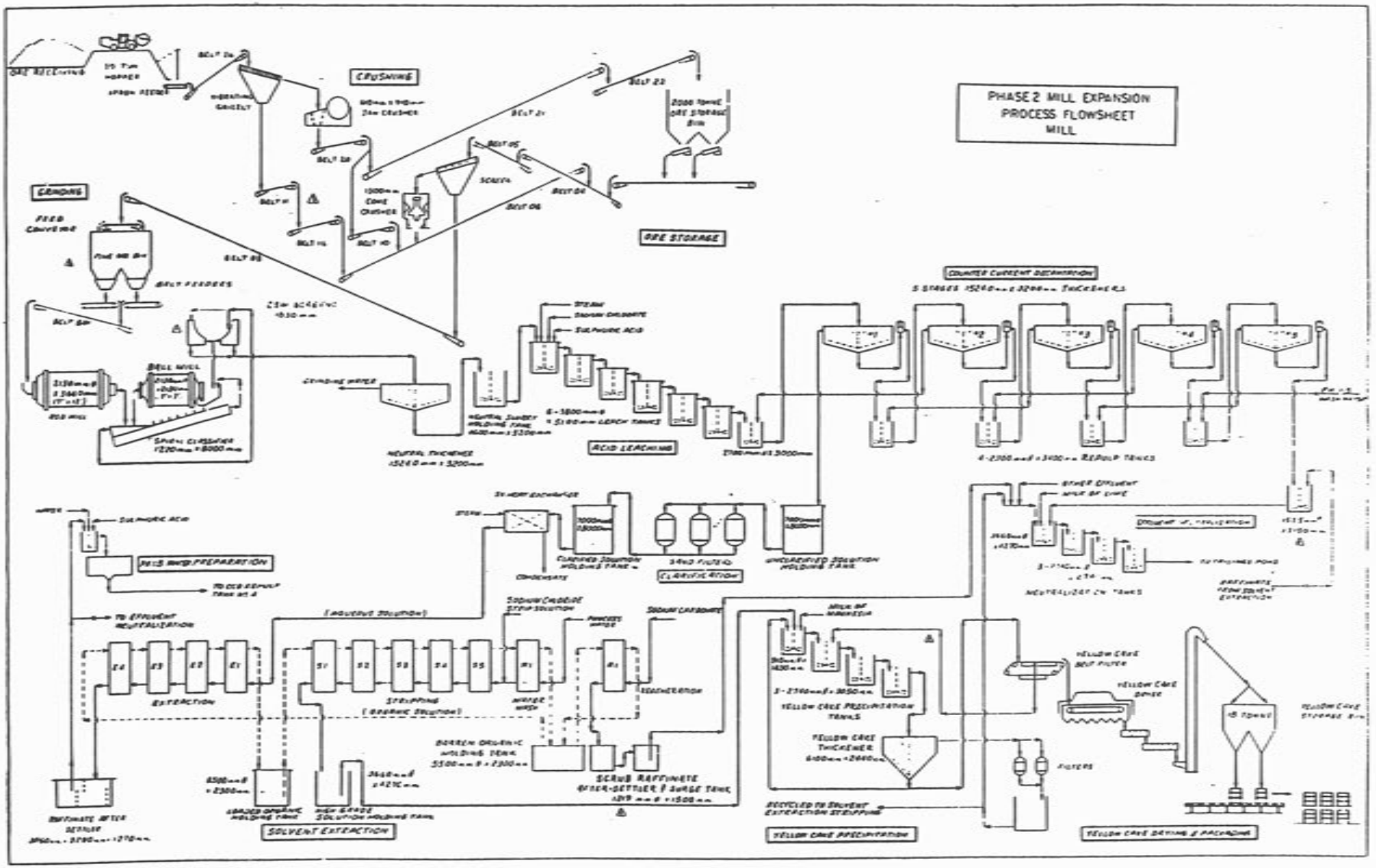
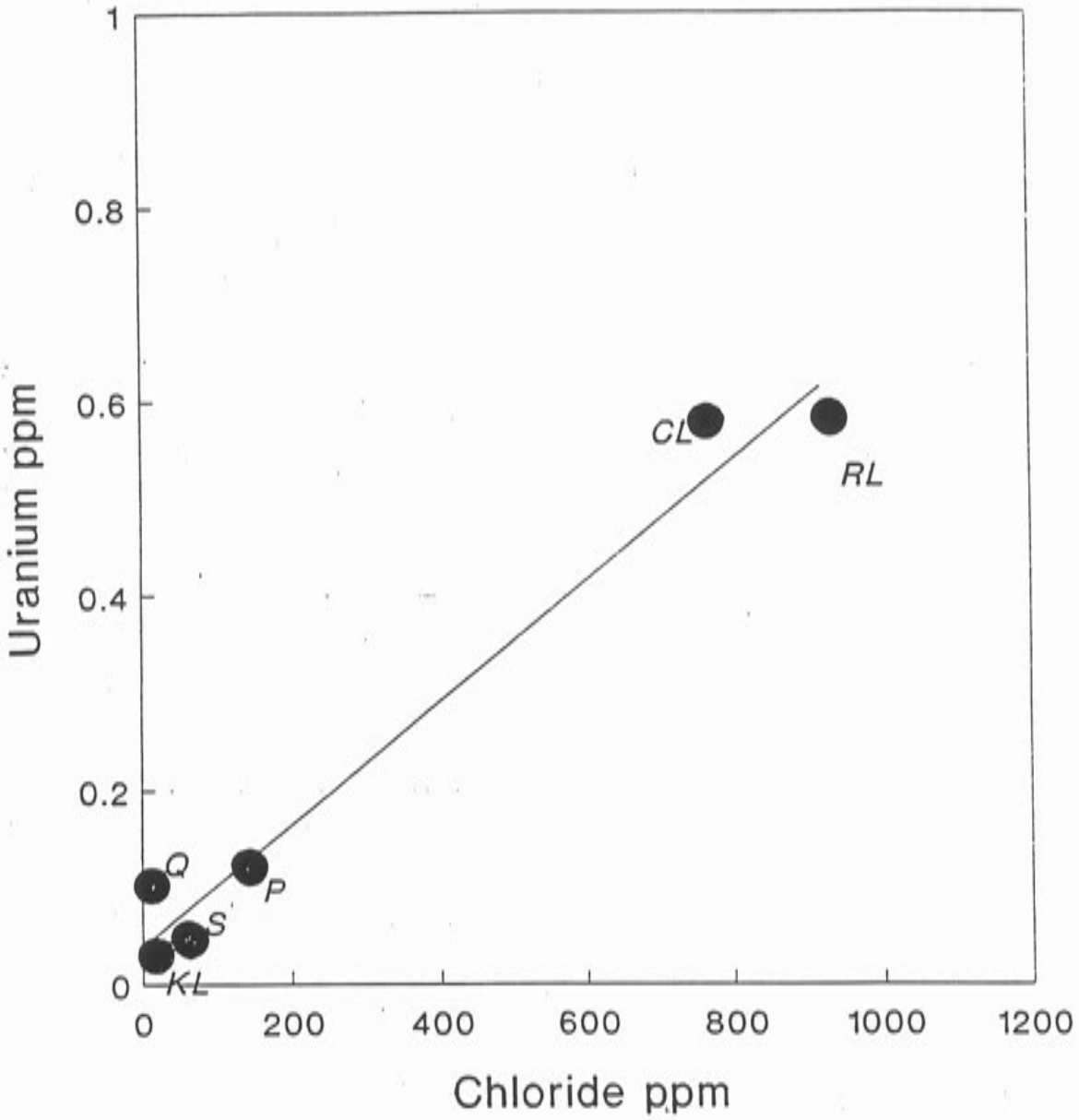


FIGURE 2: CORRELATION OF URANIUM AND CHLORIDE IN SOLUTION




KEY: Saskatchewan Mines: CL = Cluff Lake, RL = Rabbit Lake, KL = Key Lake.

Ontario Mines: P = Panel, Q = Quirke, S = Stanleigh.

FIGURE 3: KEY LAKE PROCESS FLOWSHEET

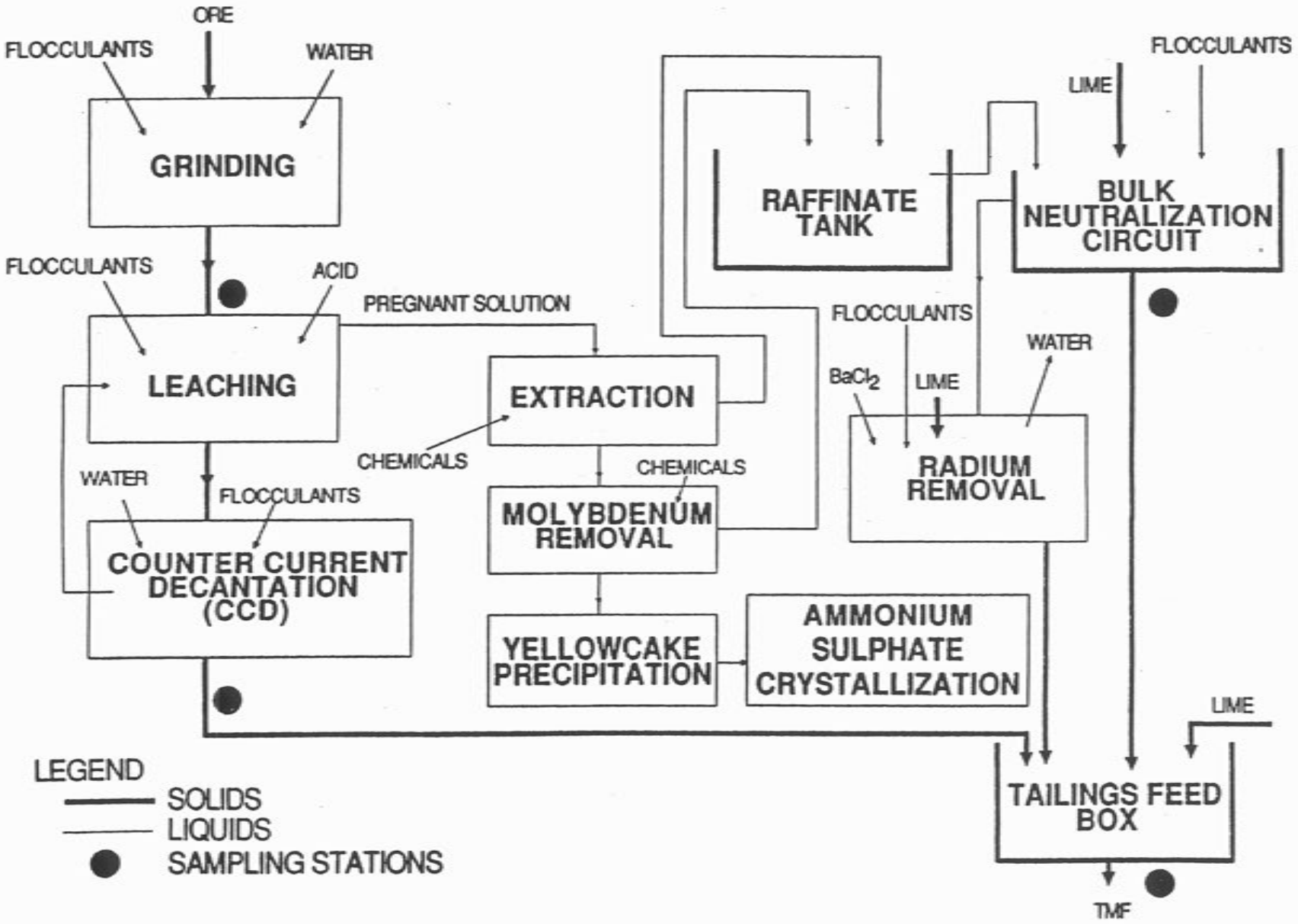


FIGURE 4: KEY LAKE - MOLYBDENUM EXTRACTION FROM URANIUM STRIP SOLUTION

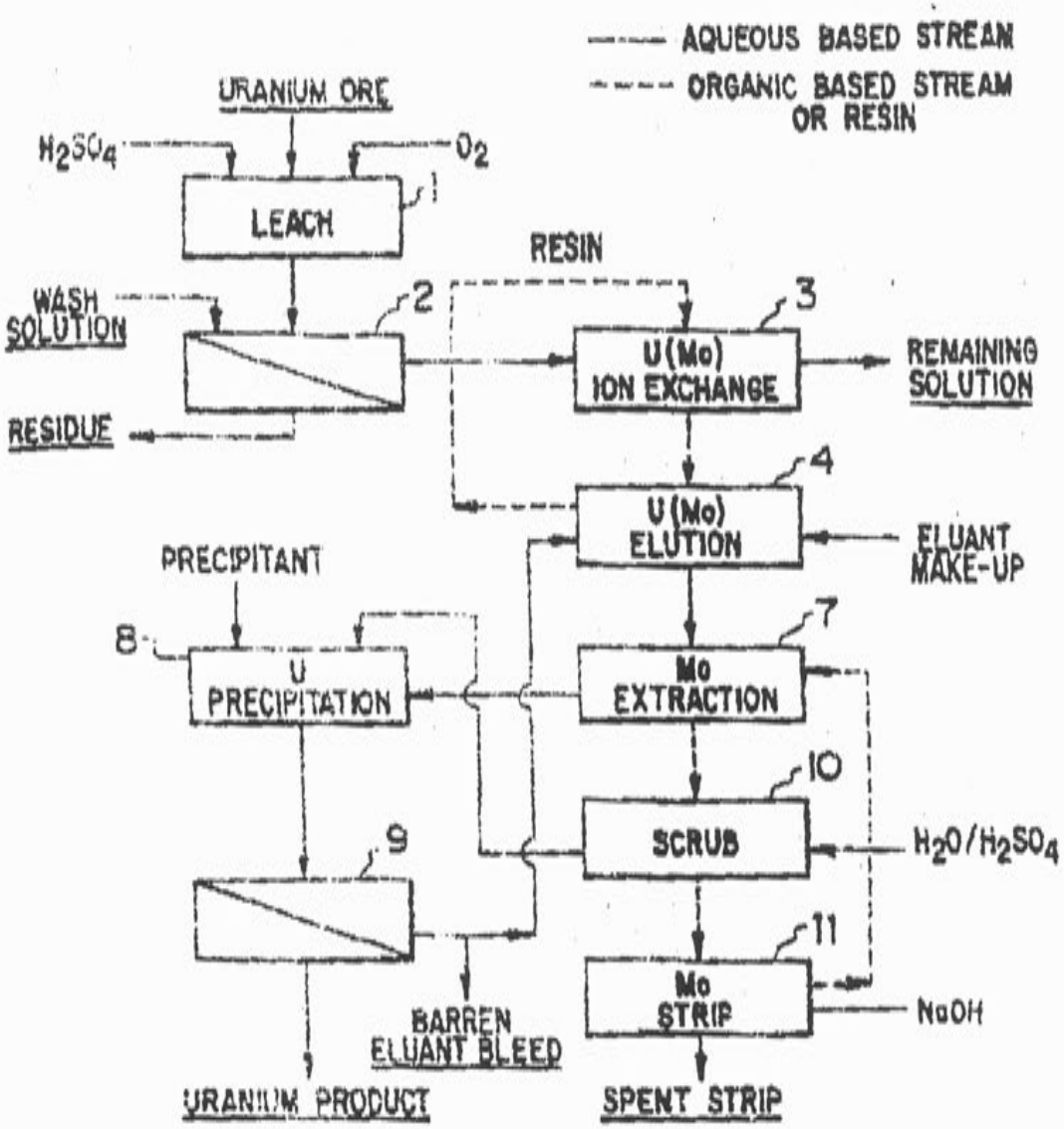


FIGURE 5: RABBIT LAKE PROCESS FLOWSHEET

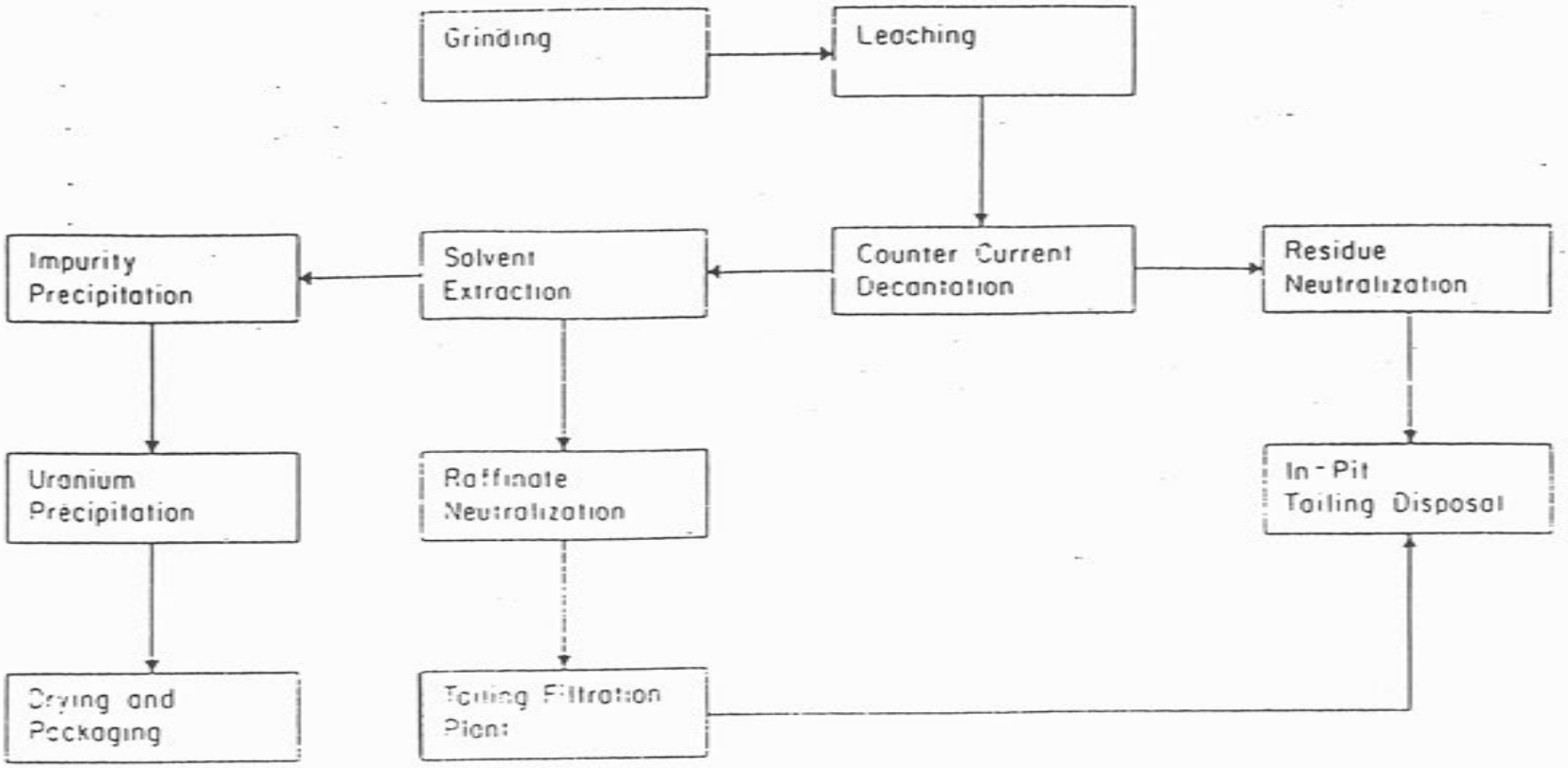


FIGURE 6: EFFECT OF TEMPERATURE ON AMINE EXTRACTION OF URANIUM

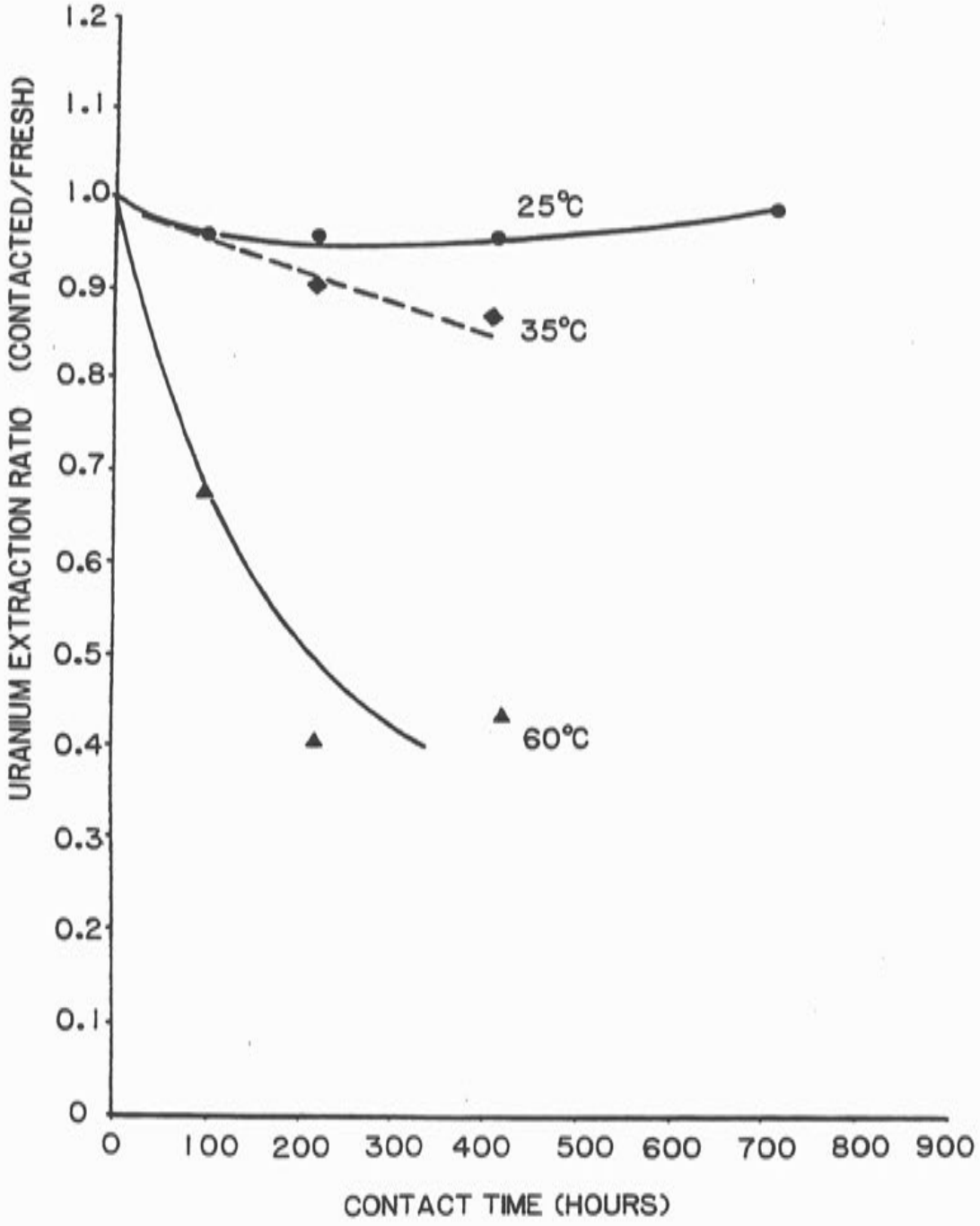


FIGURE 7: RABBIT LAKE WASTE TREATMENT SYSTEM

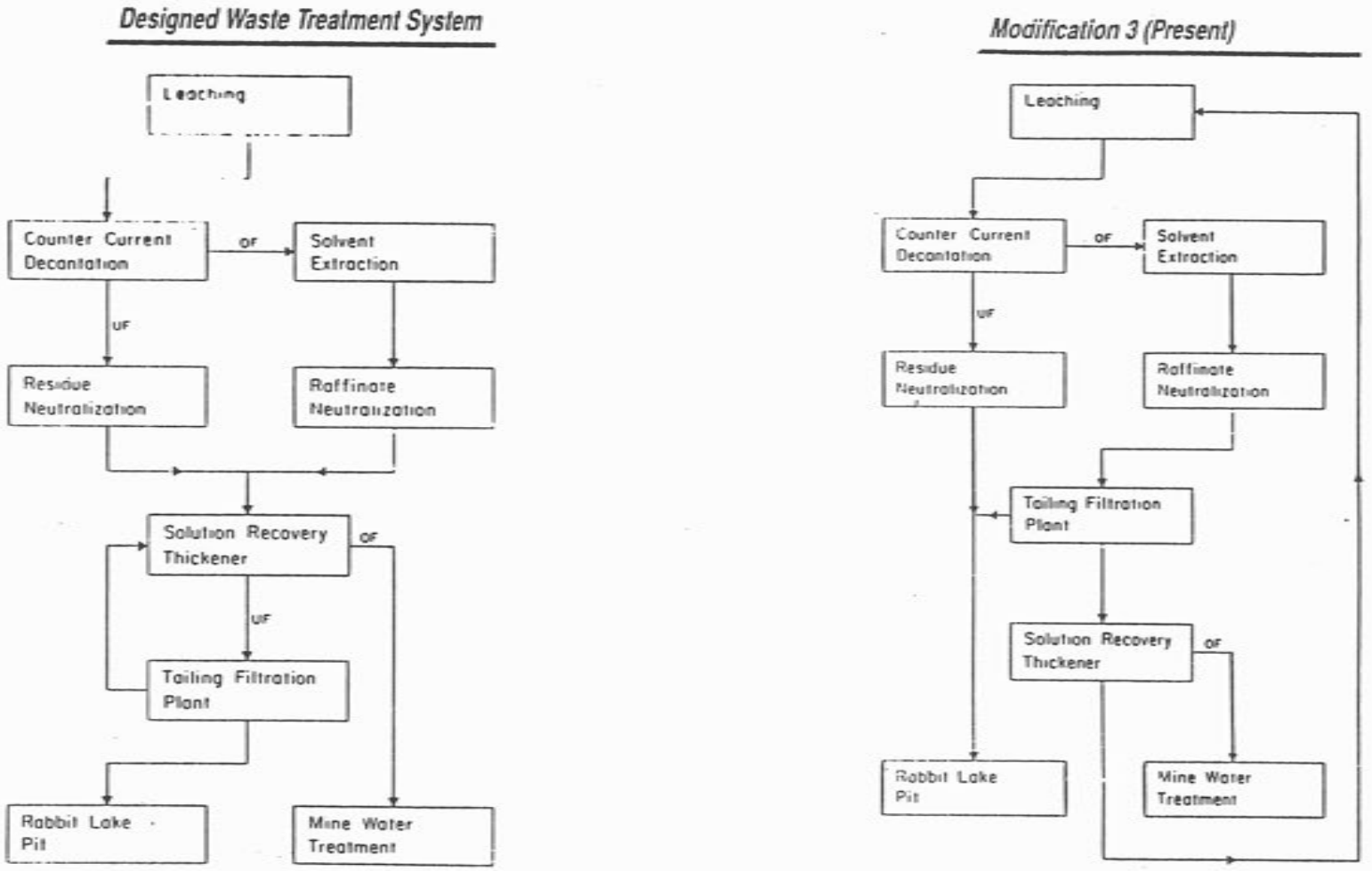


FIGURE 8: MCCLEAN LAKE PROCESS FLOWSHEET

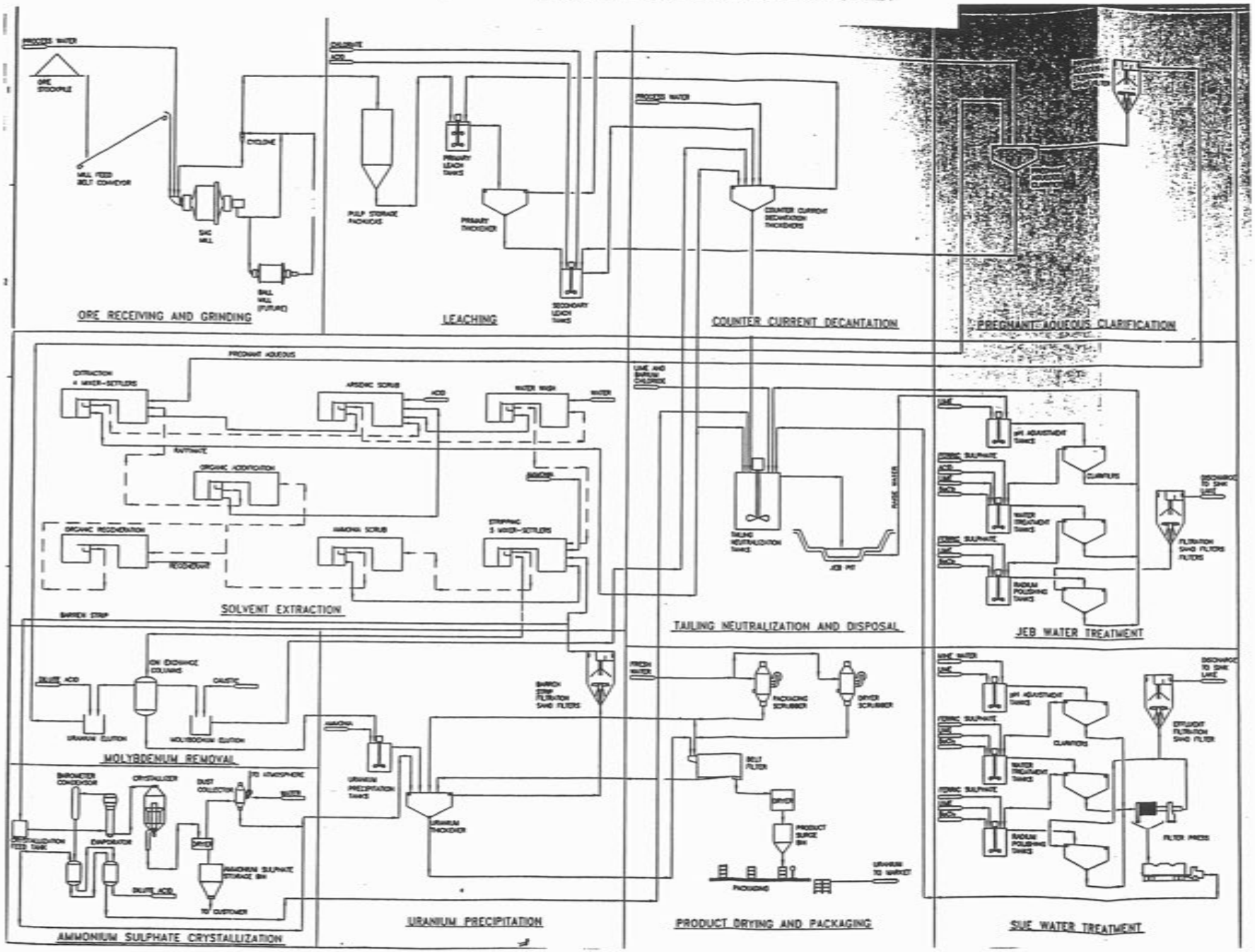


FIGURE 9: MCCLEAN LAKE MILL
MIDWEST AND CIGAR LAKE LEACHING FLOWSHEET

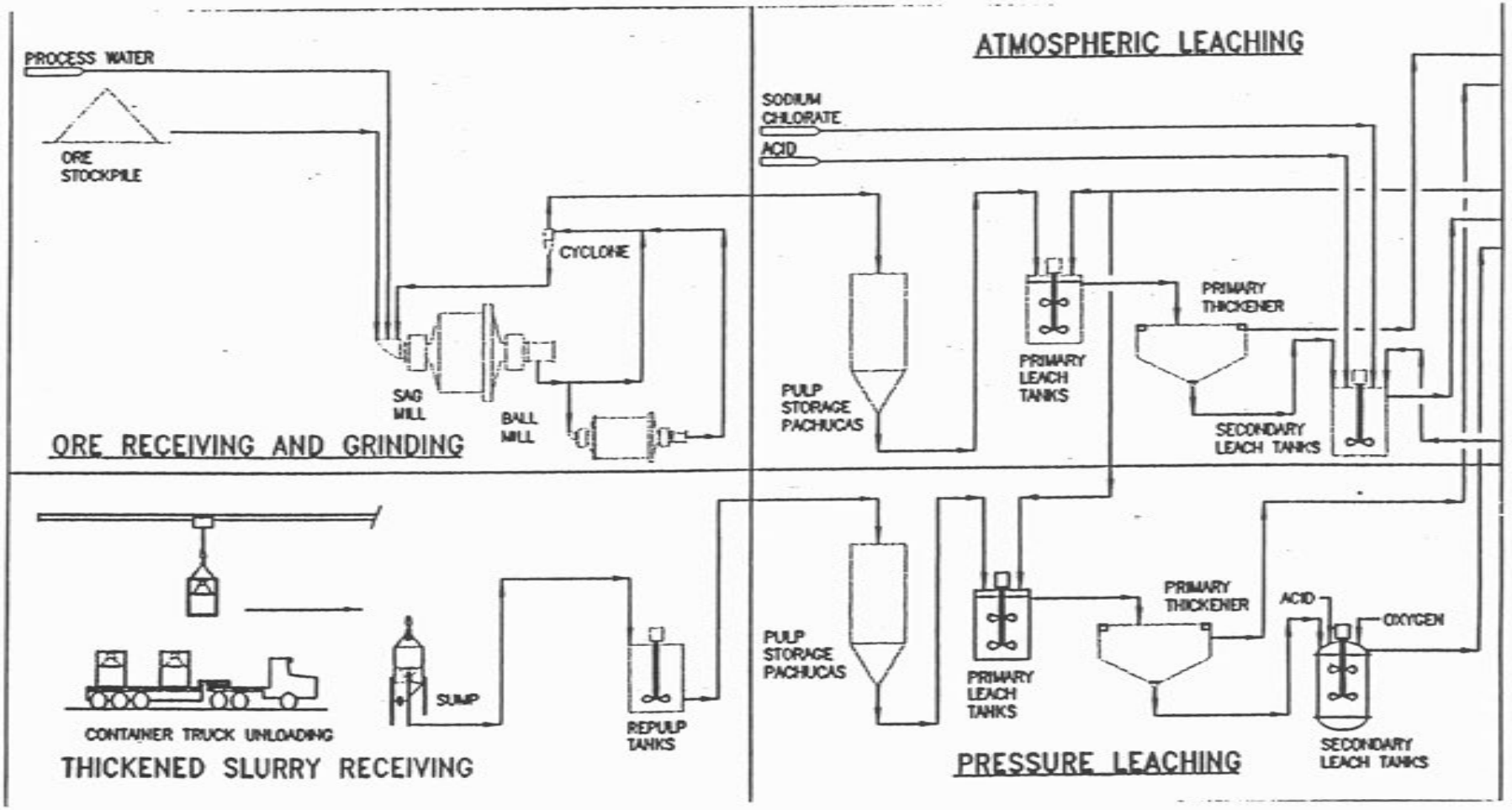


FIGURE 10: TYPICAL UNDERGROUND GRINDING PROCESS FLOWSHEET

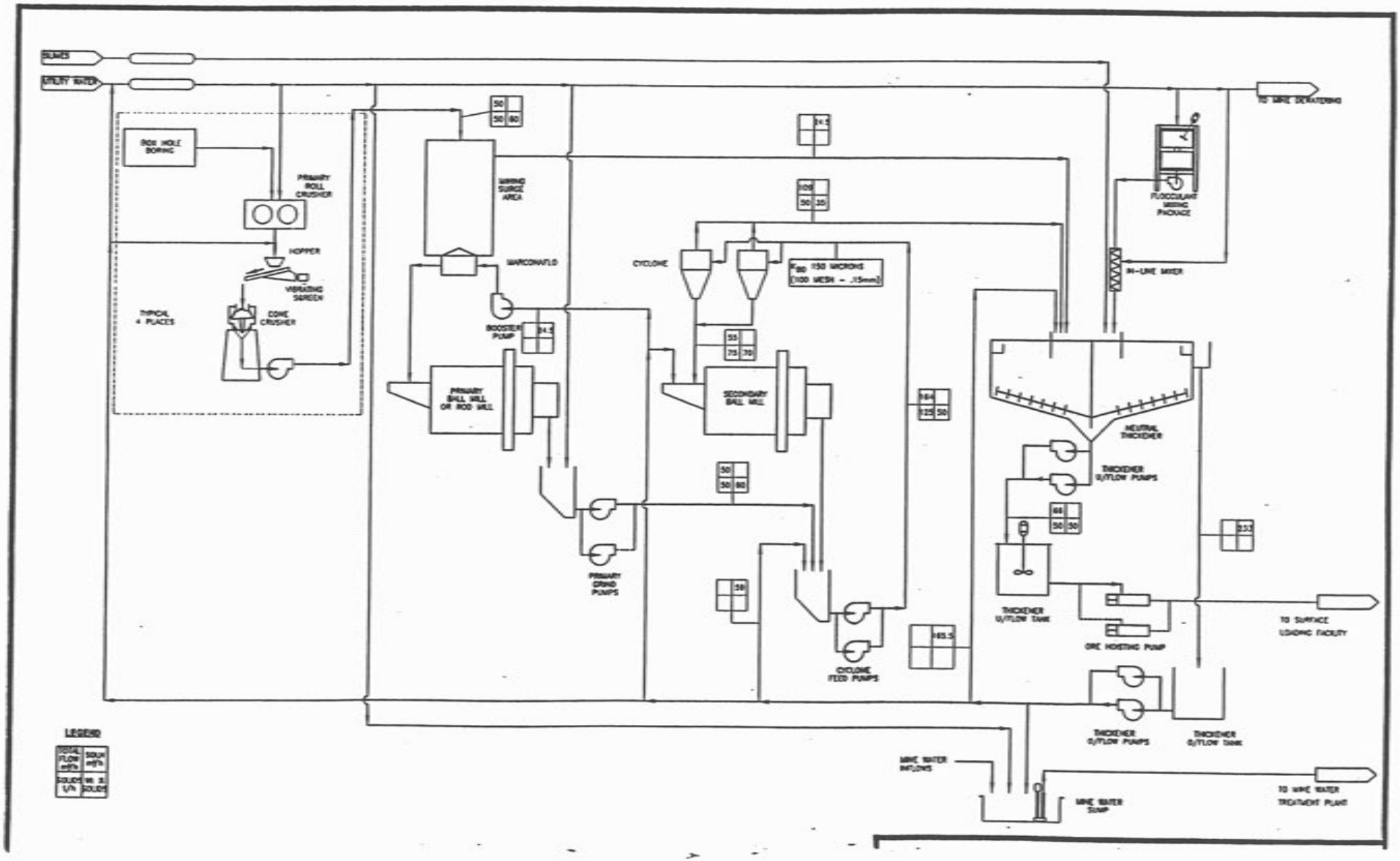


FIGURE 11: TYPICAL SLURRY LOADING FLOWSHEET

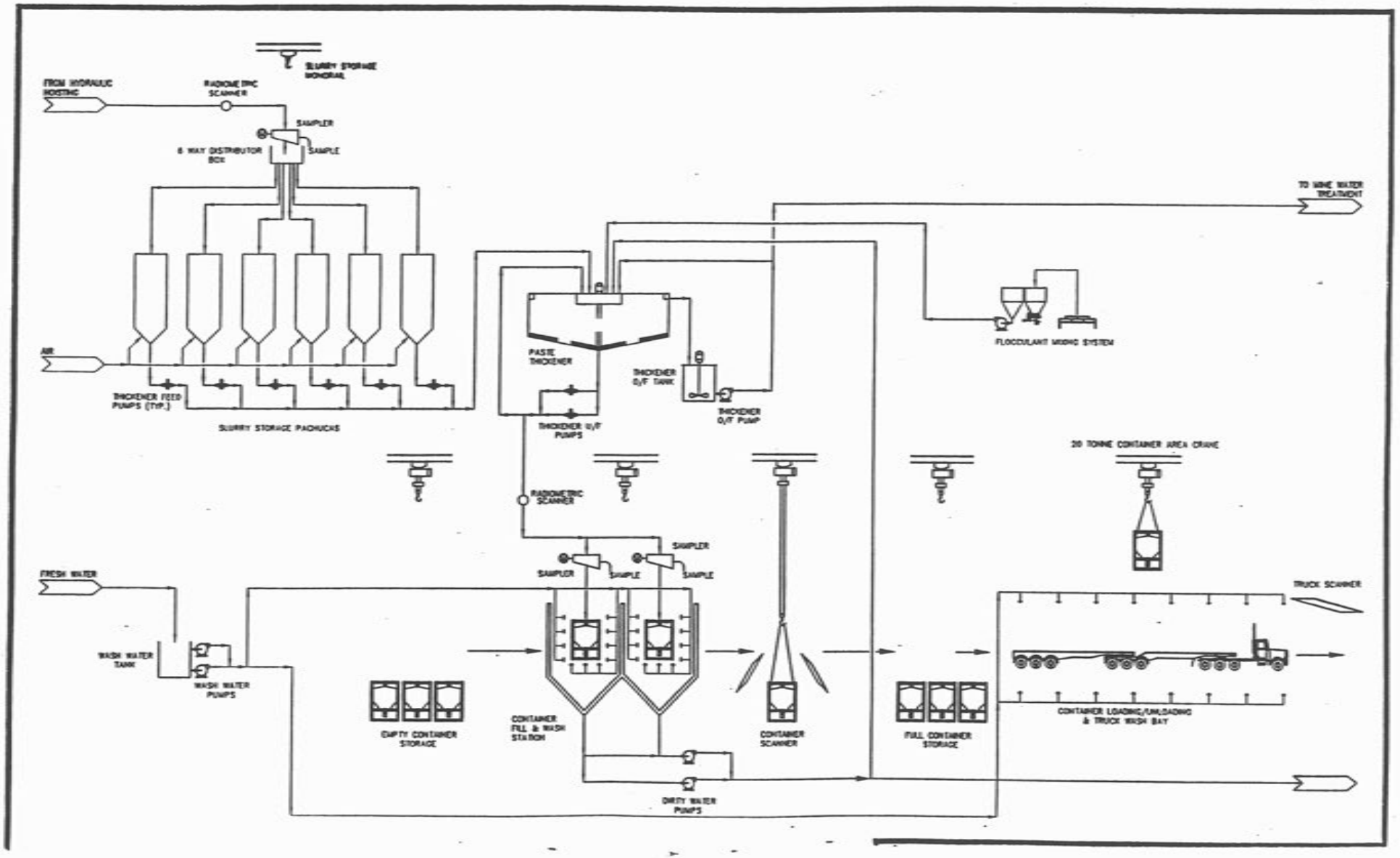
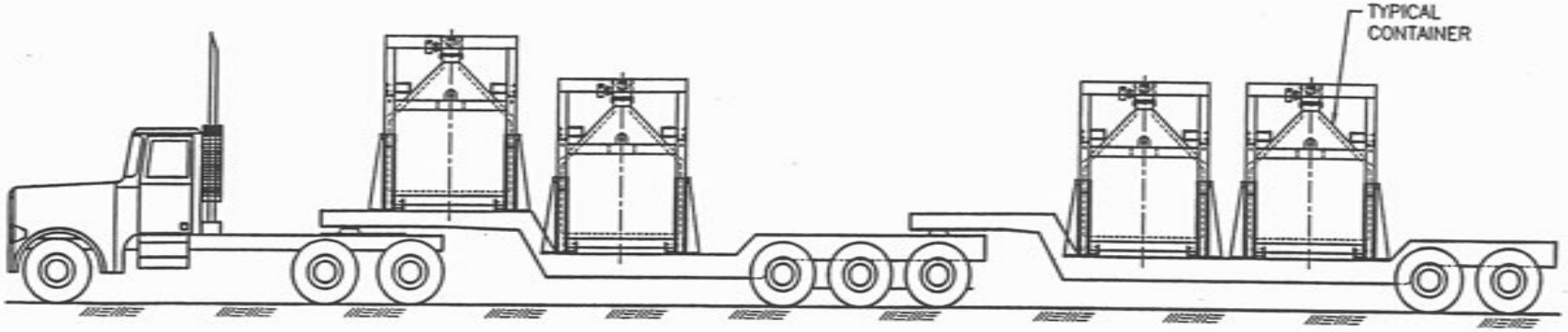


FIGURE 12: TYPICAL ORE HAULING UNIT



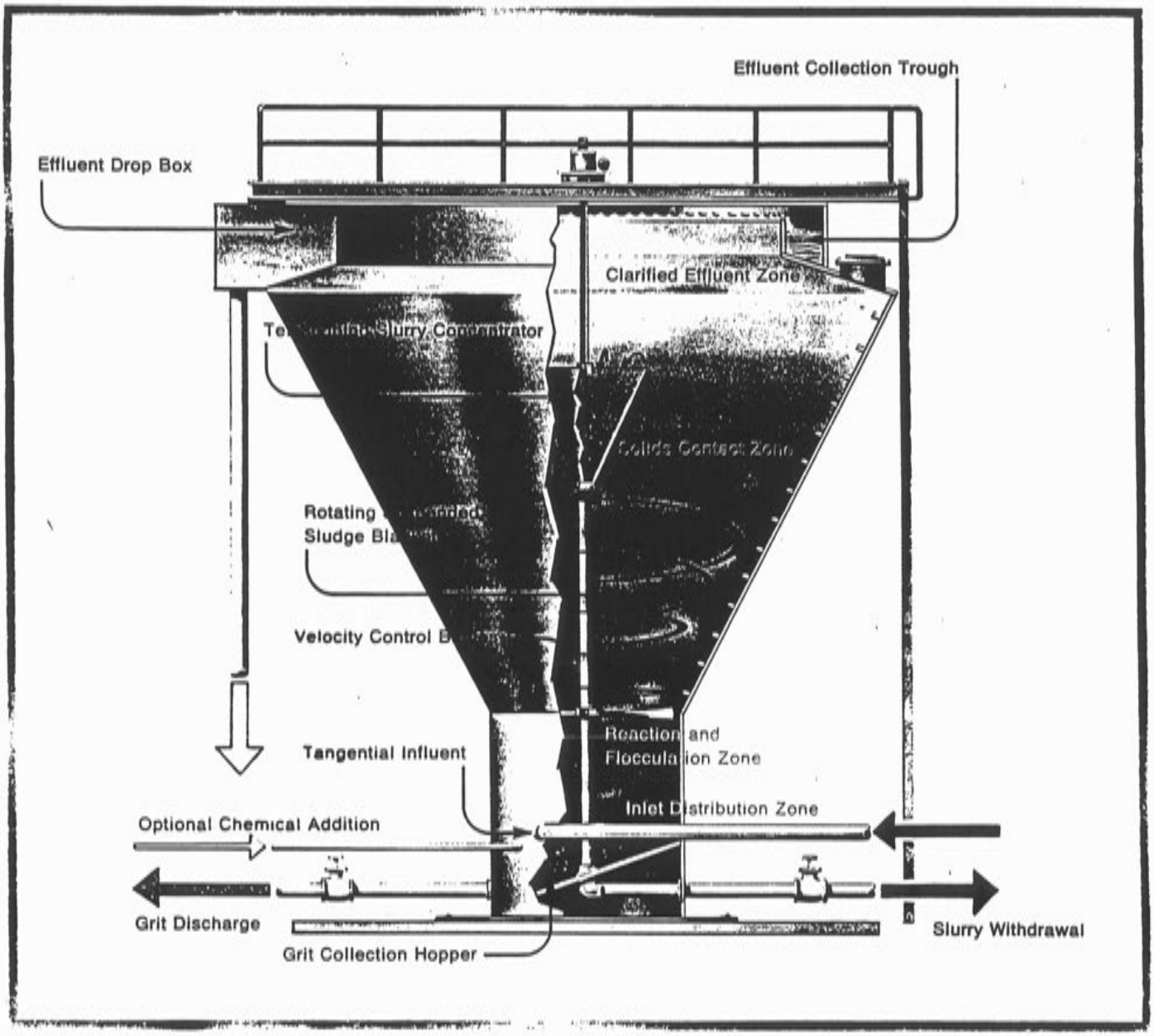

SIDE VIEW

FIGURE 13: WALKER CLARICONE

The ClariCone reactor clarifier can be applied to any liquid-solid separation process that would use a conventional upflow solids contact reactor-clarifier. These units are most commonly used to treat potable water, industrial process water, and wastewater. However, as discharge limitations become more restrictive, upflow solids contact clarification processes are being used extensively in municipal sewage treatment—especially in tertiary applications.

The ClariCone unit is available in above grade, below grade or partially buried designs and the layout and design can be tailored to suit individual plant needs.

There are eight standard units available with capacities ranging from 0.25 MGD to 3.0 MGD (2,366 m³/D to 28,388 m³/D). "Capacity" is based on a rise rate of 1.0 GPM/ft² (40.8 l/min/m²) measured at the major diameter of the ClariCone reactor clarifier unit.



# A NEW Concept in Sand

FIGURE 14: CONTINUOUS UPFLOW SAND FILTER

## Continuous Sand Filtration

The DynaSand Filter is a continuous backwash, upflow, deep bed granular media filter. The filter media is continuously cleaned by recycling the sand internally through an airlift pipe and sand washer. The regenerated sand is redistributed (right) on top of the sand bed allowing for a continuous uninterrupted flow of filtrate and reject water.

Feed is introduced into the bottom of the filter, then flows upward through a series of riser tubes and is evenly distributed into the sand bed through the open bottom of an inlet distribution hood (A) (Fig. 1). The influent flows upward through the downward moving sand bed (B) with the solids being removed. The clean filtrate exits from the sand bed, overflows a weir (C) and is discharged from the filter (D). Simultaneously the sand bed, along with the accumulated solids, is drawn downward into the suction of an airlift pipe (see Fig. 2) which is positioned in the center of the filter. A small volume of compressed air is introduced into the bottom of the airlift (E). The sand, dirt, and water are transported upward through the pipe at a rate of about 200 gpm/ft². The impurities are scoured loose from the sand during this violently turbulent upward flow. Upon reaching the top of the airlift (F), the dirty slurry spills over into the central reject compartment (I). The sand is returned to the sand bed through the gravity washer/separator (G) which allows the fast settling sand to penetrate, but not the dirty liquid. The washer/separator is placed concentrically around the upper part of the airlift and consists of several stages to prevent short circuiting (Fig. 3). By setting the filtrate weir (C) above the reject weir (J) a steady stream of clean filtrate flows upward, countercurrent to the sand, through this washer section and acts as a liquid barrier that carries away the dirt and reject water (K). Since the sand has a higher settling velocity than the dirt particles, it is not carried out of the filter. The sand is redistributed by means of a sand distribution cone (H). The sand bed is continuously cleaned while both a continuous filtrate and a continuous reject stream are produced.

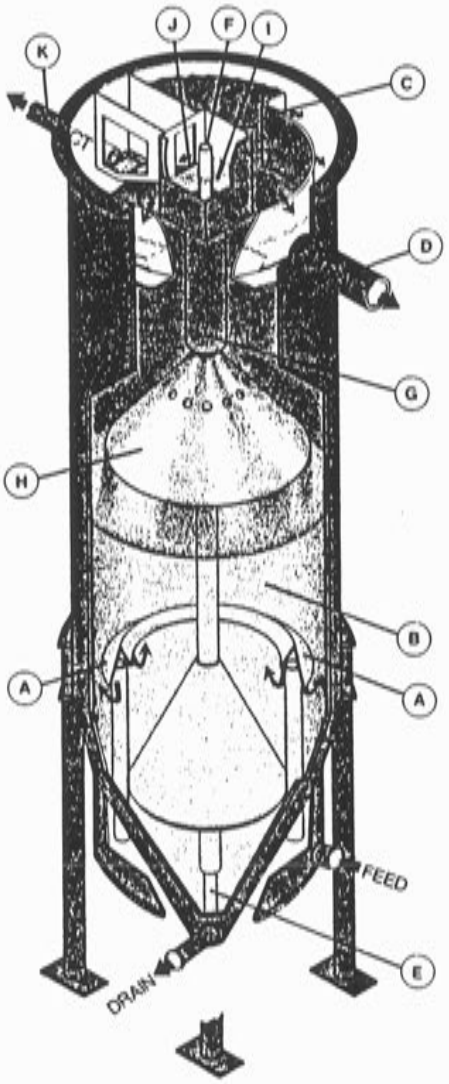
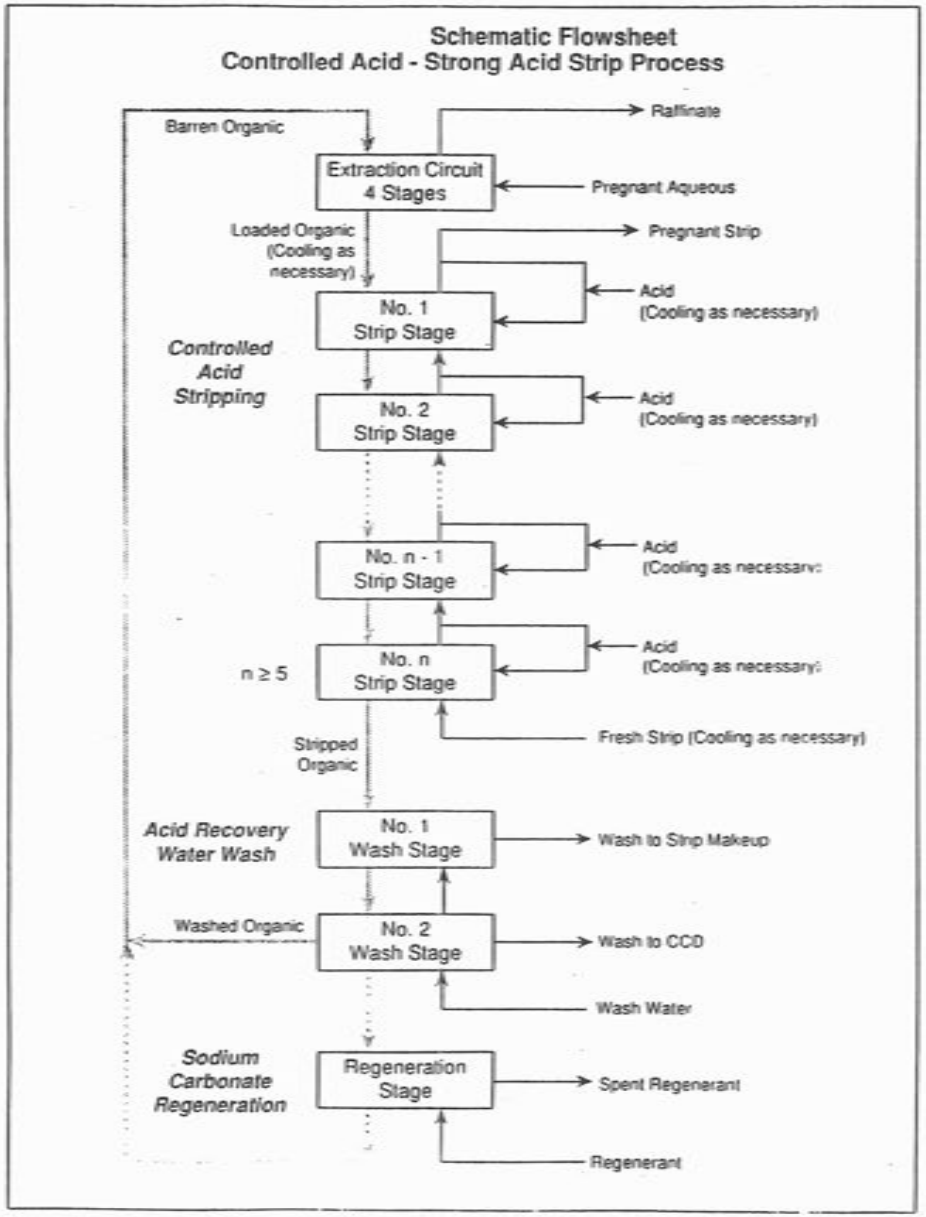


FIGURE 15: CONVENTIONAL STRONG ACID STRIP AND CONTROLLED ACID - STRONG ACID STRIP



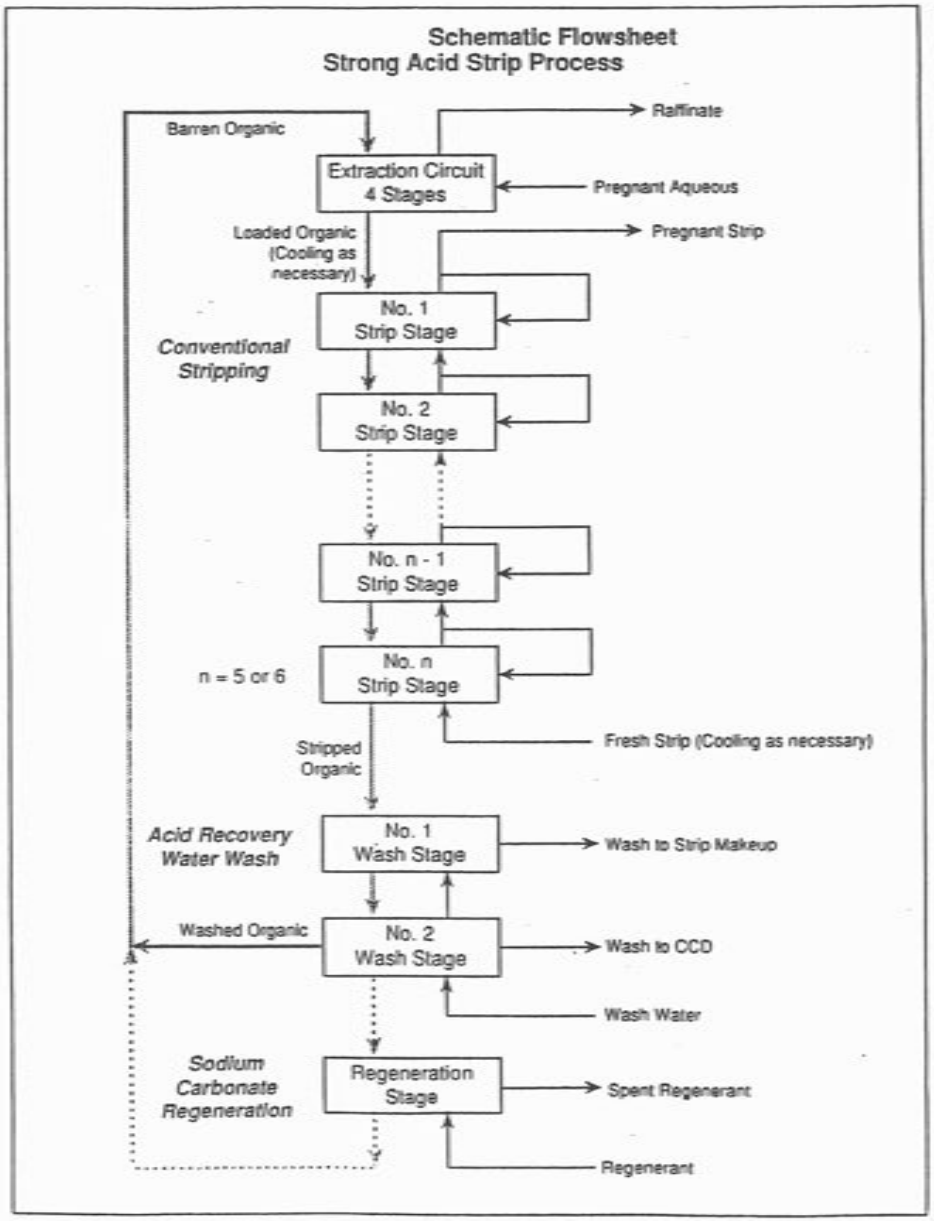
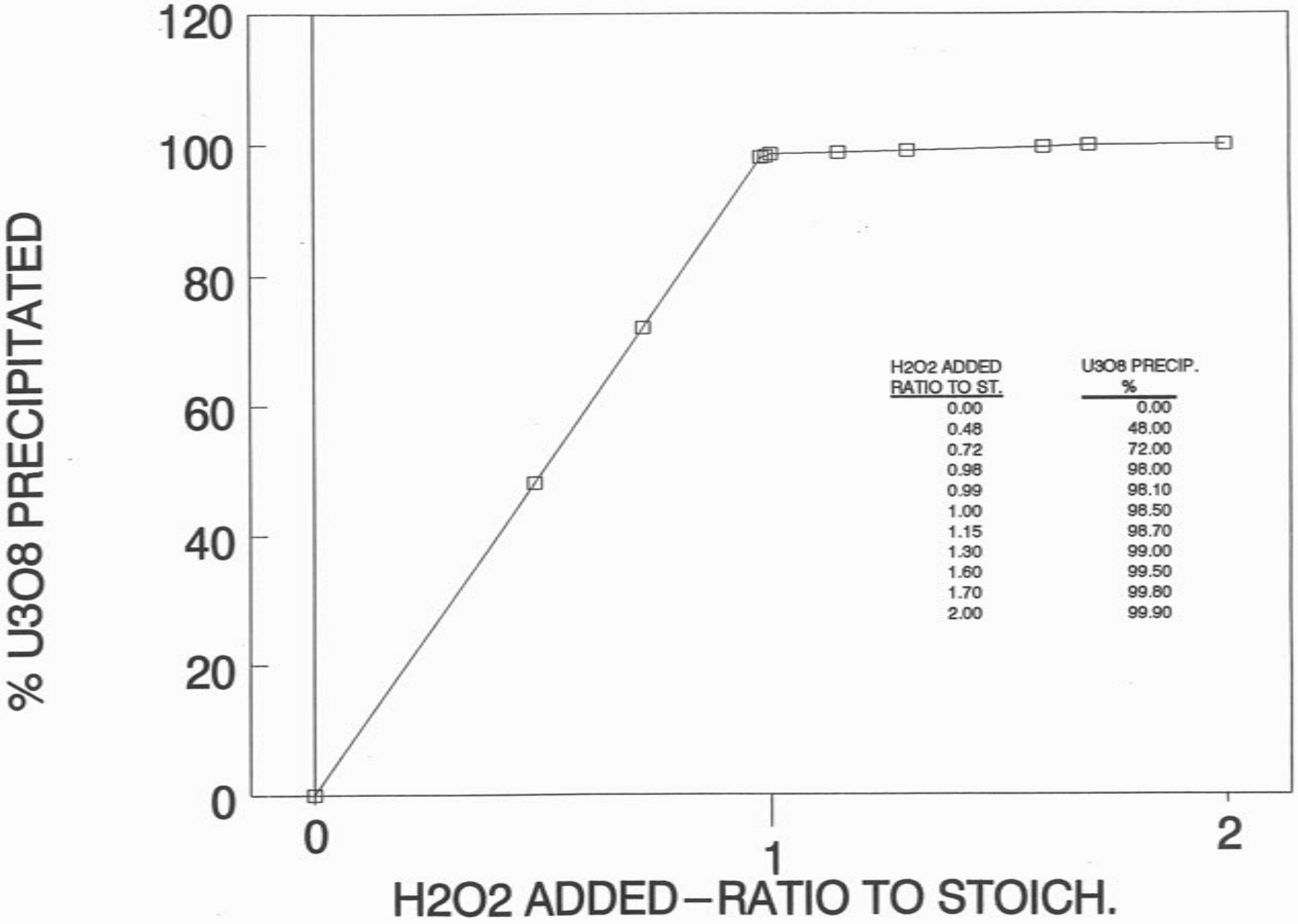



FIGURE 16: % $U_3O_8$ PRECIPITATION VS $H_2O_2$ ADDITION




| H2O2 ADDED RATIO TO ST. | U3O8 PRECIP. % |
|---|---|
| 0.00 | 0.00 |
| 0.48 | 48.00 |
| 0.72 | 72.00 |
| 0.98 | 98.00 |
| 0.99 | 98.10 |
| 1.00 | 98.50 |
| 1.15 | 98.70 |
| 1.30 | 99.00 |
| 1.60 | 99.50 |
| 1.70 | 99.80 |
| 2.00 | 99.90 |

FIGURE 17: SPLIT PEROXIDE PRECIPITATION FLOWSHEET

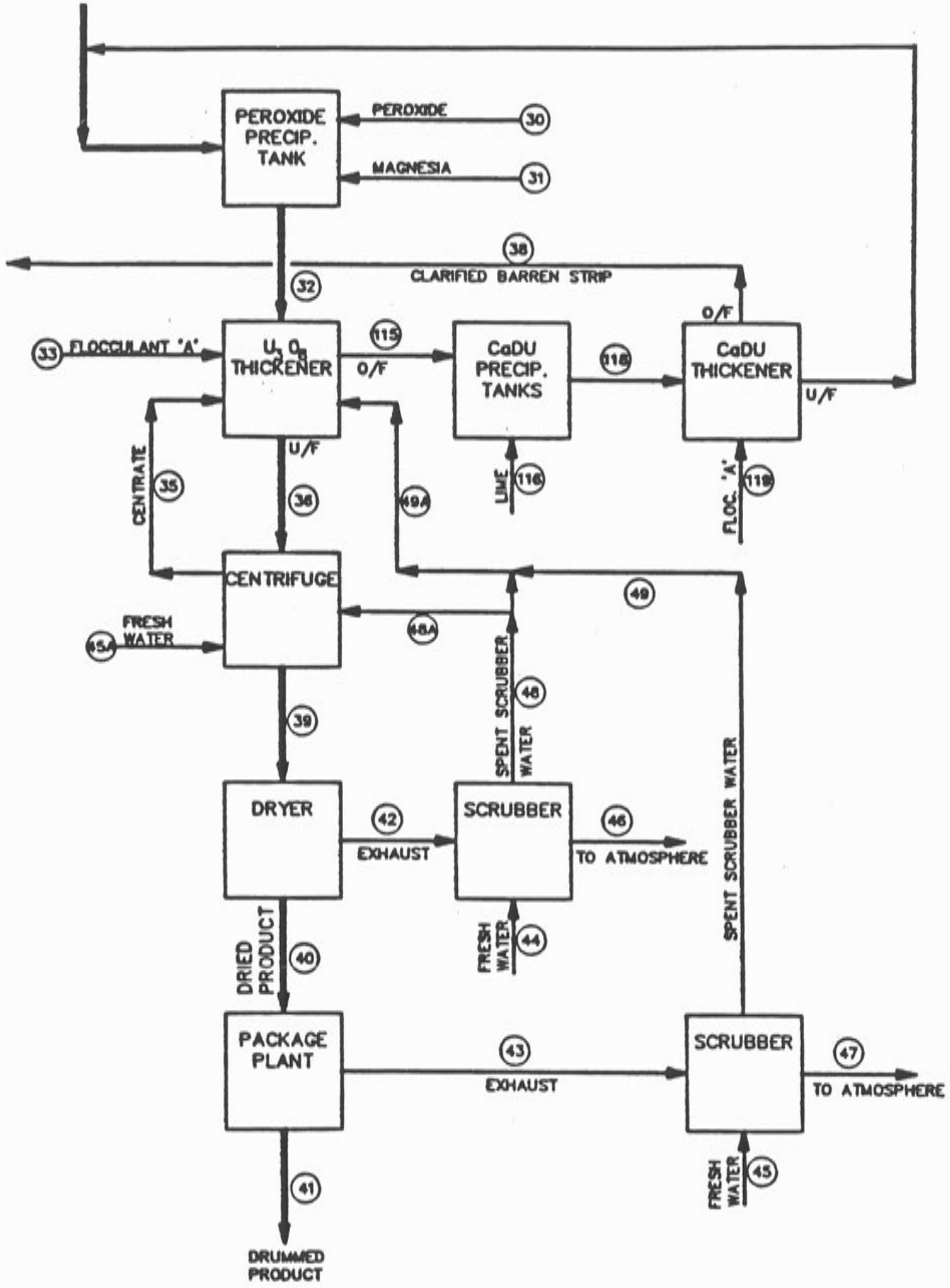
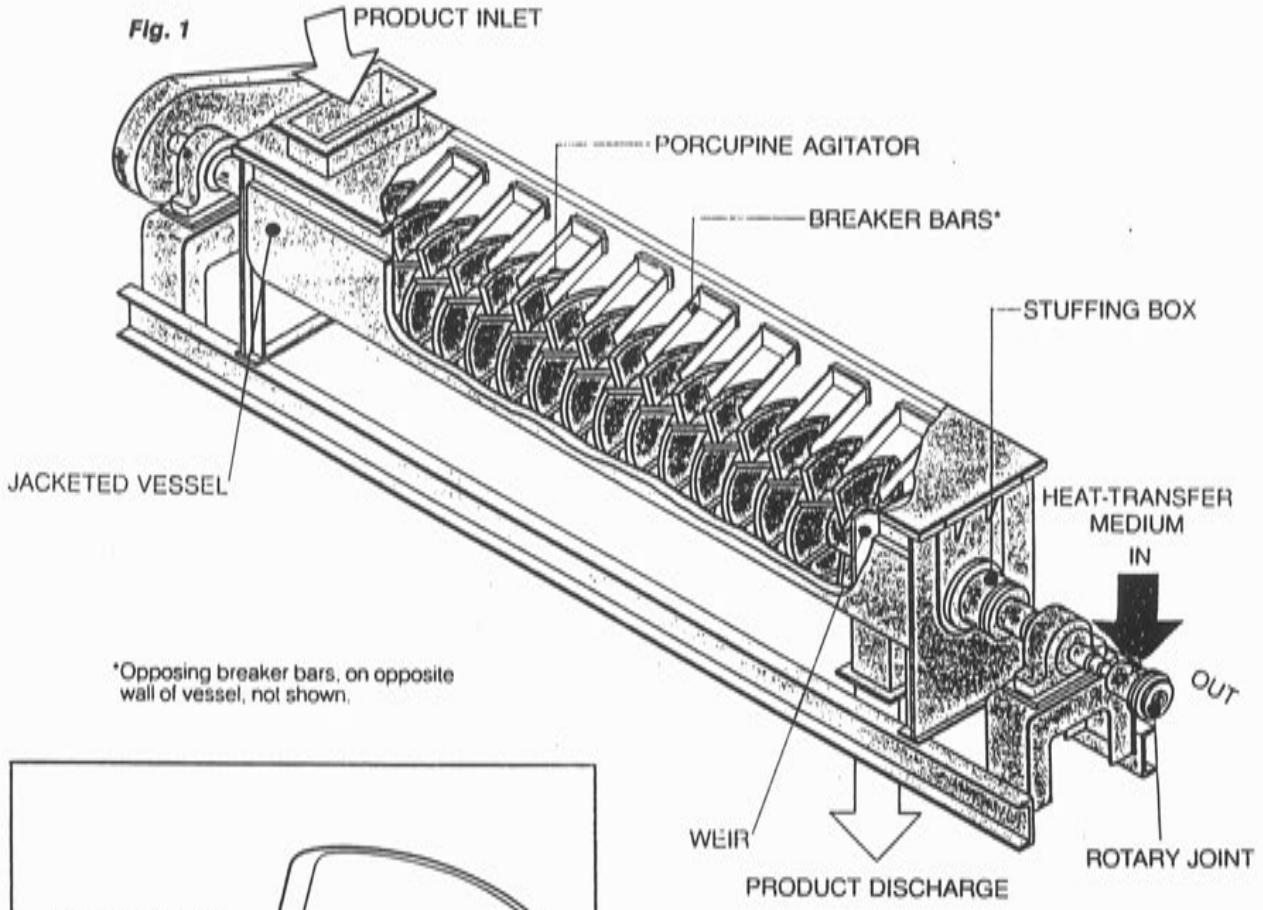


FIGURE 18: PORCUPINE DRYER

# SINGLE-SHAFT PORCUPINE® PROCESSOR

*Cutaway shows unitized design.*
*Breaker bars (optional) enhance local mixing and assure self-cleaning, when required.*



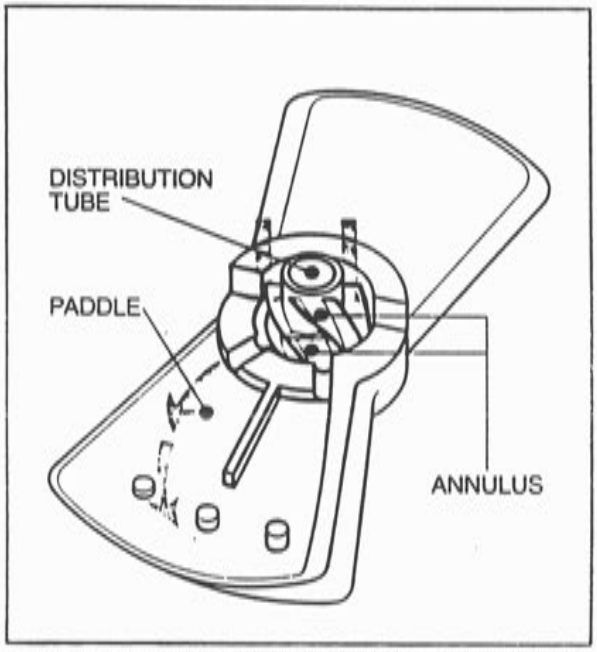




*Fig. 2 Paddle cutaway indicates flow of heat-transfer medium from paddle to paddle.*

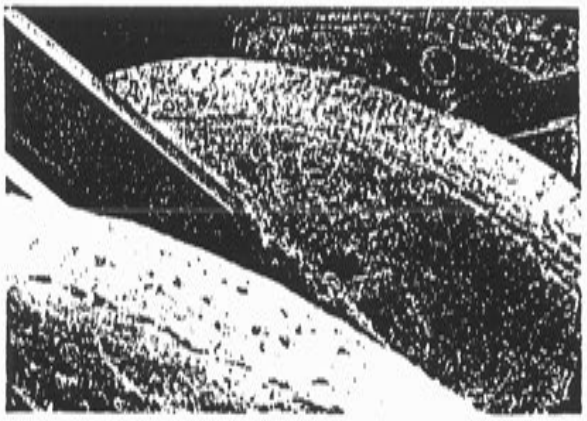


*Fig. 3 For severely abrasive applications, blade tips can be protected by hard surfacing. (Hard surfacing can be re-applied if severe wear occurs.)*

# PART II

# URANIUM ORE PROCESSING IN AUSTRALIA AND TECHNOLOGICAL DEVELOPMENTS

by
M.L. Jansen

International Project Development Services
Pty Limited

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# 1. OLYMPIC DAM

Olympic Dam , 100% owned by Western Mining Corporation, is situated in South Australia, 560 km NNW of Adelaide. It is a producer of high quality copper and gold products in addition to uranium.

Olympic Dam consists of a large underground mine and a complex processing plant.

Discovered in 1975, production began in June 1988 - almost 13 years later. It is one of South Australia's leading business enterprises and is the state's largest long term development project.

Ore throughput is currently 3 million tonnes per annum. Current mine reserves are 580 million tonnes at 2.1% Cu, 0.6 kg/t U and 2.2 g/t Au. Annual production is about 84,000 tpa copper cathode, 1500 tonnes uranium, 30,000 ounces gold and 400,000 ounces silver. Estimated uranium reserves are 360,000 tonnes of uranium.

The orebody consists of haematite-rich breccias containing medium grained disseminated copper sulphides and fine grained disseminated pitchblende. The uranium minerals predominate in the haematite and silicate gangue but there is also some association with copper/sulphide gangue composites. The uranium is mostly present as uraninite, and traces of coffinite and brannerite.

After primary crushing underground, the ore is ground in a circuit consisting of an autogenous mill, ball mill and pebble crusher, and treated in a bulk sulphide copper flotation plant. About 80% of the uranium minerals report to the flotation tail, from which they are recovered in an acid leach. The remaining 20 % are recovered in a copper concentrate, which is also processed for uranium recovery by acid leaching prior to final concentrate production as flash smelter feed.

Coarse tailings along with rock waste from the underground mine are used as backfill. The fine fraction still containing potentially valuable minerals (rare earths etc) is emplaced in tailings dams covering about 200 hectares on the lease.

The hydrometallurgical processing plant consists of the following facilities for yellowcake production and acid leachable copper production:

- concentrate leaching
- concentrator tails leaching
- flue dust leaching for copper recovery and radionuclide disposal
- counter current decantation

- clarification and filtration
- copper solvent extraction
- uranium solvent extraction, drying and packaging
- tailings desliming
- acidic liquor recycling plant

A simplified block process flowsheet is shown in Fig 1.

The plant is being expanded to handle 8.5 million tpa ore throughput by early 1999. After expansion the yellowcake production capacity will increase to about 3700 tpa U3O8.

The expanded plant will include a single train CCD circuit followed by clarification and sand filtration, producing up to 2200 m3/h filtered aqueous feed to two new trains of copper SX followed by uranium SX.

The existing uranium recovery plant includes two trains of Krebs FRP fully enclosed mixer settlers for both CuSX and USX, handling about 550 m3/h combined aqueous flow. Subject to satisfactory performance from a single train full scale uranium pilot plant extraction pulse column, the uranium expansion program is expected to include Bateman pulsed columns for uranium extraction, and conventional mixer settlers for three-stage scrubbing and four-stage stripping.

Stripped solvent is acidified in a mixer settler followed by continuous regeneration on a 10% solvent bleed stream.

Loaded strip solution from both the existing and new plants will be precipitated in 2 new tanks followed by thickening and washing of the precipitate in existing equipment.

A new surge tank will take thickener underflow and feed two duplicate centrifuge and calciner trains, one of which is an existing train. Drumming of yellowcake will be carried out in the existing packaging line.

Equipment innovations in the current uranium plant include :

- SX extraction of copper (Acorga M5640) from a combined copper and uranium PLS, followed by SX extraction of uranium (Alamine 336) from the copper circuit raffinate
- Krebs SX plants for both copper and uranium extraction

Process innovations include:

- operation of the USX (and CuSX) circuits at 40-50 C

- leach solution composition adjustment ahead of CuSX to minimise solids deposition and crud formation in CuSX

- radionuclide recovery from smelter dust

Process disappointments have included:

- unacceptably high solvent losses in CuSX (up to 400 ppm)

- excessive consumption of ammonia in yellowcake precipitation (inefficient gas dispersion)

- unacceptably large variations in Cu and U3O8 liquor feed composition caused by upsets in upstream CCD and copper refinery operations, and consequent higher Cu and U3O8 losses than design

- high solvent losses from Jameson cells installed for organic recovery from CuSX raffinate

Subject to ongoing detail design and technology reviews, process and equipment innovations in the Olympic Dam expansion program are expected to include:

- ROM ore blending and reclaiming stockpile, to smooth out mine grade variations

- expanded PLS storage ahead of CuSX to further reduce grade variations to CuSX and USX

- Bateman pulse columns for uranium extraction to reduce solvent losses in the presence of solids carryover from CuSX

- conventional mixer settlers for CuSX extract, strip and scrub and USX strip and scrub, to reduce solvent losses, and minimise piping runs

- fully enclosed HDPE lined concrete settlers and surge tanks with common settler walls to reduce settler area footprint and plant capital cost

- coalescers to minimise organic losses from raffinate

- continuous on-line Cu and U analysis for key aqueous streams

In summary Olympic Dam has demonstrated process innovation in the selection of the overall process flowsheet and equipment innovation in the original selection of Krebs SX technology for copper and uranium extraction. The new uranium plant is expected to show further equipment innovation with the use of Bateman pulse columns for USX extraction and the installation of either conventional mixer settlers or reverse flow mixer settlers for all other SX stages. The settlers are expected to be HDPE lined concrete as used on numerous projects in South America but not yet applied in Australia.

# 2. RANGER

Ranger Uranium Mines Pty Ltd, 100 % owned by Energy Resources of Australia Ltd (ERA) which is 66% owned by North Broken Hill Peko, has been operating an open pit uranium mine at a site near Kakadu, about 250 km east of Darwin, since 1981. The deposit was discovered in 1969 and consists of two ore bodies, Ranger 1 and Ranger 3.

Estimated reserves are 75,900 tonnes of uranium and the rated capacity 3,000 tonnes of uranium per annum. For a while the Ranger 1 mine was producing ore for only six months each year, with 1993-4 output at 1400 tonnes of uranium.

North Ranger 2 in the Northern Territory ( formerly known as Jabiluka and purchased from Pancontinental in July 1991) has estimated reserves of 90,400 tonnes of uranium at a grade 50% higher than Ranger 1 and 3, and is one of the world's larger high grade uranium deposits. North Ranger is 20 kilometres north of Ranger on the edge of the floodplain of the Magella Creek, a tributary of the East Alligator River.

The mineralisation occurs as finely disseminated pitchblende, which is more concentrated in disturbed, breciatted and contorted zones of quartz chlorite schists.

Nominal ore throughput at 3000 tpa U3O8 production rate is 1.150 Mt ore per annum averaging 0.29% U3O8.

The process flowsheet consists of primary and secondary crushing, rod and ball milling, neutral thickening, acid leach in pachucas with Caro's acid ( H2O2 in concentrated sulphuric acid) as oxidant, CCD, clarification and sand filtration, SX, precipitation, drying and packaging., and tailings neutralisation. In the early stages of the operation, pyrolusite (MnO2) was used as an oxidant rather than Caro's acid, but Caro's acid was found to be more cost effective.

Sulphuric acid is manufactured on site from elemental sulphur from a 185 t/d double absorption acid plant.

Process innovations include the use of Caro's acid. No major equipment innovations appear to have been used.

Process innovations considered for the expansion included the use of peroxide rather than ammonia for yellow cake precipitation. The benefits of peroxide include the production of a coarser product from uranium precipitation, which can be calcined at a lower temperature than ammonium diuranate. However it is not known at this stage whether a decision was made to use peroxide or not.

Process disappointments are understood to have included periodic crud formation in both the extraction and strip stages of solvent extraction, due to presence of solids in the leach solution or from unwanted yellowcake precipitation during SX strip. Drier capacity is also understood to have been limited at times due to excessive moisture in the product from the yellow-cake centrifuge, possibly due to maintenance limitations. These shortcomings and others are believed to have been overcome in the existing plant and/or the proposed expansion project to process Ranger North ore.

In summary the Ranger Uranium plant is a relatively conventional plant with limited process innovations, other than use of Caro's acid as a leach oxidant.

# 3. KINTYRE

Currently at the final feasibility and ERMP preparation stage, the Kintyre project is being developed by Canning Resources, a wholly owned subsidiary of RTZ/CRA.

Located on the edge of the Great Sandy Desert in the Eastern Pilbara region of Western Australia, about 1200 kilometres NNE of Perth, the Kintyre project lies adjacent to the northern boundary of the Rudall River National Park, the largest national park in Western Australia, and the second largest in Australia.

Discovered in 1985, the project contains a resource of 36,000 t U3O8 in vein type mineralisation. Initial production output is projected at 1,500 tpa U3O8 from 280,000 tpa ore at a feed grade of 0.58% $U_3O_8$.

The main mineral is coarse pitchblende with minor accessories such as native bismuth, copper, lead and zinc sulphides, gold, platinum and palladium.

The current schedule calls for construction to begin in 1997 and production to commence in the second half of 1999. The mine will be operated on a 14 days on, 7 days off basis with personnel commuting from Perth to the mine site by aircraft. The process plant will be operated 2@12 hr shifts per day - 7 days per week.

The mine will be a conventional open pit, up to 150 m depth.

Capital cost of the project has been estimated to be $120 million and annual revenue $60-70 million.

The total area disturbed, including up to five small open pits, will be about 300 ha, with the treatment plant occupying about six hectares. An additional 100 ha will be required for infrastructure.

Ore will be segregated into high, medium and low grade zones in a stockpile, with a minimum capacity of 4 months.

The vein type ore is readily upgraded over 4-fold by radiometric sorting and gravimetric methods, which reduce the tonnage to the hydrometallurgical plant to an annual tonnage of 60,480 tpa at a feed grade of 2.16% $U_3O_8$.

The flowsheet includes:

- crushing
- ore upgrading by sorting and HMS
- grinding

- acid leaching
- iron precipitation with lime
- iron precipitate releach
- uranium precipitation with peroxide and alkali
- product filtration
- non-contact drying
- automated packaging

Process innovations include:

- ore sorting and HMS for:
  - ore upgrading
  - reduction of wet plant size, capital cost, operating cost and manning
- impurity rejection by lime precipitation rather than SX
- U3O8 precipitation by peroxide and an alkali rather than ammonia
- U3O8 solids recovery by filtration rather than centrifuge
- U3O8 drying by non-contact low temperature calciner rather than contact high temperature calciner
- fully automated robotic packaging
- tailings solids disposal as filter cake rather than slurry
- no tailings dam
- separate impoundment areas for:
  - wet filter cake storage
  - bleed solution storage
- maximum off-site modular construction
- high degree of process control automation

No piloting of the process flowsheet has been carried out, although a mini-plant demonstration of the process is reportedly being planned.

Process risks presumably could include:

- ore sorting efficiency and/or availability turning out to be less than expected
- uranium coprecipitation with iron being higher than expected, resulting in higher lime and acid demand
- iron rejection from precipitation feed being inadequate
- unexpected variability being encountered in ore types from different mining areas

Economics are expected to be sensitive to:

- scale of operation
- unit acid consumption by upgraded ore
- U3O8 recovery efficiency
- capital cost per annual tonne U3O8

## 3.1 ORE SORTING AND HMS OPERATING CONDITIONS

Ore sorting is planned at three sizes:

- -100 mm +50 mm (coarse)
- -50 mm +75 mm (medium)
- -25 mm +12 mm (fine)

The high grade accept fraction will go to the secondary crusher. The reject fraction goes to the reject stockpile for transfer to the waste dump.

HMS (Heavy Media Separation) involves a -12mm + 0.075 mm fraction from the secondary screening plant being fed to the HMS plant, using ferrosilicon media at density 3.0. HMS floats (rejects) are dewatered and transferred to the rejects conveyor. HMS sinks (accepts) are dewatered and stored in a fine ore bin.

## 3.2 RADIOMETRIC SORTING

First prototyped in the late 1980's, radiometric ore sorting designs have been successfully applied at mines such as :

- Bicroft and Beaverlodge in Canada

- Schwartzwalder and Energy Resources in the USA and
- Mary Kathleen in Australia.

A new design concept has been followed by Canning Resources employing:

- relatively simple and modular electronic components
- high reliability
- simple periodic maintenance procedures
- unit components which are suitable for application in remote areas and underground areas where limited support can be expected.

### 3.2.1 Principle of Operation

By reference to a block flow diagram Fig 4, it can be seen that:

- every particle passes through the sorter detection zone
- each particle moves in a single file with sufficient separation
- the scintillation detector is exposed to only one particle at a time
- particle area is measured by camera as the particle passes off the slide plate
- a processor delays the count in order to associate it with its corresponding rock area
- compensation is needed for background radiation
- counting divided by the area gives the grade estimation
- the grade is compared with the cut-off grade
- particles exceeding the cut-off grade are, after an appropriate delay, blasted by air valves across the splitter plate onto the accept belt

### 3.2.2 Sorter Components

#### *3.2.2.1 Feed Elements*

- external belt loader
- small feed hopper

- flat bed primary feeder control over sorter feed rate

- troughed secondary feeder to separate feed into:
  - several parallel streams
  - nose to tail arrangement as the feed particles pass along the slide plate

- particles accelerate down the slide plate

*3.2.2.2 Detector*

- individual radiation measurements by scintillation detector

- ore detector for each feed channel

- housing with lead shielding to reduce contribution of background and adjacent particle radiation

*3.2.2.3 Camera*

- single, line scan camera

- measurement of position and area of each particle as it passes over lamp at end of slide plate

*3.2.2.4 Processor*

- PC based processor housed in air conditioned cabinet

- processor actions:
  - sorting function
  - control of feed rate to sorter
  - monitor performance
  - alarm if maintenance required

- operating parameters and performance monitoring accessed from central control room if required

- high speed air blast valve array individually controlled by processor

*3.2.2.5 Manufacturer*

- CRA Advanced Technical Development Centre

- Group Special Equipment Division

- Bundoora, Victoria

In summary, the Kintyre project has adopted a number of process and equipment innovations to ensure that the project economics are as attractive as possible. Process risks are expected to be significantly reduced by piloting the process on a continuous basis for an extended period. After piloting has confirmed the process flowsheet, the main process risks would appear to be scale up to commercial scale and the effects of unexpected ore composition changes on circuit performance and uranium extraction. These risks should be minimal, if the previous testing has demonstrated the robustness of the project over the range of ore types expected from the mine.

# 4. YEELIRRIE

The Yeelirrie project, 100% owned by WMC, is situated in Western Australia, 160 km to the east of Meekatharra, 550 km inland from the port of Geraldton and 700 km north east of Perth. The deposit is between Wiluna and Leinster and close to the proposed Goldfields gas pipeline.

Discovered in 1972, the project has had substantial laboratory and piloting of the process already carried out, an approved EIS, preliminary engineering and a definitive Project Feasibility Study completed and would be regarded as one of the early contenders for new uranium production facilities in Australia.

The reserves have been estimated at 34 million tonnes of ore containing 46,900 t U3O8 in mineralised material averaging 0.14% U3O8. The main mineral is carnotite (K2O.2U3O8.V2O5.nH2O) in calcrete and kaolinitic clay quartz. The deposit is reputedly the world's largest sedimentary deposit of its kind.

The proposed mine production rate is 1.21 million tonnes/annum at greater than 0.15% U3O8, and average grade 0.23% from a conventional open pit, of maximum depth 9m. The ore grade is expected to be 0.23% U3O8 for the first ten years and 0.09% for the subsequent 12 years. Moisture content is reported to be 25% free water and 75% combined water.

Material mined from the orebody will be classified into stockpiles alongside the open pit according to grade into three categories: prime ore (more than 0.15% U3O8), intermediate ore (0.05 – 0.15% U3O8), and waste (less than 0.05% U3O8). Each ore grade will be further separated according to sulphate and strontium content.

Capital cost was envisaged at $320 million in 1983 when plans were abandoned to proceed with the project due to political constraints on the development of more than three uranium projects in Australia at the time.

The metallurgical process is a basic carbonate pressure leach on ore yielding uranyl peroxide (UO4) at an expected uranium recovery of 91-92% for a feed grade of 0.18% U3O8.

Unit operations include:

- crushing
- grinding to -48 mesh
- sodium carbonate pressure leach 120-150C
- CCD and clarification

- uranium and vanadium precipitation as sodium diuranate (SDU) with caustic soda
- redissolution of SDU with dilute H2SO4
- silica removal as leach residue
- vanadium removal as insoluble vanadic acid with an equal amount of uranium
- releach of vanadium from vanadic acid with hot NaOH solution
- disposal of vanadium solution to tailings
- recycle of uranium filtercake as SDU
- uranium precipitation with hydrogen peroxide as uranyl peroxide dihydrate, UO4.2H2O with pH adjustment by ammonia
- product thickening, washing, filtration and drying in a hot oil hollow flight drier @ about 250C
- product packaging
- recarbonation of barren SDU thickener O/F with diesel exhaust

Process innovations include:

- use of moderate to highly saline process water to assist CCD operations by preventing dispersion of clays in the ore
- use of moderately anionic polyacrylamide flocculants of the type originally developed for the alumina industry in the CCD operations
- reagent usage and uranium loss reduction by contact of the barren SDU solution with fresh ore in the grinding circuit

The Yeelirrie process flowsheet would be the first sodium carbonate uranium pressure leach process in Australia. Although the circuit is complicated, process risks would appear to have been largely minimised by improvements in the process flowsheet through operation of three different pilot plant campaigns over a 9 year period including:

- a one tonne per day operation at Amdel in Adelaide over 4 months in 1972 using kiln dried ore as pilot feed
- a second pilot operation at WMC Kwinana Nickel Refinery in 1974 to produce product for buyer evaluation

- a 24 tonne per day fully integrated pilot plant operation which operated for an extended period at the Kalgoorlie Research Plant until December 1981.

The project would be located close to existing WMC infrastructure at Mt Keith and Leinster nickel mines and would therefore have a relatively low cost for infrastructure. Proximity of the new gas pipe line to Kalgoorlie to the project site may lead to the selection of gas turbines for steam and power generation rather than diesel generators as originally proposed.

The estimated power load of the project has been reported to be 8.5 MW peak load and normal steam requirements for process heating 9,000 kg/h low pressure steam and 13,000 kg/h high pressure steam. Overall the operation should be low cost.

# 5. KOONGARRA

The Koongarra deposit, discovered by Noranda in 1970 and now owned 100% by Cogema, is a high grade deposit with estimated reserves of 13,300 tonnes of uranium. It lies about 30 kilometres south of Ranger in the Northern Territory and 3 kilometres east of Nourlangie Rock, a major Aboriginal cultural site and tourist feature.

The upper orebody has proved and probable ore reserves with an average grade of almost 0.8% $U_3O_8$, containing14,500 tonnes of uranium oxide accessible by open pit mining. Proposed production was 1375 tonnes U3O8 per annum.

The Koongarra deposit is potentially one of the new mines that will be developed in the next wave of projects in Australia. No details are provided on the process flowsheet but it is understood to be a conventional circuit.

# 6. OTHER AUSTRALIAN RESOURCES

The following information is taken from Access Economics, A New Opportunity for Australian Uranium, July 1994, supplemented by other information from EIS submissions, The Uranium Institute and other sources, where readily available:

**Nabarlek**

- Queensland
- Discovered in 1970 by Queensland Mines
- Owned by Queensland Mines, a 100% subsidiary of Pioneer Concrete
- 600, 000 t high-grade orebody grading 1.8% U3O8 at 0.1% cut-off mined in an 18 week campaign over the 1979 dry season by contract mining
- Commenced milling operations in 1980
- SAG and ball mill comminution, H2SO4 leaching, CCD solids separation, amine SX, ammonia precipitation and final product calcination in a Skinner hearth
- Typical ore throughput 240 t/d
- Caro's acid as oxidant in late 1983, replacing pyrolusite
- Overall U3O8 process recovery 97.5%
- Heap leach on about 150,000 t deslimed BOGUM (below ore grade material) at +40mm and –150 mm commenced in 1985: 40-60% recovery in short cycle times and 70% recovery expected if left to completion.
- Plant and mine-site on a care and maintenance basis since 1989 while negotiations proceeded over the Nabarlek 2 deposits.
- plant fully decommissioned in 1993/4
- annual production 1500 tonnes U3O8 per year when operating
- Cogema owns 50% of exploration leases

**Westmoreland area:**

- Queensland
- Owned by Queensland Mines, Urangesellschaft Australia and Mt Isa Mines
- Estimated reserves 20,000 tonnes uranium
- About 400 kilometres north of Mt Isa

**Ben Lomond**

- Queensland
- 50 km west of Townsville
- Discovered in 1975 by Total
- Since 1994 owned by AFMEX, a wholly owned subsidiary of Cogema Australia
- Estimated reserves 3,000 – 5,000 tonnes uranium and about 4,000 tonnes molybdenum

**Lake Way**

- Western Australia
- Owned by Asarco Gold
- Estimated reserves 3,000 tonnes uranium
- Mineral carnotite, host clays, sand, calcrete
- Mining rate 173 - 308,000 tpa @ 900 ppm U3O8
- chloride prewash, SAG mill to 600 micron, sodium carbonate leach @ 95C, sand/slime separation, RIP/chloride strip, yellowcake precipitation by H2O2, dry and calcine at 500C

**Honeymoon**

- South Australia
- About 75 km north-west of Broken Hill
- Owned by Mt Isa Mines

- Estimated reserves 3,400 tonnes uranium
- Porous sandstone
- In-situ leach at 100 m depth, liquid waste disposal by reinjection
- Ferric sulphate leach, SX, sodium carbonate strip, ammonia precipitation, yellowcake drying and packaging
- $3.5 million pilot plant built for 25L/s on 6 km2 pilot plan site

**Beverley**

- South Australia
- Owned by General Atomics
- Estimated reserves 11,600 tonnes uranium
- Proposed production rate 500 tonnes per year
- 500 km north of Adelaide and northwest of Honeymoon

**Manyingee**

- Western Australia
- About 75 km south of Onslow
- Owned 83% by AFMEX in Joint venture with Urangesellschaft Australia and Triako Resources
- Sandstones and siltstones at 70-110 m depth
- Estimated resource 8300 t U3O8 (0.12 % ore)
- Potential candidate for in-situ leaching

# 7. EARLY AUSTRALIAN PRODUCTION

The following information on early Australian uranium production is sourced from The Sir Maurice Mawby Memorial Volume, Second Edition, Volume 2, Monograph No. 19 1993, Overview of the Australasian Uranium Industry, Richard Knight, and a recent Uranium Institute paper:

**Radium Hill**

- Ores first produced from underground in 1930 to obtain a small quantity of radium for medicinal purposes
- Production restart/finish 1954/1962
- Ore milled 970,000 t
- Grade 0.09% U3O8
- Heavy media separation and flotation to produce 0.7% U3O8 concentrate
- Concentrate treatment plant at Port Pirie, 300 km distant by rail, treating about 120,000 t of concentrate from 1956 to 1963
- Production 850 t U3O8

**Rum Jungle**

- Northern Territory
- Production start/finish 1953/1971
- Ore milled 863,000 tonnes
- Grade about 0.28-0.41% U3O8
- Production about 3530 tonnes U3O8
- Acid leach and ion exchange process until 1962
- Solvent extraction and magnesia precipitation process replaced IX after 1962 for Rum Jungle South ore
- Uranium tailings released into a poorly engineered shallow dam initially and into White's pit after 1958

- Copper concentrates (about 20,000 t) also produced by milling 360,000 t ore at plus 2% Cu from White's pit and from the Intermediate orebody

- Copper heap leach containing 260,000 t sulphide ore @ 1.7% Cu and 110,000 t oxide ore @ 2.0% Cu also leached from 1965 to 1971

- Commonwealth Government as owner and operator of site did not make any funds available for rehabilitation of site when mining ceased in 1971

- Bacterial oxidation of pyritic sulphides in the uranium waste ore and in the residual copper heap leach ore readily occurred during the monsoonal climate (1500 mm rainfall) after the site was abandoned in 1971

- Release of acids and metals occurred into the adjacent East Finniss River

- One of Australia's most notorious pollution problems by 1973/4

- Initial clean-up began in 1977

- A$16 million Commonwealth-funded rehabilitation program undertaken from 1983-1988

- Supplementary A$2 million to improve Rum Jungle Creek South waste dumps undertaken in 1990-91

**Mary Kathleen**

- Production start/finish 1958/1982*

- Ore milled about 9.2 million tonnes

- Grade about 0.10% U3O8

- Production 8,891 t U3O8

- Process initially (1958-1963 conventional acid leach with ion exchange

- Solvent extraction replaced ion exchange from 1976-1982

- Substantial rare earths content in ore, but unable to find markets to justify REO production

- Australia's first major rehabilitation of a uranium mine, completed at the end of 1985 at a cost of A$19 million

*operations suspended during the period from 1963 to 1975

**Moline**

- Northern Territory
- 50 km east of Pine Creek and 65 km from South Alligator
- Site of treatment plant for United Uranium's ore from its El Sharana and Coronation Hill mines in the South Alligator region
- Production start/finish 1959/1964
- Ore milled 128,000 t
- Grade 0.41% U3O8
- Production 520 t U3O8
- Process acid leach, SX and magnesia precipitation
- Plant owned by United Uranium
- Plant converted from a gold plant previously operated and owned by North Hercules at Moline

**South Alligator**

- Northern Territory
- Mines at South Alligator included:
  - El Sharana underground mine of United Uranium (1956-1963)
  - Rockhole Creek underground mine of South Alligator Uranium (1958-1961 and a brief period in 1962)
  - Coronation Hill open cut mine of initially South Alligator Uranium and subsequently United Uranium (1957-1964)
- South Alligator Uranium small treatment plant at Rockhole Creek (1959-1962)
- Acid leach, SX and magnesia precipitation process
- Production start/finish 1959/1962
- Ore milled 14,000 t

- Grade 1.02% U3O8
- Production 138 t U3O8

# 8. AUSTRALIAN URANIUM UNIT OPERATIONS PROCESS TECHNOLOGY ISSUES

## 8.1 CRUSHING

No major technological changes have occurred in crushing circuits over the last ten years or are expected in the near term foreseeable future.

## 8.2 ORE SORTING / HMS

Ore sorting was previously used successfully at CRA's Mary Kathleen uranium operation. A substantially improved ore sorter design is proposed for use at the RTZ/CRA future Kintyre operation where uranium minerals included in vein structures can be upgraded almost four-fold as a result of the ability of the ore sorter to reject low grade waste rocks.

HMS has been used previously for upgrading fine size fractions and is planned for use on the Kintyre project.

## 8.3 GRINDING

SAG milling is now well accepted as a standard unit operation in the uranium industry in Australia compared with reluctance to see it applied in the early days of the current generation of Australian uranium mill designs. However, as in certain gold processing plants, there may still be economic justification for the selection of rod mill / ball mill combination circuits as opposed to SAG milling where ore characteristics and optimum size for grinding dictate the need for a finer size than can be achieved by SAG milling alone.

The mineralogy of Australian ores has not led to the need for ultra fine grinding to liberate uranium minerals.

## 8.4 LEACHING

Sulphuric acid is the only commonly used leaching reagent for treatment of uranium ores in Australia at present. However basic sodium carbonate is likely to be used in a pressure leach process for extraction of uranium from Yeelirrie ore because of the high acid consumption characteristics of that ore.

The high cost of sulphuric acid delivered to remote uranium production sites in Australia has lead to sulphuric acid being generated on-site from elemental sulphur at Ranger Uranium or recovered from smelter gases at Olympic Dam. Modern elemental sulphur-based acid plants can produce substantial low cost by-product power as well as high/low pressure steam for process heating.

Oxidants currently used in Australia include Caro's acid (Ranger) and sodium chlorate (Olympic Dam). Caro's acid was also used at Nabarlek. There appear to be significant economic advantages for use of Caro's acid over pyrolusite for dilute acid leaching. Strong acid leaching or controlled acid strong-acid leaching has yet to be considered for Australian leaching operations.

Heap leaching of low grade uranium ores or tailings has not yet arisen except at the Nabarlek mine where a small quantity of low grade ore was heap leached and recoveries of 40 – 60% were obtained over a short time versus a longer term projection of 70 % recovery.

Complications in leaching can include the need to minimise co-dissolution of other readily soluble leach impurities such as iron, silica, copper, or various other cations that want to dissolve at the same time as uranium eg as in the extraction of uranium from copper concentrates or copper concentrator tails at Olympic Dam.

Releaching of uranium or associated impurities from uranium bearing precipitates produced during primary uranium purification stages and recovery of most of that uranium in one or more secondary leaching step are important stages in both the proposed Yeelirrie and Kintyre processing flowsheets.

## 8.5 SOLID/LIQUID SEPARATION

High rate thickening has become well accepted in uranium flowsheets, unlike the reluctance in the earlier days of development of local uranium projects to adopt this technology.

Horizontal vacuum belt or rotary drum filters for leach residue filtration are also likely to become more common when the Yeelirrie and Kintyre projects proceed to commercialisation. Both projects have a significant number of filters. Filters offer the ability to minimise tailings dam size for solids residue disposal, but can have high maintenance costs if the filter is improperly selected or maintained.

A rakeless thickener has been pioneered by Wrencat and a similar model is also offered by Bateman as a relatively low cost device for separation of slow settling solids and solutions.

Precipitation of saturated salts such as silica and gypsum from solution can often become a problem leading to major crud formation in SX unless the precipitation can be avoided by chemistry modification of the solutions or the solids periodically removed from solution, preferably ahead of the SX mixer/ settlers. Clarifiers can be successfully used if they include seed recycle, but sand filters have had a difficult history and gypsum fouling and plugging have been major problems. Pressure precoat filters are used where exceptionally clear solutions are required for SX feed.

The Gore-Tex back pulse filter offers promise for high solution clarity from feed solutions of variable solids contents from as low as 200 ppm to as high as 10,000 ppm. The filter is made of PTFE with 0.5 to 2 micron apertures and an appropriate substrate. The solids are periodically back-pulsed off the filter to form a high density sludge for discard or subsequent processing.

## 8.6 IMPURITY REJECTION AND URANIUM CONCENTRATION UPGRADING AND PRECIPITATION

Solvent extraction with an amine has been common for uranium extraction from sulphate leach liquors. The organic will often need washing to remove aqueous entrainment prior to stripping with ammonia/ammonium sulphate to produce a strip solution for yellowcake recovery.

Uranium recovery from the pregnant strip aqueous by precipitation with ammonia has been the main practice in Australia but future circuits in several of the proposed grass roots new plants are likely to produce uranyl peroxide precipitate by a combination of peroxide precipitation and magnesia for pH control.

Iron precipitation from strong leach liquors followed by hydrogen peroxide precipitation of UO4 in association with either MgO or NaOH for pH control will be used as an alternative to solvent extraction for treatment of pregnant leach liquors obtained from uranium ores in the Yeelirie and Kintyre flowsheets.

Solvent extraction may be carried out in conventional SX mixer settlers, reverse flow SX (as used by Kvaerner Davy in Mexico and South America or by Bateman in Africa), Krebs SX (as currently installed at Olympic Dam), or pulse columns as proposed by Bateman for the extraction stages of the Olympic Dam uranium solvent extraction expansion circuit.

The reverse flow SX design is somewhat controversial at present due to the recent award of a US Patent on the Bateman reverse flow SX design and the application of a slightly different design by Kvaerner Davy for the design and in some cases construction of large scale SX plants in Mexico, South America and Australia. One interesting issue outside the scope of the patent issue is whether there is a limit to settler width before flow redistribution at the feed end of the settler become a constraining factor in the settler size. Such a constraint currently seems unlikely for either conventional or reverse flow mixer settlers.

A pilot pulse column design is being installed by Bateman as a full scale commercial size alternative to conventional or reverse flow solvent extraction units ( extraction units only) for the Olympic Dam expansion project. A separate paper by Bateman will provide more details of the pulse columns. A summary of claimed advantages and potential disadvantages is as follows:

**Pulse Columns: Advantages and Disadvantages**

**Claimed Advantages:**

- High efficiency
- All extraction stages in one column
- Processing of suspended solids without crud formation
- Fully automated control
- Excellent entrainment separation
- Low environment /safety risk
- No internal moving parts
- Low maintenance costs
- Metal or plastic materials of construction
- Limited foot print area
- Competitive capital cost

**Potential Disadvantages:**

- Limited specific flow rate per train ( eg 200 m3/h aqueous)
- Multiple parallel columns needed for high flow rates
- Complex piping and flow controls for large flow rates

- Limited time available for pilot testing before commercial decision
- Ability to accommodate widely varying flows uncertain
- Multi-level structure
- Limited track record in mining industry to date

Krebs SX units installed at Olympic Dam have reportedly not performed as well as expected and there has been concern that high solvent losses may be related to interactions between high solids levels in the feed solutions and mixer performance characteristics (high shear).

In modern conventional SX mixer settlers, entrainment losses as low as 30 ppm have been obtained in copper raffinate heap leach circuits, although some of these losses may be dependent on the use of after settlers to act as additional phase disengagement devices.

Commercially available units for organic recovery are supplied by Spintek, Wemco, and Jamieson for copper SX circuits. The performance of these units in uranium circuits is not known but presumably their performance in copper circuits could be taken as a guide. Various low cost coalescers have been developed by copper SX operators to decrease organic carryover. These units include chopped plastic or PVC in holding tanks or settlers. Costs and performance of these systems vary widely.

The Olympic Dam copper-uranium operation has a copper SX circuit followed by a uranium SX circuit. There is potential for cross contamination of solvent extraction reagents due to carryover of copper extractant in the copper raffinate to the USX circuit which uses an amine extractant for uranium recovery. The extent of carryover needs to be minimised as far as possible to prevent high costs for reagent losses and to avoid potential deterioration in the performance of the amine.

The use of hydrogen peroxide as an alternative to ammonia precipitation for uranium precipitation has been proposed by Solvay Interox. Some of the advantages and potential disadvantages of hydrogen peroxide use are as follows:

**Hydrogen peroxide as uranium oxide precipitant:**

**Claimed Advantages:**

- Coarser and more easily filterable product
- Centrifuge not required
- Indirect product drying at lower temperature than traditional direct contact calciner
- Less dust and worker exposure

- Use of MgO for pH control avoids release of ammonium sulphate to tailings stream

- Improved capacity of existing equipment

- Capital cost savings on new filtration and drying equipment

- Possible sale of product without need for drying

**Potential Disadvantages:**

- Care is required in handling ammonia and peroxide in the same process – explosion potential if gaseous ammonia and liquid peroxide mixed together without first being dispersed in aqueous strip solution

- Operating cost savings over ammonia precipitation costs are relatively small

## 8.7 DRYING AND PACKAGING

Conventional dryers for yellowcake have been multi-hearth direct contact furnaces operating at around 600C. Peroxide precipitation of uranium produces a low dusting product which can be dried by indirect gas or hot oil heating at temperatures reported to be closer to 250C.

Kintyre is planning a fully robotic packaging system to handle yellowcake output in drums.

## 9. REFERENCES


1. Mines Paper No 1, Australia's Uranium Mines, Uranium Information Centre Ltd, September 1996
2. A New Opportunity for Australian Uranium, Access Economics, July 1994
3. Kintyre Uranium Project -Uranium Recovery, Project Brochure, Canning Resources, December 1996
4. Olympic Dam In Profile, Copper-Uranium Division, WMC, May 1996
5. The Yeelirrie Uranium Project, David L Bradfield, Practical Hydromet, Chapter 8, 1983
6. Environmental Review and Management Program for Proposed Metallurgical Research Plant at Kalgoorlie Initially for Yeelirrie Uranium Ore, Western Mining Corporation
7. Overview of the Australasian Uranium Industry, Richard Knight, p 1157, Australasian Mining and Metallurgy, The Sir Maurice Mawby Memorial Volume, Second Edition, Volume 2, Monograph Series No. 19, 1993
8. Uranium Ore Treatment at Queensland Mines Ltd, Nabarlek, NT, Brian R Olver, p 1165, same reference source as 8.6 above
9. Uranium Ore Processing at Ranger Uranium Mines Pty Ltd, Jabiru, NT, Russell K Edwards, p 1168, same reference source as 8.6 above
10. Acid solution will mine SA Uranium, Engineers Australia, July 23, 1982
11. Personal Communications, Mal Jansen, 1996-1997
12. Bateman Pulse Column, Alta 1996 Copper Hydrometallurgy Forum
13. Reverse Flow Mixer Settlers, Wayne R Hopkins, Alta 1996 Copper Hydrometallurgy Forum

Fig 1 Olympic Dam Simplified Block Process Fowsheet

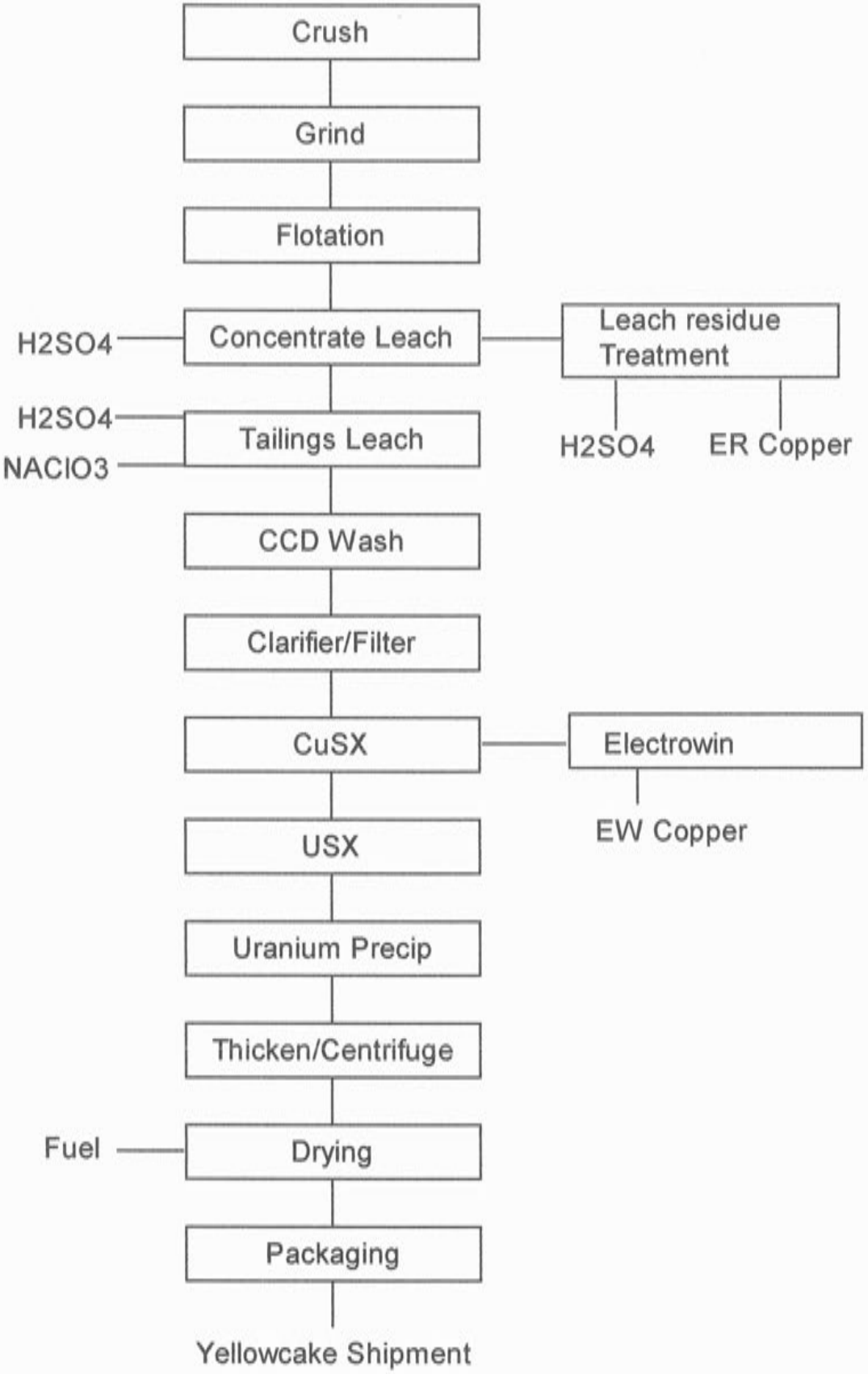


Fig 2 Ranger Uranium Simplified Block Process Fowsheet

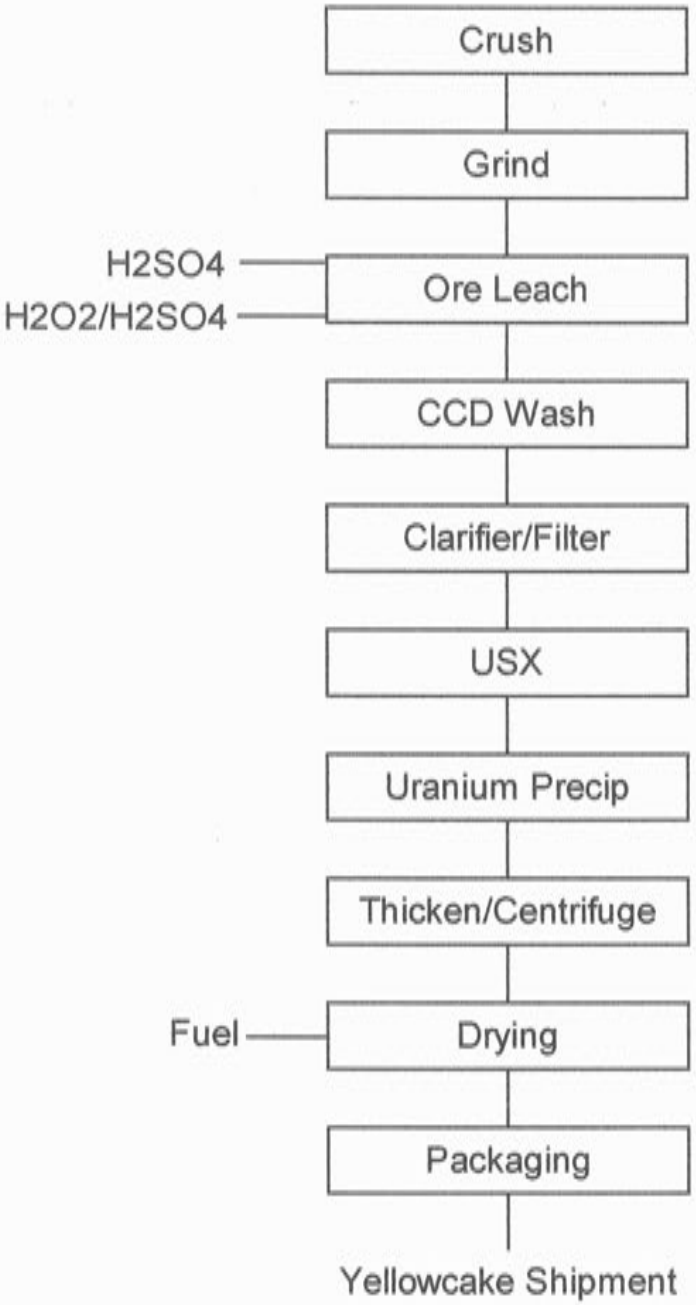
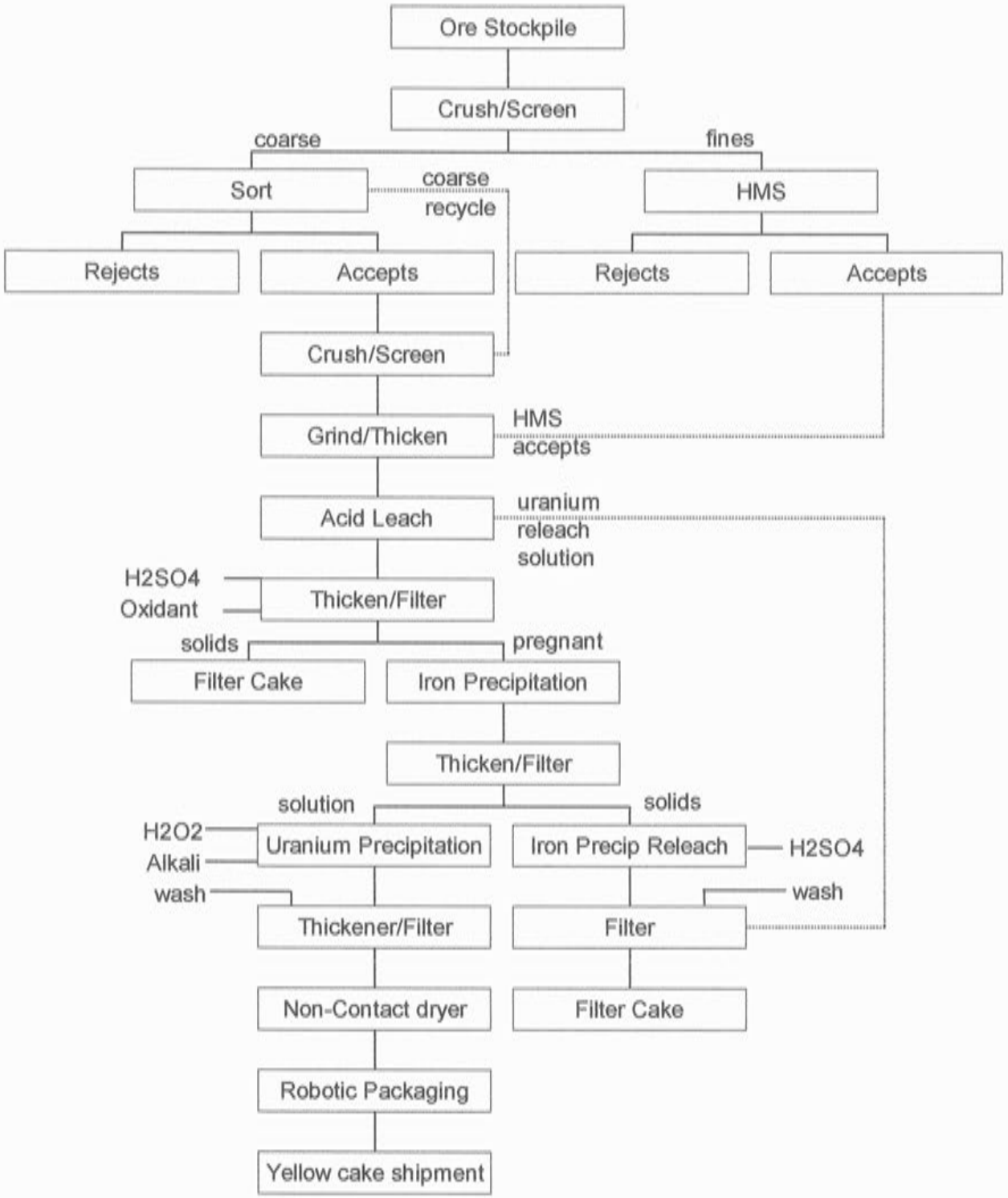


Fig 3 Kintyre Simplified Block Process Flowsheet



# Fig 4 Kintyre Radiometric Ore Sorter

## Block Flow Diagram

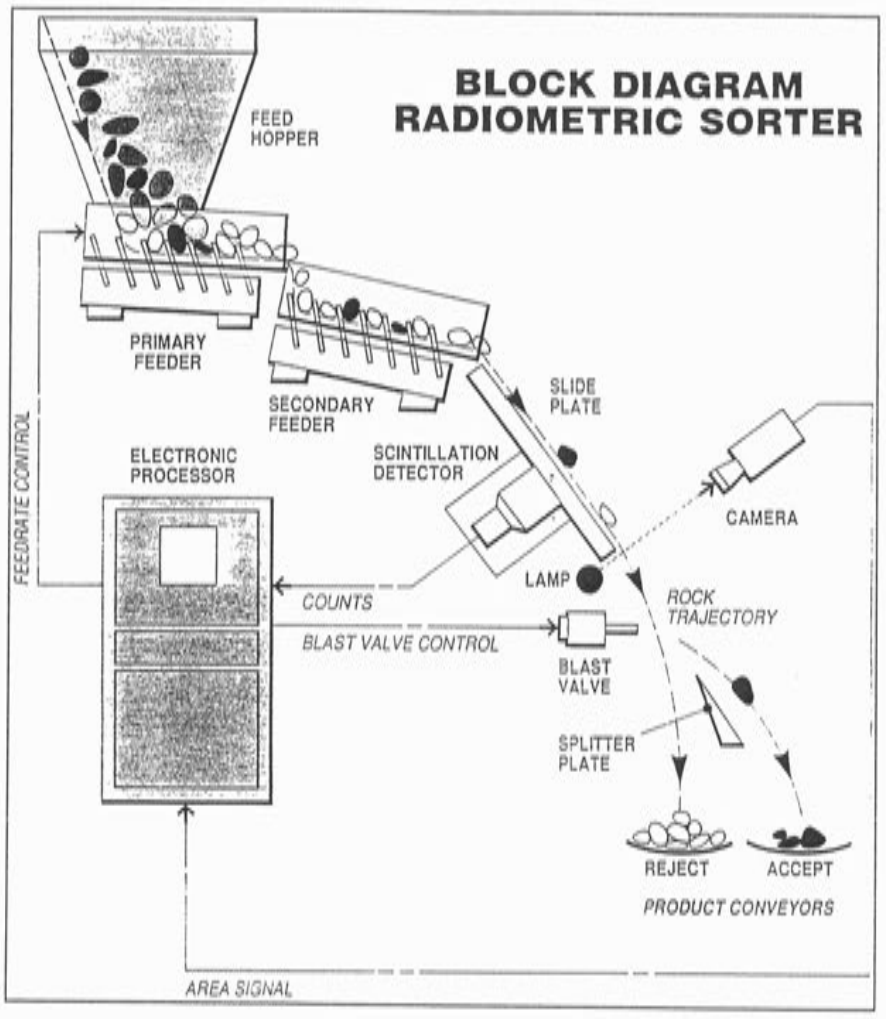
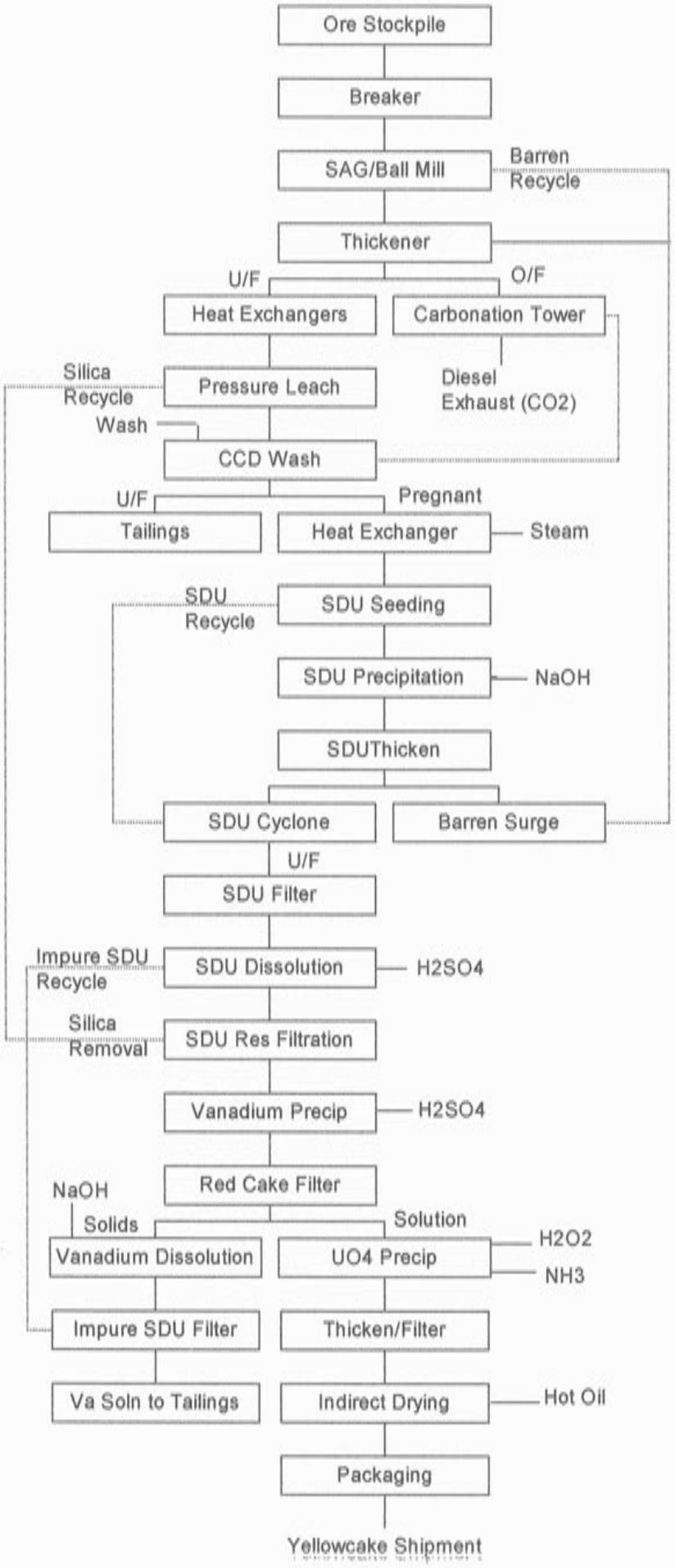


Fig 5 Yeelirrie Uranium Simplified Block Process Fowsheet



# SOLVENT POISONING AT THE RANGER MILL: A CASE HISTORY

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## ABSTRACT

The Ranger Uranium mill is a conventional acid leach-solvent extraction plant producing about 3,500 tpa of pure $U_3O_8$ concentrate from an ore containing about 3,000 ppm U.

The solvent extraction plant extracts uranium from acidic solution using Alamine 336 which is a straight chain tertiary amine with chain length $C_8$-$C_{10}$. The concentration is about 3 per cent by volume in a hydrocarbon diluent, Shellsol 2046.

Stripping is achieved by partial deprotonation of the loaded amine with ammonia at pH 3.

Both extraction and stripping are performed in four stages, counter-current, using stainless steel mixer-settlers.

In January 1994, following a seven month shutdown of the mill, the solvent extraction plant was restarted but was inoperable because the loaded solvent could not be stripped. No known treatment was able to induce any stripping whatsoever. When additional amine was added to the solvent the plant could be operated but with a very high circulating load of uranium which was lost during regeneration. Iron was also being extracted and this contaminated the $U_3O_8$ product so severely it became impossible to produce on-specification concentrate.

Laboratory tests quickly established that the system contained a poison which had been introduced during storage, and that the poison reported to the diluent when amine and diluent were separated.

Extensive investigative testwork led to the hypothesis that the poison was a sulfonate group on a lipophilic hydrocarbon molecule - a liquid cation exchanger capable of extracting iron and exchanging it for the uranyl ion $UO_2^{2+}$ which becomes the dominant cation on the strip side (uranium is extracted by amine as an anion and stripped as a cation).

This paper describes the empirical testwork and organic chemistry employed in the investigation. Some of the conclusions are really assumptions as they do match the hypothesis and the observations but cannot be proven. In addition, some of the postulated chemistry changes in the system cannot be explained in terms of normal organic chemistry. For example, the cleavage of one of three tertiary amines to form a secondary amine was proven to have occurred but was inexplicable.

This case history describes a severe problem which could occur in other mills, and it is the intent of this paper to make the knowledge obtained in this study generally available within the uranium industry.

# 1. INTRODUCTION

The Ranger mining and milling operations are situated in the Northern Territory about 260 km east of Darwin.

The mill is a conventional acid leach-solvent extraction plant producing about 3,500 tpa of uranium oxide from an ore containing about 3,000 ppm $U_3O_8$.

Figure 1 shows the plant schematic and Figure 2 the process chemistry. These show pyrolusite as oxidant, although the plant has recently been modified to utilise either pyrolusite or hydrogen peroxide ( in the form of Caro's acid).

The solvent extraction plant is a vital part of the process, separating uranium from other dissolved species in the leachate. The tertiary amine Alamine 336 is used as an extractant, made up as a 3 per cent by volume mixture in Shellsol 2046 diluent. No third phase modifier is necessary in this system.

Table 1 shows the plant description and operating parameters.

There is no pre-protonation of the amine in this plant although this will be introduced as part of the mill expansion in 1997. The extraction mixers are therefore used for both protonation and extraction, with the protonation acid being added to the pregnant liquor. Stripping is accomplished by partial deprotonation of the loaded solvent using ammonia at pH 3.

The entire solvent extraction plant is stainless steel construction.

In January 1994 the plant became inoperable as a result of solvent poisoning which occurred when the solvent was stored in stainless steel vessels for seven months while the plant was shut down. The poison interfered with the stripping chemistry to the extent that no stripping was possible using ammonia, and uranium could only be removed by regeneration with sodium carbonate or sodium hydroxide at pH >12.

This paper described the investigative testwork which led to the hypothesis of the poison's structure and ultimately to the solution of the problem.

The hypothetical structure of the poison was never proven, but remains the "best guess" to fit the observations.

## 2. BACKGROUND

In 1990 continuous milling operations were ceased after 10 years in favour of campaign mining and milling. The mill was shut down in July 1990 and restarted in January 1991.

At start-up a curious phenomenon was observed: the solvent extraction stripping efficiency was very poor with around 1 g/L $U_3O_8$ remaining in the barren organic liquor after experiencing supposedly ideal stripping conditions which would typically yield about 10 - 30 ppm retention. Some iron transfer from extract to strip was also observed. This caused concern at first, but the stripping efficiency improved quite quickly, allowing operations to proceed. The barren organic $U_3O_8$ assay had returned to normal levels after about four weeks.

An investigation at that time suggested the presence of an anionic poison possibly originating with humic acids growing in stockpiled ore. No further action was taken as the problem had gone away and was not causing any process difficulties.

Similar phenomena were observed during the 1992 and 1993 start-ups but again there were no serious process problems except for a small amount of iron-contaminated product which was easily blended off to maintain quality specifications.

As expected the phenomenon reoccurred during the 1994 start-up but this time with a difference - it did not go away. Loaded solvent and barren solvent uranium assays were the same - about 1.1 g/L $U_3O_8$ - and no improvement occurred within the first five days. Uranium losses were minimised by lowering the head grade while waiting for the poison to flush out as it had in previous years. This did not happen.

Laboratory assays indicated that the solvent contained only about 1.7 per cent total amine compared to about 2.5 per cent at the time of shutdown (the reason for this loss was never established). There was hesitation about adding more amine because if the stripping reaction was being blocked this would achieve nothing except further amine loss if the solvent had to be discarded. Consideration was given to discarding the whole solvent inventory (900 $m^3$) by mixing with diesel and burning in the power station engines. However, laboratory tests indicated that additional amine would extract and strip in the normal manner leaving only the 1.1 g/L $U_3O_8$ baseline in the barren solvent. The net result would be uranium losses during regeneration, but plant operation would be possible.

The only remaining problem was that the amine delivery was delayed and was still three weeks away. There was no fresh amine on site. Clearly the plant was inoperable.

At that point a major failure of the rod mill shut the plant down for four weeks. During this time additional amine was added to the circuit and the solvent extraction plant was able to be restarted when the rod mill repairs were complete.

This did not entirely solve the problem. The total amine content of the solvent was about 3.7 per cent yet small amounts of uranium (~5 ppm) remained unextracted in the raffinate. The barren solvent contained about 1 g/L $U_3O_8$ which suggested that about 1.2 per cent of the total of 3.7 per cent amine was loading but not stripping - yet still demanding acid and ammonia. Regular solvent regeneration is essential in this type of solvent extraction plant and this is where uranium losses occurred. Regeneration with sodium carbonate completely removed uranium, but this clean solvent would simply reload uranium and strip to only 1 g/L.

The worst problem, however, was product quality deterioration. The product assayed only about 95% $U_3O_8$ compared to typical assays of about 99.5% $U_3O_8$. The contaminant was iron, which is a specification element at all conversion plants except BNFL. More than 80 per cent of our product was at that time being converted at Allied-Signal which has the tightest iron specification of all the converters. The Allied specification is 1 per cent Fe maximum and some of our product contained three times this amount.

The mill laboratory was closely monitoring iron levels in product and was able to provide some blends of drums just on specification for containerising and despatch to Allied. Some other material was containerised for other converters, but most of the production had to be stored uncontainerised awaiting good quality production for making up on-specification mixtures. This was a long time coming. A further difficulty was the need to make up a shortfall in production resulting from four weeks rod mill downtime.

X-ray fluorescence analysis of the solvent extraction organic liquors clearly showed that iron was being transferred by solvent extraction and not, as first thought, by aqueous entrainment. The mechanism of this extraction was not then understood, as the equilibrium between ferric iron and the complex iron sulfato anion is heavily dominated by the cation which could not be extracted by amine.

The flushing out of the poison was a very slow process but ultimately a divergence between loaded and barren solvent uranium assay began to appear and iron levels in product fell to below specification. It took several months for the barren solvent assay to fall and by the time the plant was shut down to begin the mining phase in June the barren solvent $U_3O_8$ assay was still 0.35 g/L - more than ten times the typical value.

The January start-up was awaited with some apprehension.

# 3. INVESTIGATION

## 3.1 MILL LABORATORY TESTWORK

With the onset of the problem and the urgency of a resolution an extensive campaign of laboratory testwork was undertaken. A simple test was devised to measure the stripping efficiency in a separating funnel. The loaded solvent was contacted with 10 per cent ammonium sulfate solution doped with sufficient ammonium hydroxide to give a terminal pH of about 4 after extraction. The organic phase was then filtered through a Whatman PS1 phase separator and analysed for uranium by x-ray fluorescence. The stripping efficiency measured this way gave similar results to that being observed in the plant, while freshly prepared amine/Shellsol mixture was 100 per cent strippable.

A number of solvent treatments were tried in an attempt to induce some strippability in the plant liquor. Strong alkali regeneration removed the loaded uranium but when reloaded the solvent would still not strip. Acids, alkalis, reductants, oxidants, ethanolic hydroxides and most of the other reagents on the shelf had no effect. Following these treatments the appearance of the organic liquor was superb: pale straw-coloured, bright and very clear. But it would not strip.

A most significant outcome was achieved when the amine was separated from the diluent. Contact with warm 50 per cent sulfuric acid causes the amine to separate out quantitatively as a third phase which can be easily removed from the diluent in a separating funnel. This diluent would not load any uranium from PLS, confirming that the amine separation was complete. The separated amine, when mixed with fresh diluent loaded and stripped without difficulty but the separated diluent when doped with fresh amine would not strip.

Clearly the problem was confined to the diluent and this is why none of the solvent treatments had worked: they are intended to clean up the amine.

The presence of a carboxylic acid was suspected as iso-decanol had been added to the solvent mixture in earlier years, although this had been discontinued about four years before the stripping problem occurred. It was thought that any residual decanol in the system may have somehow transformed to the carboxylic acid during storage.

It was decided to treat the solvent with a soluble hydroxide of a heavy metal in an attempt to remove any carboxylic acids as insoluble soaps. A 4 per cent solution of barium hydroxide was used but no soaps separated. Instead barium was solvent extracted, and the presence of a cation exchanger was proven.

## 3.2 ORGANIC ANALYTICAL CHEMISTRY

The mill laboratory has few facilities for organic analysis (and not much expertise!) so it was decided to send samples out to CSIRO Mass Spectrometry Laboratory in the Division of Chemicals and Polymers. The choice of analytical techniques was left to the CSIRO experts. They tried infrared spectrometry (IR), nuclear magnetic resonance (NMR) and gas chromatography-mass spectrometry (GCMS) but only the latter was successful. Both IR and NMR were swamped by strong absorption bands in the Shellsol.

The GCMS results were astonishing. Figure 3 is the gas chromatogram of unused solvent showing that Alamine 336 is a mixture of three straight chain amines:- tri-n-octylamine, n-decyl-n-octyl-octylamine and n-octyl-n-decyl-decylamine. Figure 4 is the gas chromatogram of the plant solvent showing that the concentration of the n-octyl-n-decyl-decylamine was considerably diminished with respect to the other two, and the presence of a large quantity of the secondary amine, n-octyl-decylamine. These peaks are of course not quantitative but their relativity to each other is significant.

The source of the secondary amine was unknown but the potential formation of n-nitrosamines was immediately of great concern. N-nitrosamines had been discovered in an African uranium mill and had been reported to interfere with stripping.

At that time the power station engine jacket cooling water was being treated with nitrite and the blowdown from this system was sent to a pond which was sometimes used as process water. In acid solution, secondary amines can react with nitrite to form n-nitrosamines, the short chain molecules of which are highly carcinogenic. The carcinogenicity of the $C_8$-$C_{10}$ n-nitrosamines is unknown but is suspected to be much less than that of the short chain ones. Nevertheless, these compounds could conceivably pose a health risk and are considered highly undesirable in any solvent inventory.

Both CSIRO and Henkel were able to confirm the absence of n-nitrosamines by mass spectrometry and this line of investigation was ceased. It was considered, however, that a potential health hazard had been identified, and nitrite-based cooling water treatment was discontinued in favour of a molybdate type treatment.

Although the mill laboratory has few facilities for organic analysis it does have an x-ray spectrometer and this was used to scan the solvent for inorganic elements. The only significant difference between the plant liquor and unused solvent was a residual sulfur peak after regeneration with alkali. This was not quantified but it did prove the presence of a sulfur-containing impurity in the plant solvent.

## 3.3 EMPIRICAL EXAMINATION - THE BUCKET TESTS

An attempt was made to simulate plant storage conditions to determine whether stripping inefficiency could be induced in laboratory samples. The plant solvent had been stored in the protonated form in stainless steel vessels for seven months at ambient temperatures of about 35 - 40°.

A freshly prepared mixture of 3 per cent amine in Shellsol was divided into four portions and stored in plastic buckets under the following conditions:

a. unprotonated without stainless steel

b. protonated without stainless steel

c. unprotonated with stainless steel

d. protonated with stainless steel

The stainless steel was simply a 10 cm square of 316 plate, acid washed and placed in the plastic bucket. A small amount of water was also added to each bucket.

Bucket (d) was the only one to show any evidence of poison growth. After three months it stripped to 0.061 g/L $U_3O_8$ and after seven months to 0.109 g/L. Although these values are nowhere near the observed plant value of about 1 g/L, the conditions in the bucket were probably not as favourable as those in the plant. The important thing was that poison growth had been stimulated in one bucket under one set of conditions. The material in the other three buckets showed no sign of stripping inefficiency.

# 4. THE HYPOTHESIS

Uranium is extracted as an anion:

$$pUO_2(SO_4)_3]^{4-} + 2(R_3NH)_2SO_4 \rightarrow (R_3NH)_4UO_2(SO_4)_3 + 2SO_4^{2-}$$

and is stripped as a cation:

$$(R_3NH)_4UO_2(SO_4)_3 + 4NH_3 \rightarrow UO_2^{2+} + 4R_3N + 2(NH_4)_2SO_4 + SO_4^{2-}$$

It is simply not possible for this stripping reaction not to proceed in the presence of excess ammonia.

However, if a **cation** exchanger were present it might extract iron which is the most abundant cation on the extraction side and exchange it for the uranyl ion which becomes the most abundant cation after the stripping reaction is complete.

The net effect would be an apparent loss of strippability as the uranyl ion is held in the organic phase by the cation exchanger. Iron carryover would also occur, as iron is easily extracted by most reagents over a wide pH range, and would be deposited on the strip side by ammonia.

These conditions reflect exactly what has been observed and, considering that barium was also extracted in a laboratory experiment, it appears most likely that an amphipathic cation exchanger is the poison.

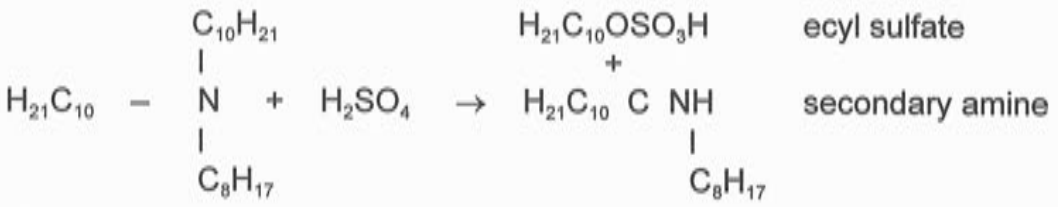
The remaining question is, of course: how did a cation exchanger enter the system during a period of storage?

The possibility that it originated as isodecanol which somehow oxidised to the carboxylic acid could not be discounted. This was considered unlikely, however, because both isodecanol and isodecanoic acid have appreciable solubility in water, and no residual would be expected after four years of operation without a phase modifier being added.

Sulfonic acids are also potential cation exchangers, and this type of compound was considered to be a good possibility because a sulfur-bearing impurity had been positively identified in the plant liquor.

The presence of a large amount of secondary amine in the liquor may provide a clue to the formation of a sulfonate.

As mentioned earlier, the n-octyl-n-decyl-decylamine content was considerably diminished in concentration relative to the other two tertiary amines in Alamine 336. Since the secondary amine was n-octyl-n-decylamine it would appear to have formed by cleavage of the n-octyl-n-decyl-decylamine with the loss of $C_{10}$ chain:




Only the n-octyl-n-decyl-decylamine appears to have degraded because there was no evidence of any di-n-octyl secondary amine and the concentration of the di-n-octyl-decylamine was unchanged relative to the tri-n-octylamine. The reason why only one of the three tertiary amines has partially degraded to the secondary amine is a mystery. Furthermore, although the chromatogram is not quantitative, the peak height of the secondary amine suggests that the quantity is too great to match the loss of n-octyl-n-decyl-decylamine.

It is suggested, therefore, that degradation of this tertiary amine to the secondary occurs during normal operation and was not necessarily the result of storage.

The presence of the secondary amine is in itself not a problem in the process. Indeed, the early solvent extraction plants used secondary amines to extract uranium.

Less certain is what happens to the $C_{10}$ chain separated from the tertiary amine. It will certainly not form the free alkane and, in a sulfuric acid system, will most likely form decyl sulfate or bisulfate. These compounds could be weak cation exchangers and might explain the initial problems with stripping efficiency after the first three shutdowns. The alkyl sulfates may be forming during routine operations but are being constantly washed out with the raffinate. After storage this washing out may take a few days or weeks to complete.

There was still no explanation why the problem had progressed from merely a curiosity in the first years to a plant shutdown situation in early 1994.

There was one thing different about the 1993 storage conditions - water had been sprayed onto the roofs of the settlers used to store the liquor in an attempt to minimise evaporation losses. Some of this water had seeped into the settlers forming a thin aqueous band between the stainless steel substrate and the organic liquor. Although originally thought to be of no consequence, this water would have become extremely acidic. The acidity of protonated amine is often not fully appreciated. With a residence time of seven months at 45° temperature some etching of the stainless steel may have occurred, setting up reducing conditions which may have transformed the decyl sulfate to decyl sulfonate. Traces of chromium and vanadium may also have been liberated, and these might assist the reduction catalytically:

$$H_{21}C_{10}OSO_3H + H_2 \xrightarrow{Cr,V} H_{21}C_{10}SO_3H + H_2O$$

Although decyl sulfate would be a relatively weak cation exchanger, the sulfonate would be very strong. Sulfonates are fundamental to IX resin technology, exchanging cations at almost any pH.

In summary, the poison was thought to be decyl sulfonate, formed by reduction of decyl sulfate resulting from cleavage of a tertiary amine. The mechanism of poisoning was thought to be cation exchange, with iron being transported to the strip side and exchanging with uranyl ion which is the most abundant cation after stripping. Uranium would be held in the organic phase giving the appearance of loss of stripping efficiency.

Although a sulfur-bearing impurity had been detected by XRF it was not possible to prove that it was decyl sulfonate. Nor could decyl sulfonate be measured by gas chromatography as it would decompose to decane at the high temperature of the injection port of the chromatograph. Figure 5 shows the chromatograms of new and used solvent in the region of Shellsol hydrocarbons. Decane is clearly present in the used solvent chromatogram but absent in that of the unused solvent. It is not possible for the used solvent to contain free decane as it is absent in Shellsol 2046 and, even if it had been introduced by some chemical reaction, it would be quickly lost by volatilisation. The decane in this chromatogram is clearly a degradation product of another compound.

Evidence in support of the decyl sulfonate theory is summarised as follows:

- The concentration of tertiary n-octyl-n-decyl-n-decylamine is diminished with respect to the other tertiary amines.

- The corresponding secondary amine n-octyl-n-decyl-amine is abundant despite its absence in Alamine 336.

- In a sulfate system the broken-off $C_{10}$ chain, if intact, would most likely form the sulfate.

- Storage of the organic liquor in 1993 was under much more reducing conditions than in previous years. Catalysed reduction of alkyl sulfate to sulfonate is implied.

- Presence of significant quantities of decyl sulfonate would explain the observed behaviour of the solvent extraction plant.

- A sulfur-containing organic compound is present in the used solvent but absent in fresh solvent.

- A compound which degrades to n-decane in the injection port of a gas chromatograph is present in the used solvent but absent in fresh solvent.

# 5. THE REMEDY

At the start of the 1994 storage period it was decided to deprotonate the solvent inventory and store it in the free amine form. It was not practical to deprotonate 100% as our plant uses bleed stream regeneration. However, after running the solvent through several sodium carbonate regenerations over about one week, it was estimated that about 90% deprotonation had been achieved.

The water sprays on the settlers had been effective in reducing evaporation losses the previous year and this practice was continued.

The 1995 start-up was similar to those of 1991 to 1993. Initial stripping efficiency was poor but quickly recovered to workable levels. It is generally believed that if the deprotonation action had not been taken the plant would not have been operable at 1995 start-up.

# 6. CONCLUSION

Although this poisoning virtually crippled the solvent extraction plant there were some positive aspects - particularly the amount of information gathered and an improved understanding of the process chemistry.

There are warnings here for other producers and would-be producers who may be required at some stage to shut down solvent extraction plants for extended periods.

It may well be that stainless steel solvent extraction plants are dinosaurs of the past and that newer epoxy construction plants will not suffer these problems (our bucket tests are a good indicator of this). Nevertheless, it is strongly recommended that any amine-based organic liquors be deprotonated before extended storage.

A potential serious safety hazard was also identified as a result of this incident. It seems that the formation of secondary amine is normal in an operating Alamine 336 circuit and usually causes no problems. It is also common practice to use nitrite-based water treatments such as Nalco/Alfloc 2000 in cooling waters, and at Ranger the blowdown from the cooling system can enter the process water. Nitrite in contact with secondary amine could form potentially carcinogenic n-nitrosamines such as those discovered in an African mill some years ago.

Nitrite treatment should not be used in the proximity of an amine solvent extraction plant.

By far the best way to avoid solvent poisoning is to keep the plant running. The Ranger mill resumed continuous operation early in 1996, and by December the barren organic assay was below 100 ppm $U_3O_8$ and still falling.

Hopefully with the improved market conditions, campaign mining and milling will never again be necessary in this operation.

# 7. REFERENCES

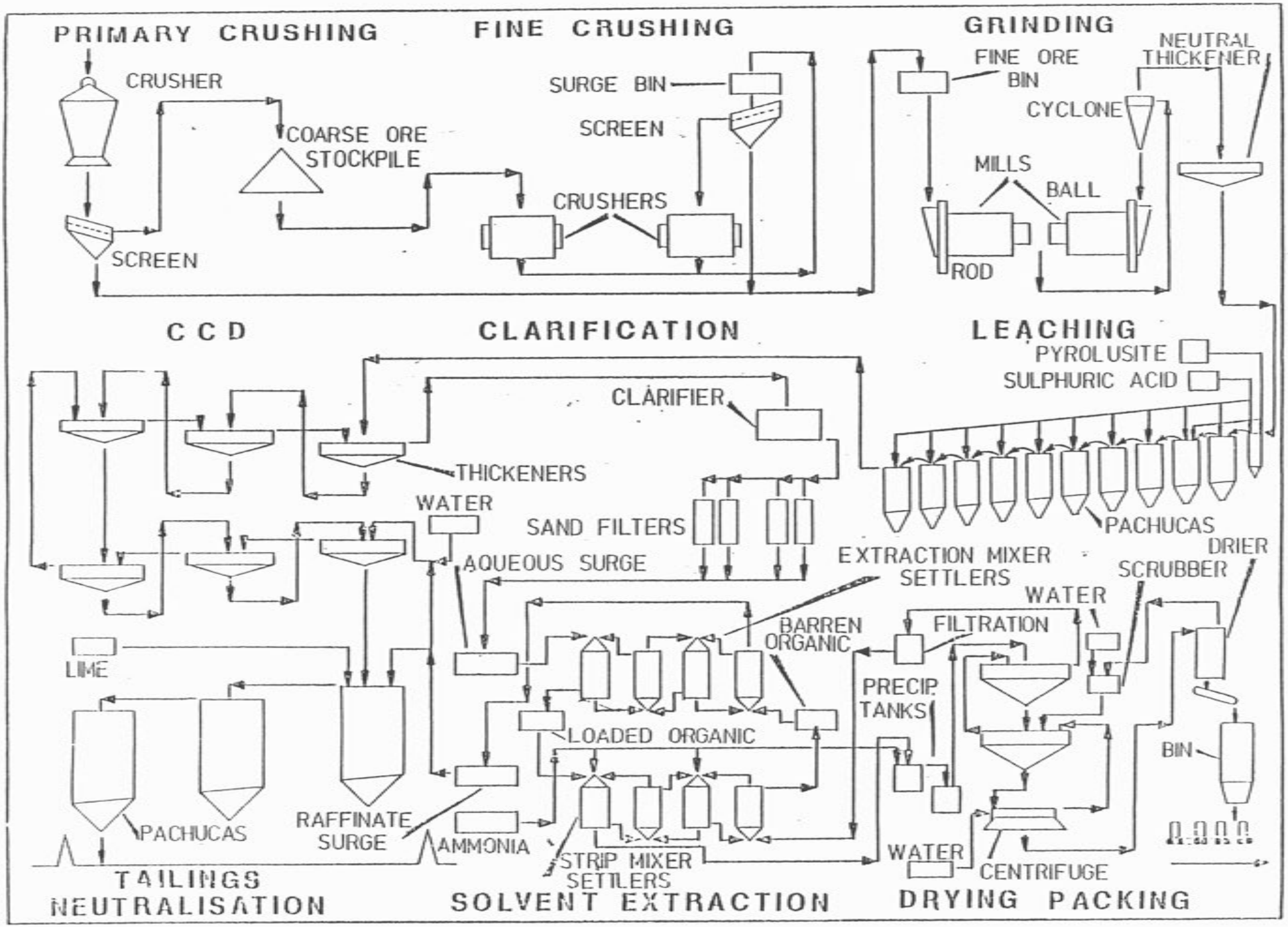
1. Vit, I. Identification of Contaminant in Ranger Mine Extraction Liquor, *CSIRO Report*, March 1994.
2. Mackenzie, M. Henkel Australia Pty Ltd, private communication.

## TABLE 1

### SOLVENT EXTRACTION PLANT PARAMETERS

| | Extract | Strip |
|---|---|---|
| Number of Stages | 4 | 4 |
| Mixer Volume ($m^3$) | 17.7 | 21.2 |
| Settler Volume ($m^3$) | 459 | 124 |
| Settler Cross Area ($m^2$) | 20.2 | 11.2 |
| PLS Flow ($m^3$/hr) | 500 | - |
| PLS Grade (g/L $U_3O_8$) | 1.0 | - |
| PLS pH | 1.6 | - |
| O/A Ratio | 1.5/1 | 3/1 |
| Continuous Phase | Organic | Organic |
| Strip Liquor Flow ($m^3$/hr) | | 25 |
| Strip pH | - | 3.0 - 3.5 |

FIGURE 1



# THE CHEMISTRY OF WINNING YELLOWCAKE

FIGURE 2

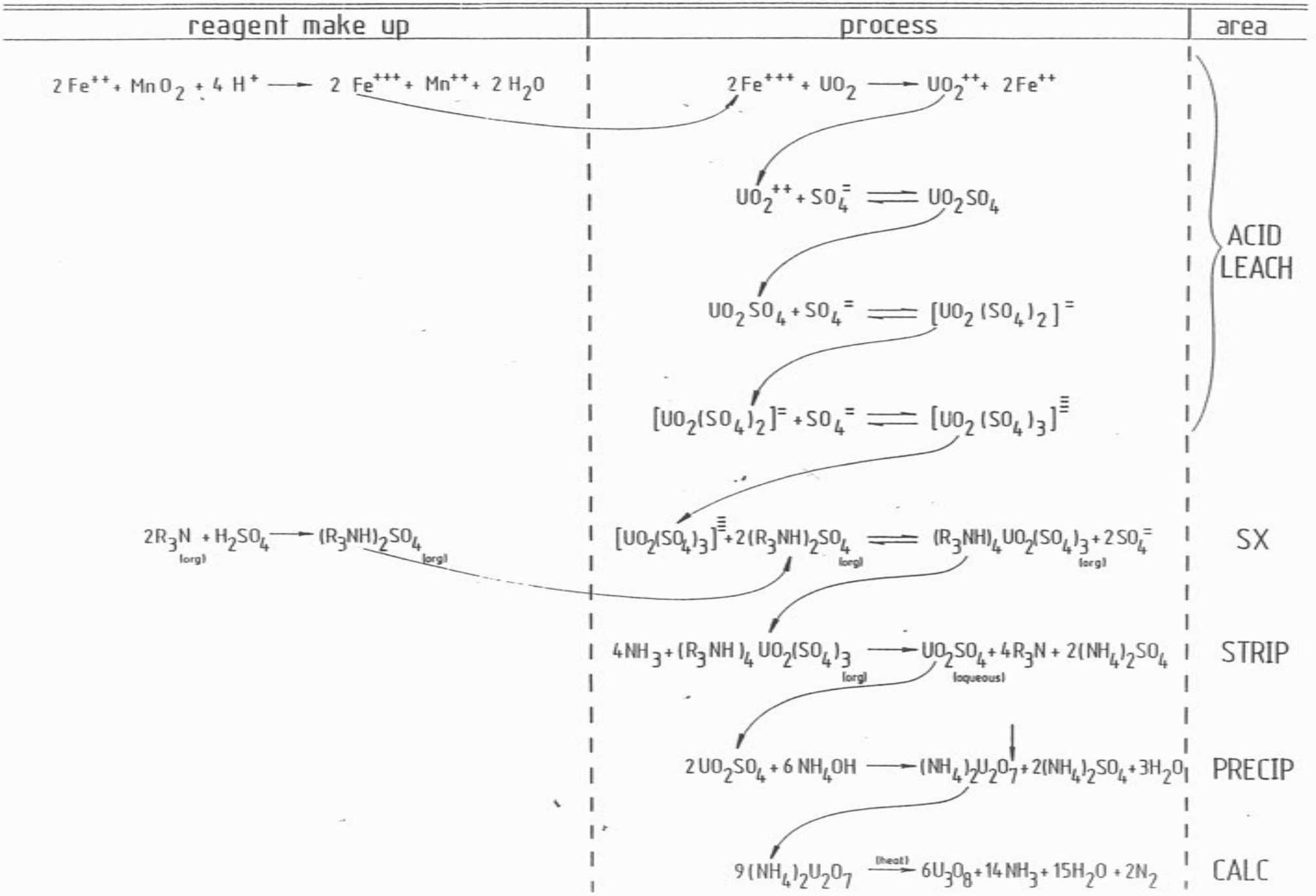


FIGURE 3

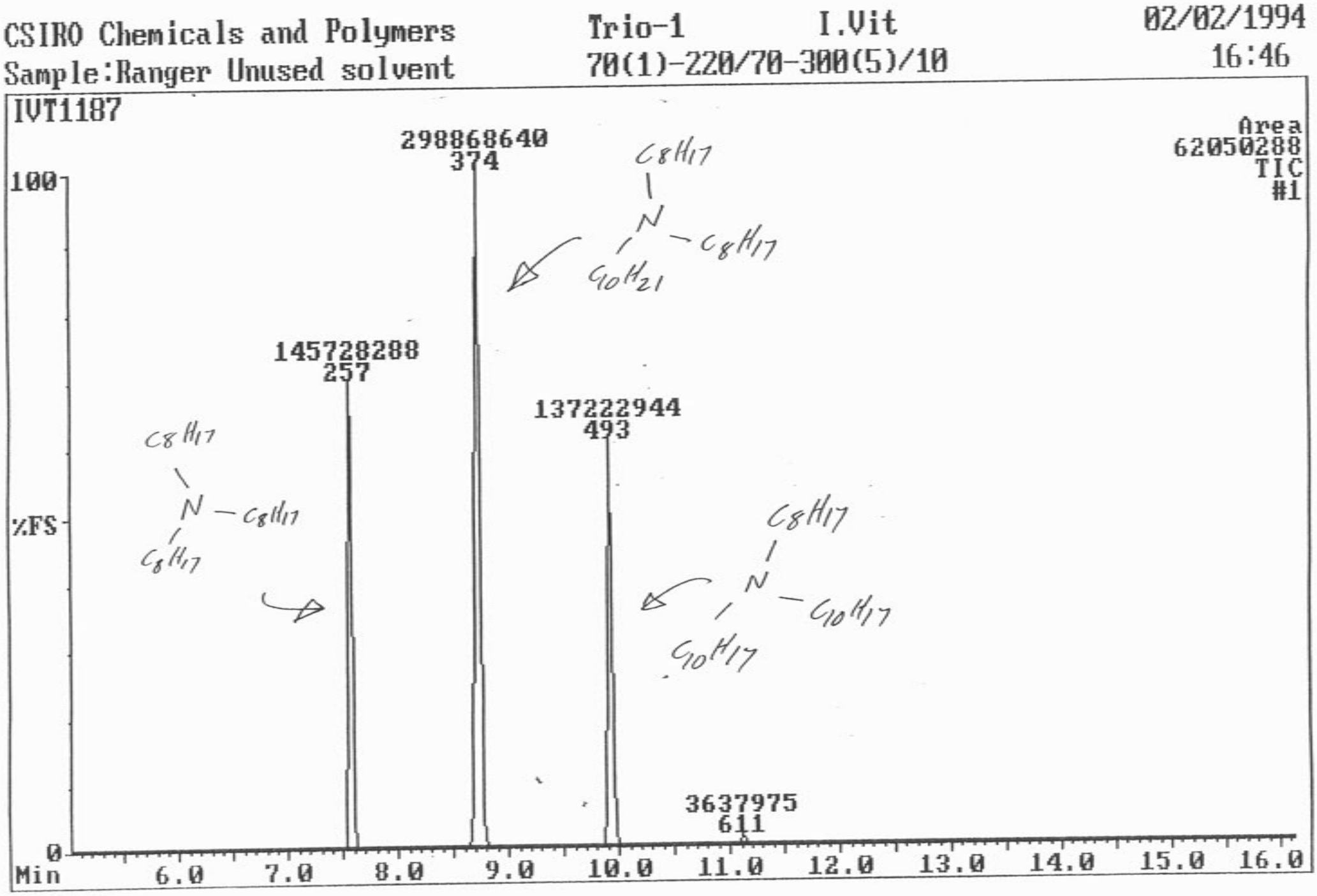


FIGURE 4

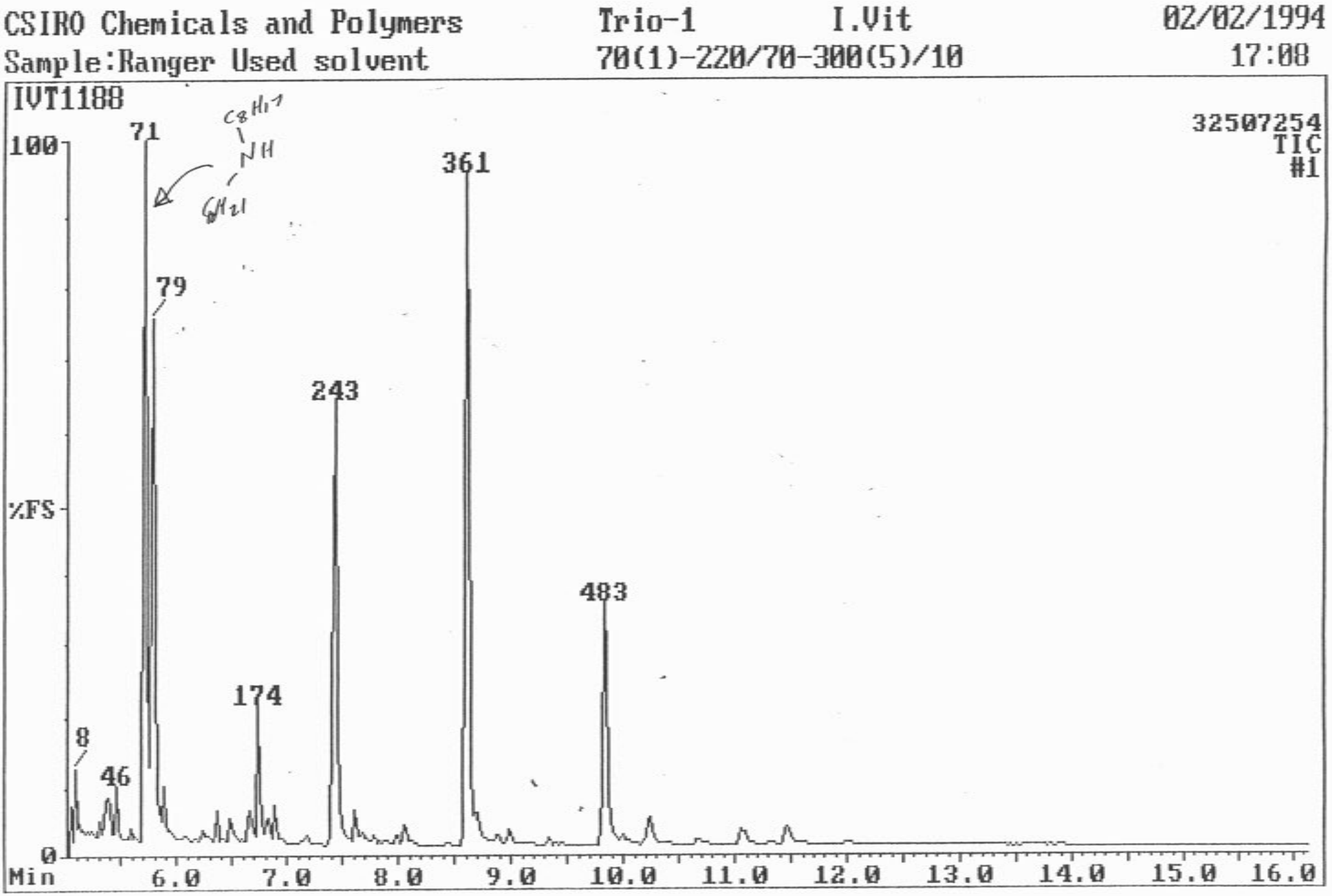
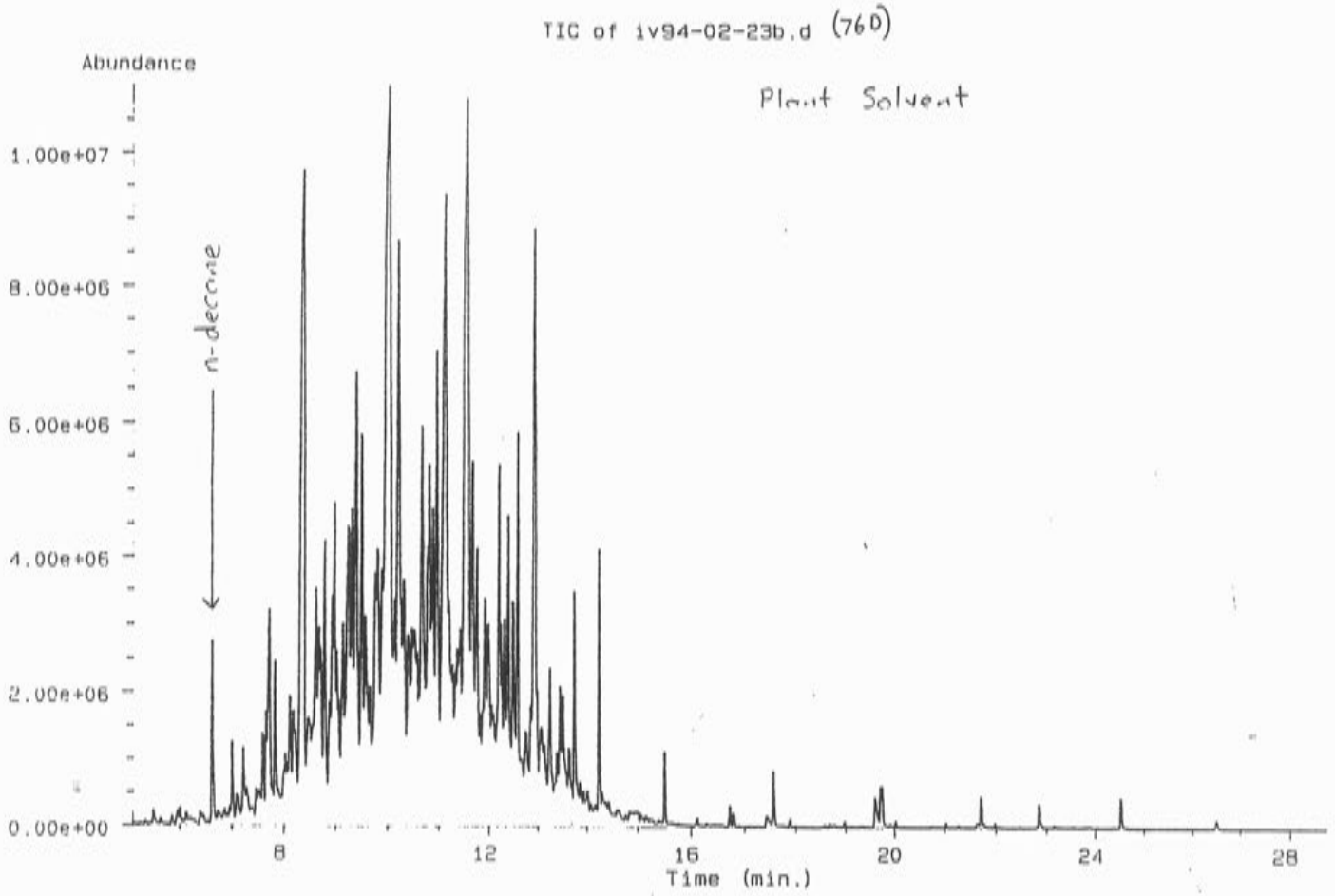
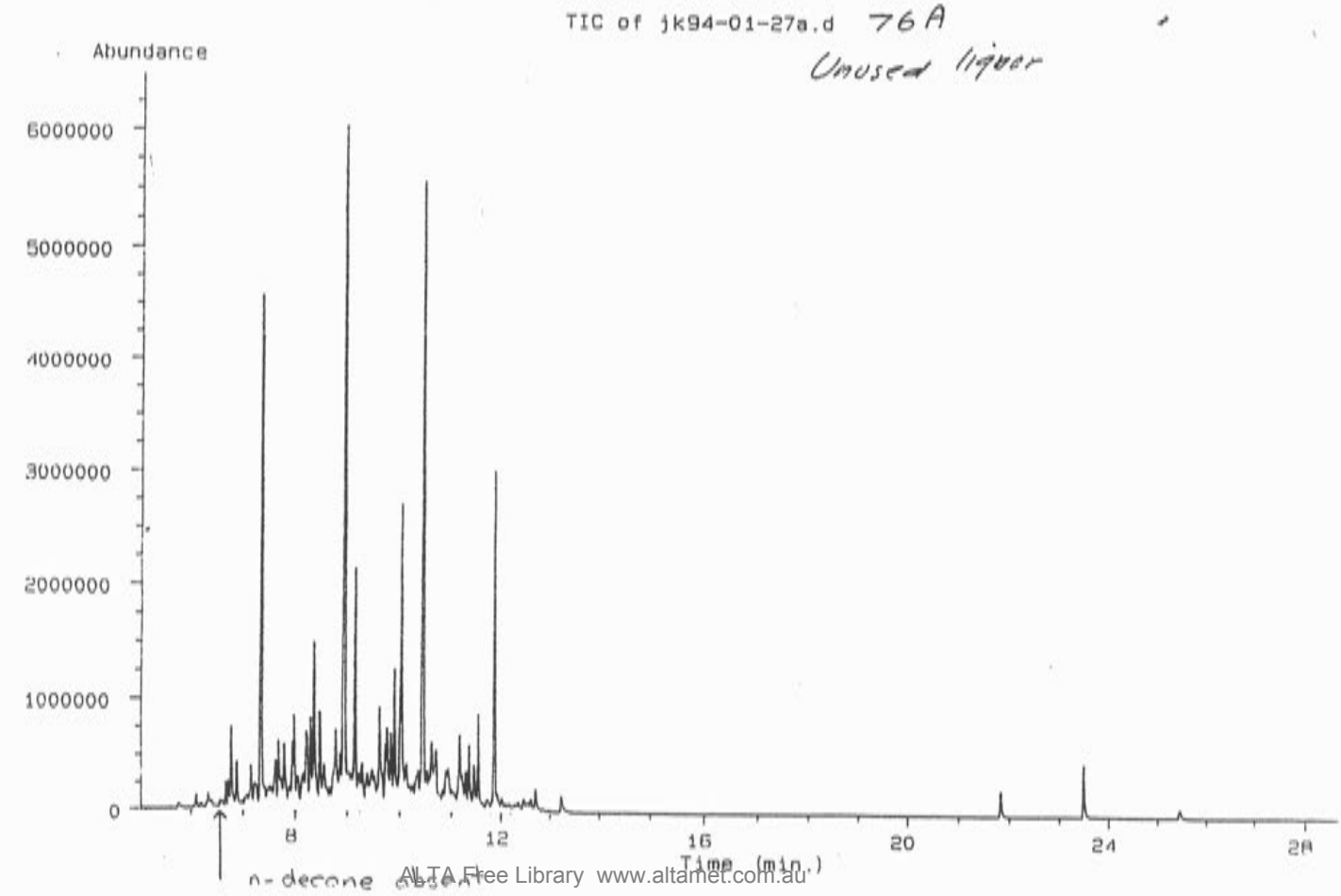


FIGURE 5



# TESTWORK PROGRAMS FOR URANIUM PROJECTS

by
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# 1. INTRODUCTION

From a metallurgical point of view uranium ores are no different from any other ore types so the approach to a laboratory test program has many aspects in common with development testwork on a gold or base metal project. However because of the constraints imposed by regulatory authorities and the need for the miner to ensure that everything possible is done to satisfy, or even better those requirements, the testing of uranium ores is often more thorough, more complete in terms of detail and broader in its scope to include environmental issues such as the detailed establishment of flora and fauna and animal species data bases prior to any mining so that a measure can readily and rapidly be made of impact from mining. In many ways uranium mining in Australia, through the regulations and agreements resulting from the Fox inquiry laid the foundation for current EIS studies for mining projects in general.

Environmental issues aside the basis of this presentation is to provide an outline of how a metallurgical program might be developed from grass roots stage through to engineering approval. The issues involved are technical and non technical, although I would propose that both are of equal importance as they both relate to time, money and achieving the goals of the program. The non technical aspects of the testwork have generally common ground with any test program whilst the technical aspects are those unique to treatment of uranium ores.

There is no blueprint on how to conduct a metallurgical program as each ore, thankfully for the commercial test laboratories, is unique and requires its own set of solutions to the problems posed. It is important to keep a clear mind when approaching any new uranium resource development, applying the techniques at your disposal but keeping your prejudices in the background. The only rule is that "there is no rule". In my years doing testwork my experience has been that despite being presented with test programs for costing either for budget purposes or to present a comparative quote with other laboratories the general rule, for new deposits, is that the program changes, sometimes significantly after the first information or the first of the proposed tests is completed and the results direct a change of strategy.

# 2. NON TECHNICAL ASPECTS OF TESTWORK

## 2.1 WHY DO TESTWORK

Because no two ores are the same, testwork of some form or other is necessary for every deposit, but the reasons for doing the testwork are often as varied in purpose as are the ores. Some of the most common reasons are to determine the amenability of the ore to a particular leach process, to determine the leach efficiency for prefeasibility calculations, to provide data upon which to base engineering design parameters or to determine the compatibility of response to an existing plant. It is more than likely that in the history of a project all or most of the above reasons will come into play at particular stages.

In the initial stages of development the emphasis is usually on deciding which process route is more applicable and what degree of extraction can be achieved. Obviously the exploration effort will be encouraged if extractions of better than 90%, rather than 50%, are readily achieved. The more conventional route for uranium ores in Australia is for acid leaching i.e., Ranger, Olympic Dam, Mary Kathleen (mining ceased), Narbalek (mining ceased), Kintyre (pending development), Jabiluka (pending development).

## 2.2 WHEN TO DO TESTWORK

Testwork is generally commissioned from the early stages of development of a resource but is controlled by the degree to which the resource has be defined. The ideal would be for the complete resource to be drilled out and for mineralogical data to be available upon which to define the variability of the ore throughout the deposit. The testwork could then be structured sequentially and definitively. However this is almost never the case as;

- some idea of the uranium extraction is going to be required early on in the resource development

- drilling would most likely only target the establishment of a mineable resource and there may be potential for further reserves so testwork in the first instance would be restricted to the mineable resource

- it would be unlikely for the orebody to be drilled out if potentially limiting metallurgical problems arose in early stage testing.

The most likely scenario is that testwork from the first drill holes is generally limited to confirming which process route is applicable, what level of uranium extraction can be achieved and perhaps the characteristics of the leached pulps to solids/liquid separation.

As the drilling progresses, confirmatory tests might be carried out on mineralised intercepts followed by a more structured test program once more information is available to define ore types or zones within the reserve.

## 2.3 HOW MUCH TESTWORK IS REQUIRED

There is no definitive answer to this question. Some might say "as much as is required to get the project off the ground", but for uranium ores this begs the question. Because of the fact that any failure within the mine or processing plant could be used for political gain and could have the potential to close the operation, the amount of testwork must be sufficient to minimise the potential of the unknown event. Perhaps the best example that is available in Australia relates to the development of the Ranger orebody where development approval was the subject of a public inquiry that lasted some years. During that time laboratory testing continued in greater depth with the specific objective of ensuring that the maximum amount of information was available to ensure no planning or design oversight and to have the answers to the most detailed questions that might arise from the inquiry.

Having made the point that the amount of testwork required is open ended, that is not to say that there should not be an outline program to use as the starting point. To this end the following process unit operations are suggested.

1. Decision on the most applicable processing technique ie., an acid or alkaline treatment. For the following we have assumed that an acid circuit has been selected but a similar set of process steps would apply to an alkaline circuit.
2. Comminution data to establish the crushing hardness, abrasivity and rod and ball mill work indeces of the ore. Other issues that may arise include consideration of a Sag mill grind.
3. Leaching response is the area of the most intense testing activity in the first instance considering such variables as grind size, reagent addition, leach time, oxidant levels, temperature and pulp density. Many of the following process steps are dependent upon the leach conditions being established before they are entirely relevant.
4. Having dissolved the uranium the next aspect of testing is to establish the solids liquid separation characteristics. These are largely dependent on the gangue ore type and on the fineness of the primary leach grind. However they are important in ensuring that design, which normally utilises counter current decantation in thickeners, is sufficient to establish the number of stages for efficient uranium recovery. In some cases filtration may be considered as an alternative to thickening.
5. Purification and concentration of the uranium leach liquor are the next stages of testing and these are normally achieved using solvent extraction. Testwork may consist of simple small scale shake tests in flasks through to more complex continuous operation pilot plant runs. For dilute solutions ion exchange testwork may be considered.
6. The final stages of testing relate to product preparation and specification. They are probably best left until the preceding unit operations have been optimised and in the initial instance are more important from a marketing point of view although some data is necessary for design and costing.

## 2.4 WHO SHOULD SUPERVISE THE TESTWORK

Any metallurgical test program should be supervised by either an experienced in house project metallurgist or a consultant metallurgist selected for his/her particular expertise that complements the project, but not by the commercial laboratory personnel. This is a strong statement made after many years of consideration and, coming from someone who manages a testing laboratory, a slightly inflammatory statement. The fact is that the testing laboratory, provided it has been selected for its expertise, is quite capable of managing and directing the test program. However I do not feel that the test laboratory will necessarily direct the program efficiently or provide the client with the level of professionalism and security that they require. Let me explain;

I stand to be corrected but, any commercial laboratory under my management has as its main objective turning over as many tests in as short a time as possible. By inference this means that either the laboratory may have a tendency to recommend and carry out more tests than required or fail to interpret the data correctly as it becomes available. In addition the client may feel, rightly or wrongly, that they are exposed to exploitation by the test laboratory, particularly if they do not have any expertise in the area. The other factor that can come into play is that the hours charged by the laboratory for managerial or supervisory costs are often considered excessive, particularly on top of the charges for testwork.

For these reasons the technical control of the test program is better of in the hands of someone slightly divorced from the actual testwork. If the development company does not have their own metallurgist then use of a consultant is the better option. Often the metallurgical mill superintendent elect is appointed when the commitment to mining has been made but they will still benefit from the support services of a good consultant. The consultant is more closely associated with the mining company, who is paying their fees, rather than the test laboratory, so the mining company usually feels much more at ease accepting their advice and their fees structure.

When the Ranger project was being developed Peko Wallsend had the services of their own in house metallurgist, the input from the metallurgical laboratory plus extensive use of an international consulting firm in A. H. Ross & Associates who provided expertise and a link with recent developments at other mines. A similar approach was taken by Pancontinental Mining with the Jabiluka uranium deposit until that project was put on hold by the then government of the day.

## 2.5 TAILORING TESTING TO MEET THE REQUIREMENTS

After consideration of all the above factors the decisions still have to be made as to what testwork to initiate and how that testwork should be managed. I have made a list of possible situations that might be given consideration;

Testing of intercepts - during initial exploration, throughout the development drilling and possibly continuing after mining has started but extensions to the orebody are being proved. Testing of intercepts is often restricted to the main extraction step and maybe to settling or filtering if that aspect has been shown to be a key variable.

Testing of ore type composites - as a development from the testing of intercepts and in conjunction with mineralogical classification ore type composites may be prepared and subjected to a more detailed test program looking at all the metallurgical or engineering process design aspects. This may develop into larger scale testing, particularly if it is considered desirable to run a continuous solvent extraction rig or produce larger quantities of yellowcake for marketing purposes.

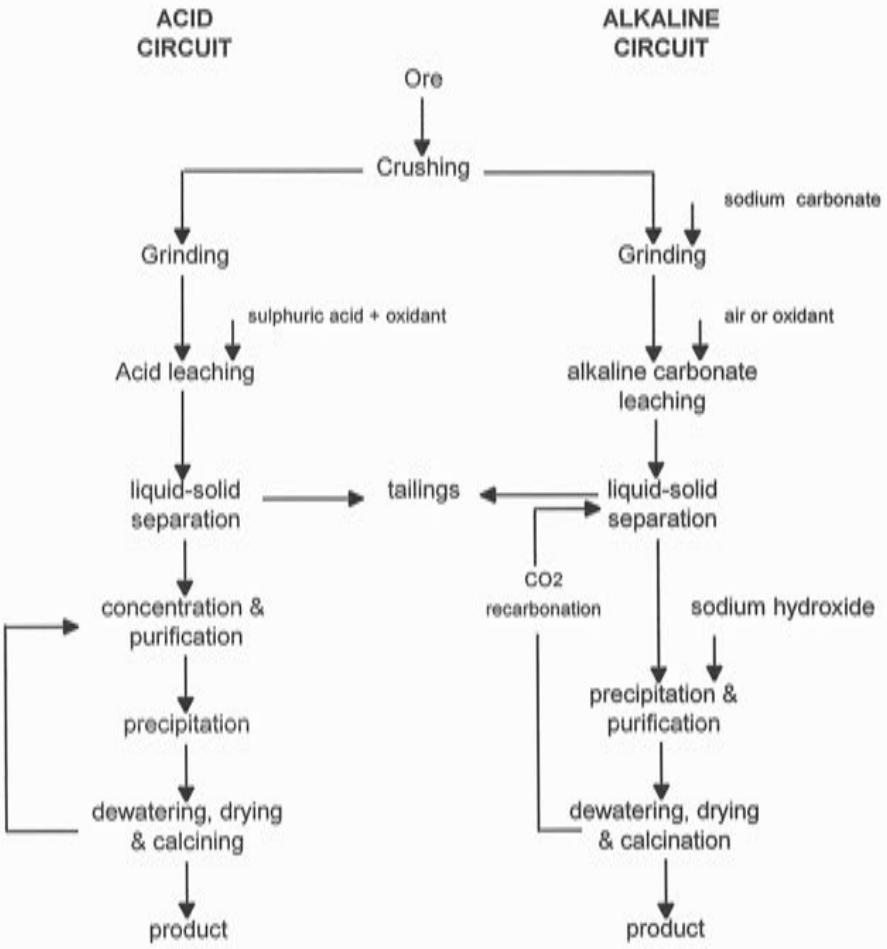
Testing of ore zones - particular attention may be warranted to look at ore zones rather than ore types. Some examples of these classifications might be year 1, 2, 3, 5 to 7 ore, oxide, transition, primary or high grade ore. It may well be that the majority of the design testwork is carried out on 'average' ore but, if sufficient testwork is not carried out, the plant may well be found wanting when treating 'typical' ore. Most teething troubles are encountered when starting up the plant and if the properties of the early mill feed ore (year 1 ore) differ from the development ore samples then the situation can be exacerbated.

Ancillary process options may also be considered - a typical example of this might be the response of marginal or below ore grade zones to heap leaching as a subordinate treatment method. Some knowledge of the potential response to this form of treatment can influence how low grade or waste stockpiles are constructed or on how that material is treated during the mining stage. For example it may prove expedient to screen out fines from low grade ore and stack the oversize onto a packed clay or membrane base for future development as a heap leach operation.

# 3. CHOICE OF PROCESS ROUTE

The major choice in processing of uranium ores is between an acid and alkaline leach medium. Sulphuric acid is used in the majority of mills as it is more effective with most ores and generally does not require as fine grinding as does carbonate leaching. Alkaline leaching with sodium carbonate is however more selective than acid leaching and is more applicable to acid consuming ores so that the choice of which route to use is most often decided on the basis of the gangue mineralisation rather than on the uranium minerals themselves. A simplified flowsheet for each option is shown schematically in Figure 1.

**FIGURE 1**
**ACID AND ALKALINE LEACH PROCESSING CIRCUITS**



## 3.1 URANIUM MINERALS

The polyvalence of uranium and the relatively high solubility of the hexavalent form leads to a large number of minerals or hybrid minerals containing varying amounts of uranium. Some 500 minerals have been identified; examples of the more common ores listed below where they are grouped on the basis of chemical type into oxide, salts, silicates, phosphates etc.

| Type | Name | Composition |
|---|---|---|
| Simple Oxides | Uraninite | $UO_2$ |
| | Pitchblende | variety of uraninite |
| Hydrated oxides | Becquerelite | $7UO_2.11H_2O$ |
| | Gummite | alteration product of uraninite including silicates, phosphates and oxides. |
| Complex oxides | Brannerite | $(U,Ca,Fe,Th,Y)(Ti,Fe)_2O_6$ |
| | Davidite | $FeTi_3O_7$ |
| Silicates | Coffinite | $U(SiO4)_{1-x}(OH)_{4x}$ |
| Phosphates | Autunite | $Ca(UO_2)_2(PO_4)_2.10H_2O$ |
| Vanadates | Carnotite | $K_2(UO_2)_2(VO)2.H_2O$ |
| Hydrocarbons | Thucholite | uranium complex with hydrocarbons |

Uraninite and pitchblende are mixtures of $UO_2$ and $UO_3$, the ratio depending on the conditions of formation and subsequent changes. The two names are often used synonomously. Alteration of these two oxides by hydration and the chemical environment often leads to a great variety of secondary minerals exemplified in the Table above. Pitchblende has a hardness of 5 ½, a specific gravity of 9-9.7 and is black or pitch like with a submetallic lustre. Thorium can substitute for uranium with small amounts of lead and rare earth elements often present.

## 3.2 MINERALOGY AND CHEMICAL ANALYSIS

Mineralogy should be, but is usually not, the starting point for any investigation. The information sought by metallurgists tends to differ significantly from the usual information sought by geologists, something that is not often appreciated by geologists. I can well remember attending a course when I had recently graduated, whose name "Mineralogy for Metallurgists" appropriately summed up the situation. The information revealed by a combination of mineralogical and chemical analysis can provide valuable information that will steer the direction of the testwork by:

a. Identifying the uranium minerals present which can then be related to known behavior and give an indication, based on experience and their physical characteristics, about possible process options. In most cases the secondary uranium minerals are soft and friable and occur as coatings and fillings on grains and in fissures and cracks of the host rocks.

b. Give an indication of the mode and occurrence of the uranium minerals which can be translated to grind size. For uranium mineralisation of the type above or for ores with a sandstone type gangue, grinding need only be as fine as is necessary to expose the minerals ie. relatively coarse compared to that required for say gold leach plants or for base metal flotation.

c. Identifying the associated minerals and gangue which can have a major influence on the selection of treatment method. For instance a carbonate gangue with more than say 15% carbonate mineralisation will almost certainly preclude an acid leach because of the high cost of acid required. As a rule of thumb about 1kg of sulphuric acid is required to treat each kilogram of carbonate mineral present.

d. Revealing relationships of the uranium minerals with the host minerals. The uranium minerals may occur as discrete grains or as intrusions or deposits along rock fractures. It can be important to ascertain which minerals the uranium is associated with as the properties of those minerals may provide an avenue for preconcentration or change of technique. Much testwork was carried out on both Ranger ore and Mary Kathleen ore to introduce an ore sorting preconcentration step based on the properties of the uranium associated gangue. At Ranger ore sorting of a type was finally introduced based on radioactivity measurements made on the trucks leaving the pit but the early testwork was based on ore sorting of individual rocks based on recognition of the host rock colour. At Mary Kathleen radiometric ore sorting was carried out in the process plant with each rock scanned after primary crushing.

e. Finally chemical analysis can be used to confirm the results of the mineralogy and to identify any other potentially value added minerals present. The Jabiluka deposit and to a lesser extent the Ranger deposit in the Northern Territory both have potentially economic gold associations.

# 4. CARBONATE LEACHING

## 4.1 ADVANTAGES AND DISADVANTAGES

As mentioned previously most uranium plants in Australia incorporate a sulphuric acid leach to extract uranium. This is generally the preferred route unless the particular ore contains amounts of carbonate or other acid consuming minerals, making that approach economically less attractive. Carbonate leaching does however have some other advantages over acid leaching;

The carbonate leach tends to be more selective than an acid leach so that the introduction of gangue contaminants, which is so pronounced in acid leaching, is reduced. Oxidised uranium minerals are readily soluble. The purity of the leach liquor means that in some cases precipitation of uranium direct from solution is possible. Carbonate solutions are also relatively non corrosive and safer to handle than acid solutions so that there are savings in materials of constructions costs and in general safety.

The disadvantages of the carbonate process are that;

- The carbonate leach solutions are less agressive and finer grind sizes are often required to expose sufficient uranium mineral surface for good extraction and acceptable leaching rates.

- Carbonate leaching of the silicate type uranium minerals which require some breakdown of the gangue are not as effective whilst the method is reportedly not effective with the highly refractory minerals in the complex oxide group.

- Minerals containing uranium in the tetravalent state usually require oxidation over an extended time at high temperature before dissolution is achieved.

- The high temperatures necessary may extend into the requirement for pressure vessels.

- Carbonate leaching also requires an integrated closed circuit where the leach solutions are recycled

## 4.2 ESSENTIAL PROCESS STEPS

The uranium ore is generally leached in an aerated pulp containing 40-50g/l sodium carbonate and 10-20g/l sodium bicarbonate. After leaching the solids are separated from the pregnant solution by filtration or counter current decantation and the uranium is precipitated by adding an excess of sodium hydroxide which neutralises the bicarbonate. The sodium uranate precipitate is dried and calcined whilst the sodium carbonate solution is regenerated with $CO_2$ in packed towers to restore the carbonate-bicarbonate concentrations and reintroduced into the circuit during the CCD washing stage.

As with acid leaching uranium in the tetravalent state needs to be oxidised into the hexavalent state in which it is readily soluble, forming tricarbonate ions i.e,

$$2UO_2 + O_2 = 2UO_3$$

$$UO_3 + Na_2CO_3 + 2NaHCO_3 = Na_4UO_2(CO_3)_3 + H_2O$$

Bicarbonate is necessary to prevent reprecipitation of some of the uranium in the leach pulp as the monocarbonate.

After solids liquid separation the uranium is reprecipitated by first neutralising the bicarbonate with sodium hydroxide and then adding an excess of hydroxide to precipitate the uranium;

$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O$$

$$2Na_4UO_2(CO_3)_3 + 6NaOH = Na_2UO_2 + 6Na_2CO_3 + 3H_2O$$

After uranium precipitation and separation the liquor is regenerated by converting the sodium hydroxide to a mixture of carbonate and bicarbonate in packed columns by bubbling $CO_2$ gas before being recycled back to the CCD circuit.;

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$$

## 4.3 LABORATORY TEST VARIABLES

Test variables include such factors as carbonate/bicarbonate strength, grind size, temperature, pressure and oxidant type and concentration. Leach conditions to act as a starting point might be;

- P80 = 75μm
- 50% solids pulp
- 40-50g/l sodium carbonate and 10-20g/l sodium bicarbonate
- temperature 80 degrees Celsius
- atmospheric pressure
- aeration
- 24 hours retention

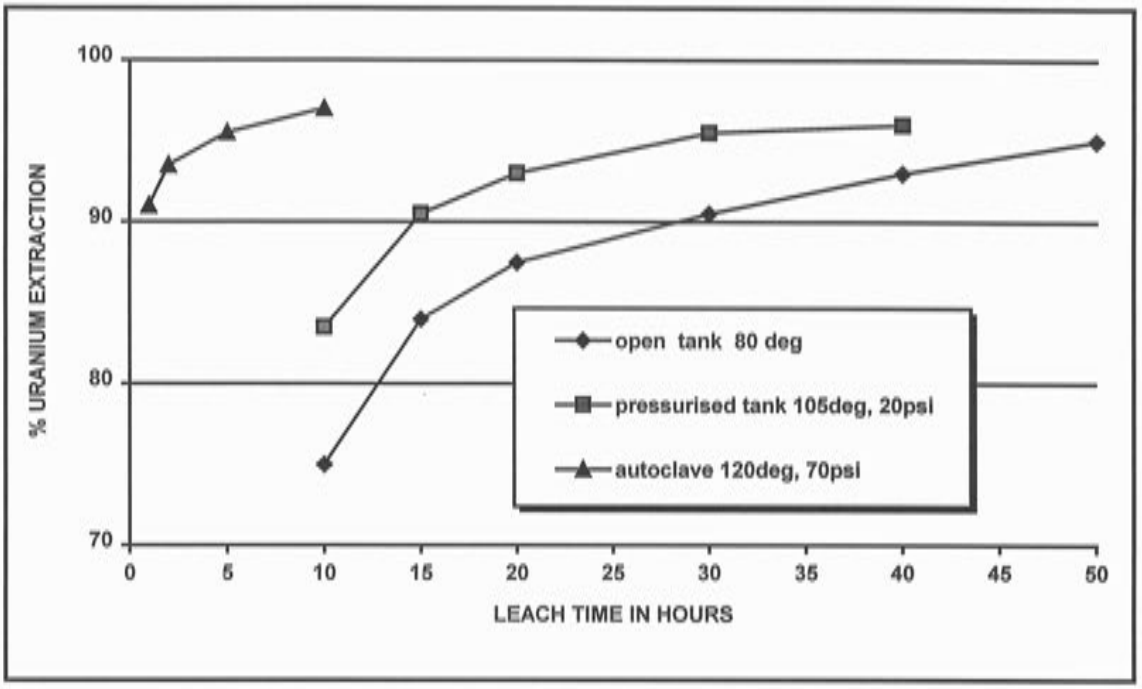
As mentioned previously the grind size for carbonate leaching may require a finer grind than that for an acid leach due to the less aggressive nature of the solvent system. Obviously if the uranium mineralisation is located as deposits between or on other substrate minerals then coarser grinds will suffice. If the uranium is within otherwise insoluble minerals then finer grinding will become important.

The percentage solids of the pulp will generally be set by the viscosity induced by the gangue minerals. This can be set by eye and quantified by viscosity measurements.

Studies, by others, have shown that within the general pH range of 9 to 10.5 the rate of dissolution of uranium is independent of the bicarbonate/carbonate ratio. However an insufficient amount of bicarbonate, as noted previously, and consequent increase in the hydroxyl ions content (pH>10.5) tends to reprecipitate sodium diuranate and thus slow the overall reaction. The amount of bicarbonate required varies between ores, mainly controlled by consumption of bicarbonate by other ions such as sulphides. The objective is to have only a small excess of bicarbonate on completion of the leach as this bicarbonate needs to be neutralised with caustic prior to reprecipitation of uranium. A minimum of 5g/l bicarbonate seems to be required. If the bicarbonate consumption is high then it may be necessary to introduce a sulphide flotation step ahead of the carbonate leach.

As a general rule uranium leaching rate tends to increase with increased concentration of the carbonate/bicarbonate reagent at least up to 20g/l concentration. Hence the base conditions may be taken as excessive in the first instance and provided a good result is obtained then the concentration can be progressively reduced.

Typical temperatures for non pressurised tanks are around 80 degrees C with temperatures up to 120 degrees C and pressures of up to 90psi typical for autoclaves. Air consumptions range widely, mainly dependant on retention time. A typical relationship that might exist between retention time and temperature and pressure is shown below.




- Reference Robert C Merritt, The Extractive Metallurgy of Uranium

An important factor in the leach process is the maintenance of an oxidising environment, not only to convert the uranium from the tetravalent to the hexavalent state but to prevent reduction back to the tetravalent state by reaction with reducing agents in the ore or from iron introduced during grinding.

Direct oxidation by air sparging is the most common form of oxidation both in agitated tanks and in pressure vessels. Even though it is less efficient than chemical oxidation it is considered to be cheaper by substituting longer leach times for the cost of chemicals. Oxygen can also be substituted for air, particularly in pressure leaching with advantages not only in oxygen availability but in reducing the off gas emission and hence heat losses.

A list of suggested chemical oxidants is given below but, many of these eliminate themselves either on the basis of cost or other downstream problems.

- Potassium permanganate is the most well known and it has a high initial efficiency but is expensive and losses its efficiency.

- Ferricyanide is also expensive and large amounts are required.

- Like permanganate hydrogen peroxide is expensive and has a tendency to decompose in solution thus reducing its long term benefit.

- Sodium hypochlorite is the most economical of the oxidants based on cost and oxidising efficiency but its concentration in solution must be maintained and it can lead to buildup of chloride ions in the recirculating solutions.

The use of the copper ammonium system has had some reported success, particularly were aeration has also been maintained. The optimum copper concentration in solution is about 0.15g/l. The ammonia acts to complex and hold the copper in solution and must be added before the copper in sufficient amounts to achieve this. Typical additions of 1kg/t copper sulphate and 3kg/t of ammonia are reported. As ammonia is volatilised rapidly at atmospheric pressure and temperatures of 80-90 degrees C this system is more efficient in pressure vessels. There are downstream disadvantages such as precipitation of copper with the uranium and interference with filtration properties.

| Oxidant | Relative efficiency when added in stoichiometric quantity |
|---|---|
| $Ag_2SO_4$ | 100 |
| $K_3Fe(CN)_6$ | 100 |
| $HgCl_2$ | 96 |
| NaOCl | 81 |
| $KMNO_4$ | 76 |
| $H_2O_2$ | 69 |
| $K_2S_2O_8$ | 65 |
| $CuSO_4 . 5H_2O + 0.15M\ NH_3$ | 64 |
| $PbO_2$ | 47 |
| air | 21 |

# 5. ACID LEACHING

## 5.1 ADVANTAGES AND DISADVANTAGES

As mentioned earlier all of the uranium plants in Australia, to my knowledge, utilise a sulphuric acid uranium leach. Sulphuric acid rather than nitric and hydrochloric acid is used on a cost basis unless there are other factors involved that increase their appeal. Nitric acid and hydrochloric acid also both introduce more expensive materials of construction problems.

The sulphuric acid leach is carried out at atmospheric pressure and at ambient temperatures unless particularly aggressive conditions are called for with a problematical ore.

## 5.2 ESSENTIAL PROCESS STEPS

As with carbonate leaching sulphuric acid leaching relies on the uranium to be in the soluble hexavalent state and so an oxidising environment is necessary to ensure that the uranium is converted to and maintained in that state. The simplified leach reactions are thus;

$$2UO_2 + O_2 = 2UO_3$$

$$UO_3 + H_2SO_4 = UO_2SO_4 + H_2O$$

Leaching is generally carried out these days in mechanically agitated tanks rather than the previously preferred air agitated pachuca tanks. After leaching the pregnant liquor is recovered in a solids liquid separation step (usually in a counter current thickener circuit). The pregnant liquor which contains higher levels of dissolved gangue ions than does a carbonate leach liquor is then clarified ahead of a solvent extraction stage designed to concentrate and purify the uranium liquor.

The uranium is then precipitated from the upgraded solution as ammonium diuranate by the addition of ammonia with the precipitate dried, calcined and drummed as the conventional yellowcake product.

## 5.3 LABORATORY TESTING VARIABLES

Most of the emphasis on laboratory testing surrounds the leaching efficiency, although at latter stages of development the solvent extraction step is often investigated. This usually involves batch contacts but might progress to a mini pilot plant in order to provide some confirmation of selected conditions and expose any unforeseen crud forming properties that can cause so much problem if not anticipated.

Suggested base conditions might be;

- P80 = 75μm grind
- 50% solids pulp
- pH 2.0 or 30kg/t of acid
- ambient temperature
- atmospheric pressure
- pyrolusite to 475mV (vs SCE)
- 24 hours retention time

As acid leaching is more aggressive than carbonate leaching and tends to dissolve a greater component of the host rock it is often possible to operate at primary grinds coarser than those indicated for the base test. I stand to be corrected but the typical grind specification for Ranger ore is around 80% passing 100μm while for Kintyre ore coarser sizes, up to 200μm, can be tolerated without loss of leach efficiency. Coarser grind sizes are desirable as they improve the materials handling and washing properties of the ore for downstream processing.

The major requirement of the leaching operation is to maintain sufficient free acid to attack the uranium minerals without dissolving an excessive amount of the associated gangue minerals. There is often a fine line between adding sufficient acid and wasting acid in dissolving aluminosilicate gangue. As a general rule this is achieved at a pH around 2. On Jabiluka ore we developed a procedure for leaching defined as "*acid added under controlled pH conditions*". Effectively this technique recognised that defining the pH alone was not sufficient to specify the leach as the amount of acid and the rate at which it was added also had an influence on acid consumption and leach efficiency. Controlling the leach by pH led to sometimes large variations in acid addition due to the influence of temperature, addition rate and pH meter drift. In the end pH was used initially to define the acid requirement and then the acid requirement became the controlling factor for further testing refinements.

The percent solids of the leach, as with carbonate leaching, is a function of the pulp viscosity and can be modified and quantified by viscosity measurements. The objective is to establish a pulp that is mobile so that good mixing and diffusion of soluble uranium is obtained.

Most acid leaching is carried out at ambient temperature and atmospheric pressure. The reaction of acid with the pulp generates some heat so that typical operating temperatures of 25 to 35 degrees Celsius are obtained. Increasing the temperature can result in increased uranium dissolution rates but has the effect of increasing acid consumption, causing higher levels of contaminants in solution and a more corrosive environment which can lead to more expensive materials of construction. Depending on the leach conditions leach times of between 4 and 48 hours can result.

Next to acid addition the maintenance of proper oxidising conditions is the most important requirement in leaching, as we are about to hear in two subsequent papers. The principle oxidants traditionally used were manganese dioxide and sodium chlorate but more recently competition has come from the use of hydrogen peroxide (in the form of Caros acid) and improved aeration efficiency as proposed by Atomaer's Filblast technology. Each of the oxidants act to oxidise iron in solution from the ferrous to the ferric state and the ferric iron in turn oxidises the uranium. Minimum concentrations of 1g/l free iron in solutions are usually recommended, such iron often coming from the ore itself or from iron introduced during milling. In a typical test program a range of oxidants and pulp potential levels would be investigated.

# 6. ANCILLARY TESTING

Having established the most applicable leaching process then the behaviour of the pulps produced during neutral thickening, CCD washing in thickeners or by filtration, selection of solvent extraction reagents and their testing become of significance because of their potential influence on the efficiencies that can be achieved and their impact on capital costs for the project. Other aspects that can become drawn into the final stages of testing are neutralisation of acid tailings, the behaviour of tailings in dams as they may affect dam design and the prepartion and properties of tailings if they are being considered for use as mine backfill.

I do not intend to spend time on those aspects in this presentation but each can become of significant importance to a project and can even lead to small scale pilot plant runs in order to produce sufficient volumes of material for testing.

It is in this overlap area of optimisation and testing that suppliers of reagents (such as oxidants, flocculants and solvent extraction chemicals) and equipment suppliers (of thickeners and filters in particular) are often called upon to play a role in prefeasibility testing. Often they supply specialist testing and recommendations at no charge in order to enhance their possibilities of gaining inclusion in the tendering process and ultimately sales of their products.

# 7. CONCLUDING COMMENTS

In the preceding presentation there are three topics that I have not touched on that are generally of concern to the management of the development company. They are;

- Sample requirements
- Costs and
- Program duration

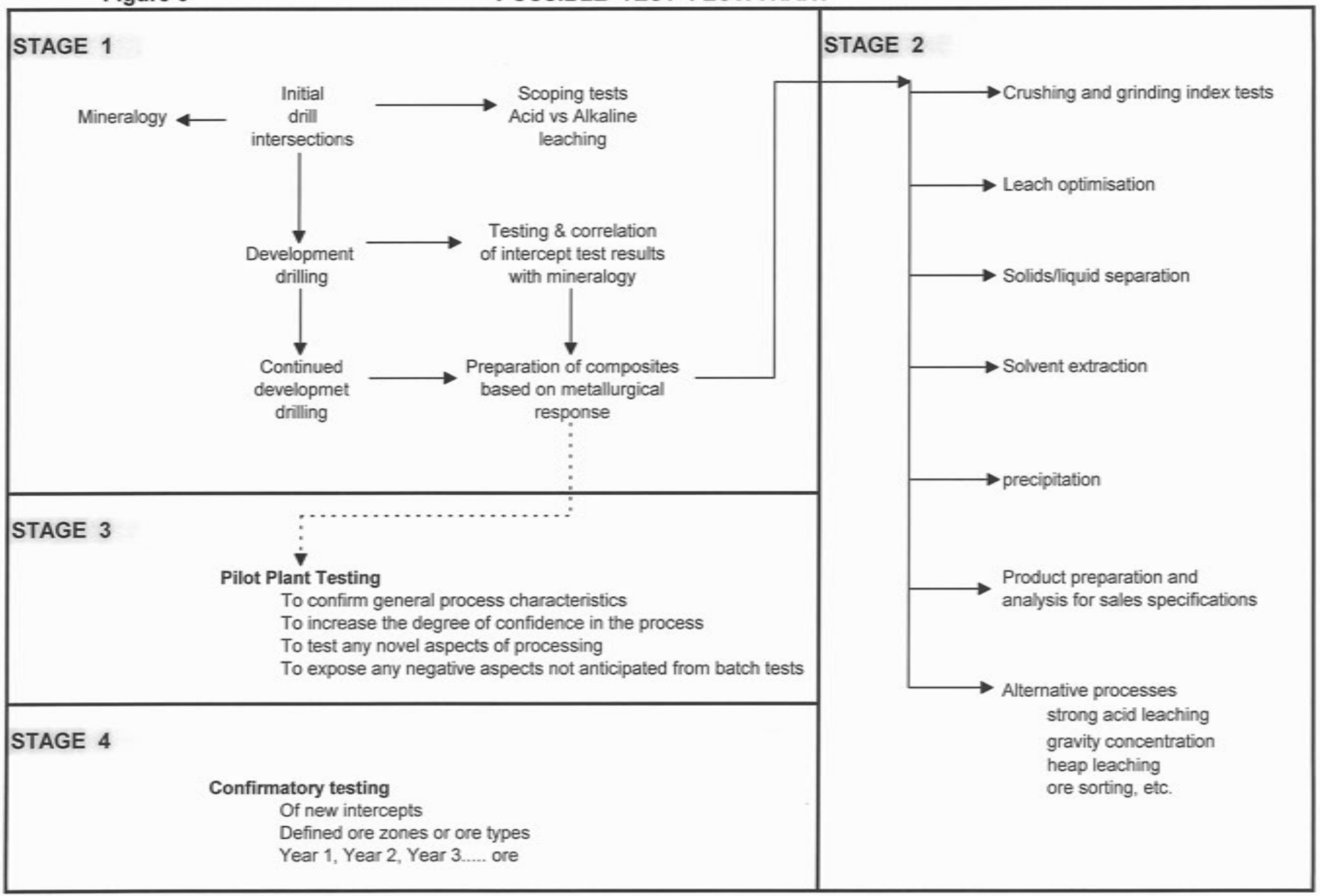
These are each difficult questions on which to give a specific answer and when asked generally cause the consultant, or the test laboratory, to stumble a bit as they do not have a crystal ball from which to predict the answers.

Testing in the first instance is generally carried out on 1kg test portions although the number of tests required to optmise a process may approach a hundred, with additional tests on individual drill increments or ore types adding another hundred. In conservative terms, for the purpose of budgeting, the cost per test for acid leaching is around A$600 in 1997 dollars, and for alkaline pressure leaching is around A$700. From this the mathematics suggest around $120 - 140,000 for a bench scale test program taken to completion. This can be doubled if small scale continuous testing is required and the management costs are added in. In the final analysis I would be suprised if you could find a miner that had spent less than a million dollars on testing before bringing a uranium project on line.

I have mentioned that in the first instance tests are generally carried out on core samples at 1kg scale bench tests. These core sections may eventually be combined into a test composite with a minimum requirement for 100 tests of 100kg. When sample for crushing and grinding properties are included, plus material for any pilot run, then up to 1 tonne or core could easily be required.

Prediction of the duration of any test program is just as difficult a question to answer. The program is generally carried out as a series of scope of work programs that develop as the project develops. A time scale for each program can often be estimated and as a guide I can suggest that pressure leach tests, because of the specialised equipment required, are generally carried out one at a time and down time for maintenance and repairs can cause delays so that progress is slow. Acid leach tests can be carried out at a faster rate but in the initial stages when the effects of the variables are being assessed this may only be twice as fast as the pressure leaching tests. Thus the best answer that I can give on timing is for say 4 weeks for an initial range of tests to anything from 1 to 2 years to completion. This may sound like a long lead time and compared to say a gold project it is long, but in reality the time scale is probably well within the lag time for the project to gain the necessary approvals. The Jabiluka deposit was discovered in the 1970's and here we are in the 1990's with the ore still in the ground.

Figure 3 POSSIBLE TEST FLOWCHART



# URANIUM SOLVENT EXTRACTION USING TERTIARY AMINES

by
Dr. J.M.W. Mackenzie

Henkel Australia Pty Ltd

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# 1. INTRODUCTION AND HISTORY

## 1.1 INTRODUCTION

Uranium was the first metal to be recovered in significant quantities using solvent extraction. Much of the copper SX equipment technology is a development of existing uranium technology. Because the kinetics of extraction via an ion exchange mechanism are much faster than for a chelation mechanism the mixer residence times are much longer for copper SX than for uranium.

## 1.2 HISTORY

Following the development of the nuclear industry during and immediately after World War II, attention was focussed on developing technologies which could be used to upgrade and purify uranium from low grade sources. Initially the nuclear industry had relied on high grade uranium ores from the Belgium Congo and Canada. One of the main participants in this development was the Union of South Africa and the then Prime Minister, Jan Smuts, visited MIT in the USA in this regard.

Research in the USA lead to the first commercial use of amines in uranium concentration at West Rand Consolidated Mines in South Africa in 1952. The amines used in this plant were in the form of a strong base resin and it was not until 1957 that the first commercial solvent extraction plant using amines was opened in the USA.

Since those early days, the development of uranium hydrometallurgical processing has developed along three main paths:

1. **Ion exchange as the sole on site purification and concentration route**
   This used a strong base (quaternary amine) functionality resin to concentrate and purify the uranium.

2. **Ion exchange followed by solvent extraction purification of the IX concentration eluate**
   Acid leaching of uranium is a non-selective leach and ion exchange using strong base resins is a non-selective extraction process so it was not surprising that metallurgists looked to ways of purifying the concentrated eluate produced by strong IX. Attempts to improve the selectivity of the uranium IX process using weak base (tertiary amine) resins were not particularly successful and a circuit based on strong base IX of the leach solution followed by solvent extraction (SX) of the conc eluate using tertiary amine extractants was developed. One of the first plants of this type was installed at Buffelsfontein Gold Mine in South Africa and this circuit is sometimes referred to as a "Bufflex" circuit.

3. **Direct solvent extraction of the leach solution**
   This circuit uses a single extraction process, solvent extraction using a tertiary amine solvent and yields a product which is as pure as circuit (2). The direct SX circuit ("Purlex") became the standard uranium circuit in Canada, Australia and the US. In South Africa both direct SX and IX-SX circuits co-existed but SX circuits predominated.

   There are some hydrometallurgical circuits for uranium which use none of the above options. These include the use of TBP to treat nitric acid leach solutions produced in nuclear fuel reprocessing [1] [2], and to treat nitric acid leach solutions produced at Palaborwa, South Africa. D2EHPA/TOPO mixtures are used to extract uranium from phosphoric acid solutions

## 2. ACID LEACH CHEMISTRY FOR URANIUM

Sulphuric acid leaching of uranium ores in the presence of an oxidising agent (usually manganese or chlorate based) which provides a leach oxidation-reduction potential of 400 - 500 mv relative to a saturated calomel electrode, results in virtually all the leached uranium being present in the U(6) valency. The uranium dissolves as $UO_2^{2+}$ and then forms two uranyl sulphate anion complexes viz:

$$UO_2^{2+} + 2SO_4^{2-} \longrightarrow UO_2(SO_4)_2^{2-}$$

$$UO_2(SO_4)_2^{2-} + (SO_4)^{2-} \longrightarrow UO_2(SO_4)_3^{4-}$$

The uranyl sulphate anion complexes are the species which are extracted by amines.

Unfortunately, the oxidising sulphuric acid leach, which is often carried out at a temperature of 40 - 80°C is aggressive and non-selective resulting in many other species besides uranium being leached.

The presence of these anionic species can present problems in uranium solvent extraction. Some of the more important species involved are:

| | | |
|---|---|---|
| Soluble silica | $Si(OH)_4$ | $Si0_2$ amorphous |
| Tungsten | $WO_4^{2-}$ | |
| Antimony | $SbO_4^{3-}$ | |
| Arsenic | $ASO_3^{3-}$ | |
| Molybdenum | $MnO_4^{2-}$ | |
| Vanadium | $VO_3^-$ | |
| Zircon | $ZrO_3^{2-}$ | |
| Titanium | | |
| Phosphate | $PO_4^{3-}$ | |

In addition, sulphuric acid dissociates in water as follows:

$$H_2SO_4 \longrightarrow HSO_4^- + H^+ \qquad K_1 = 4 \times 10^{-1}$$

$$HSO_4^- \longrightarrow H^+ + SO_4^{2-} \qquad K_2 = 1.27 \times 10^{-2}$$

Chloride ($Cl^-$) and nitrate ($NO_3^-$) anions may also be present in the leach liquor.

The problems caused by these species and possible solutions to these problems are listed in Table 1.

# 3. TERTIARY AMINE EXTRACTION OF URANIUM

There are a number of extractants which can be used to recover uranium but only the amines (tertiary and quaternary) and the organic phosphates have found widespread commercial acceptance in the recovery of uranium from ores. SX recovery of uranium is restricted to acid leach solutions. Carbonate leach recovery systems do not use SX as a recovery or purification stage. By far the most widely used extractants for uranium are the tertiary amines specifically the $C_8$-$C_{10}$ symmetrical amines. Table 2 shows the loading and stripping chemistry for these systems.

## 3.1 TYPE OF AMINE USED AND MAXIMUM LOADING CAPACITY

The tri-octyl, tridecyl amine mixtures are used almost exclusively however amines of longer chain lengths have been used.

Trilaurylamine can be used when molybdenum is present as the amine molybdate complex formed with the $C_{12}$ amine is much more organic soluble than the $C_8$ amine complex. Obviously higher molecular amines require greater mass concentrations to give the same loading capacity as the lower molecular weight amines.

The approximate molecular weight of a typical $C_8$-$C_{10}$ tertiary amine, Alamine® 336, is 388 - 391 and the product is 96% tertiary amine. Based on this molecular weight, and the specific gravity of Alamine® 336 of 0.81, it is possible to calculate the theoretical maximum loading of a 1% V/V mixture of Alamine® 336 in a diluent of specific gravity of 0.81.

The calculated maximum loading depends on the speciation of the uranyl sulphates in the leach liquor. The appropriate values are:

| | Theoretical maximum loading of 1% V/V Alamine® 336 |
|---|---|
| $UO_2(SO_4)_3^{4-}$ | 1.12 gm U or 1.32 gm $U_3O_8$ |
| $UO_2(SO_4)_2^{2-}$ | 2.38 gm U or 2.81 gm $U_3O_8$ |

Under typical acid leach conditions almost all of the uranium is present as the $UO_2(SO_4)_3^{4-}$ complex and uranium SX plants are designed on the basis of a theoretical maximum loading of 1.2 gm U per 1 vol. % Alamine® 336.

In practice the theoretical maximum loading is not attained due to the presence of competing anions in the leach liquor.

## 3.2 THE EFFECT OF COMPETING ANIONS

Ion exchange extractants are non-selective and, although the uranyl sulphate anion is very strongly extracted by tertiary amines, other anions will also be extracted.

The order of selectivity for some anions is:

$$UO_2(SO_4)_3^{4-} > NO_3^- >> Cl^- > HSO_4^- > Fe(SO_4)_2^-$$

The effect of $NO_3^-$ and $Cl^-$ ions on the extraction of $U_3O_8$ on Alamine® 336 is shown in Figure 2. Interestingly, the effect of nitrate ions is much stronger than the effect of chloride ions. Fortunately, nitrate ions are not commonly present at high concentrations in ammonia leach liquors.

The effect of pH on the extraction of $U_3O_8$ on Alamine® 336 is shown in Figure 3.

Tertiary amines have a pKa of 9.02 but they have a weak basicity with stripping commencing around pH 3.0. The increase in $U_3O_8$ extraction as the pH is decreased from 2.03 to 1.04 in Figure 3 probably reflects the increased protonation of the amine as the pH is lowered.

When the $H_2SO_4$ concentration becomes significant however, as is the case in the conc eluate of an ion exchange plant, then $HSO_4^-$ competition can reduce uranium extraction as is shown in Figure 4.

## 3.3 DILUENTS AND THIRD PHASE INHIBITORS OR MODIFIERS

The role of the diluent in amine extraction of uranium is similar to the role of the diluent in other solvent extraction systems. A good diluent will:

a. Be insoluble in the aqueous phase
b. Solubilise the extractant
c. Solubilise the extractant-metal complex
d. Not adversely alter the extraction and strip equilibrium
e. Have a flash point significantly (at least 30°C) higher than the operating temperature
f. Have a low viscosity
g. Be chemically stable
h. Have good phase separation properties
    i. Low entrainment
    ii. Not form crud and be tolerant to crud
i. Have acceptable cost
j. Be non-carcinogenic

For (c), tertiary amines impose special conditions as the $C_8$-$C_{10}$ amine - uranium complex is not totally soluble in the typical carriers containing 0-20% aromatic and third phase inhibitors or modifiers are commonly used to improve this solubility. Isodecanol is the usual third phase inhibitor employed and it is added at about 50-60% of the amine concentration. The addition of isodecanol does bring some potential problems:

1. Because of the OH group, alcohols can make phase separation of the mixed organic more sensitive to dissolved and precipitated silica. This is presumably due to a hydrogen bonding linkage between the silica and the alcohol OH group.
2. Isodecanol is a nutrient for bacteria.
3. Note also that isodecanol is much more soluble in water than amine. Typical values are:

| | Solubility in Water |
|---|---|
| Tertiary $C_8$-$C_{10}$ amine | < 5 ppm |
| Isodecanol | 150 - 170 ppm |
| Water in isodecanol | > 150 ppm |

Because of this higher solubility, the isodecanol and amine loss from a mixed solvent will often be about the same in ppm in raffinate or kg/month terms.

An alternative to isodecanol as a third phase inhibitor is to add a high aromatic content diluent (+90% aromatic) to increase the total aromatic content of the diluent to 36-40%. Such high aromatic diluents are not subject to bacterial decay and it is possible that they may be more tolerant of dissolved and precipitated silica than are the carrier isodecanol mixtures. However, high concentrations of aromatics can produce environmental problems.

## 3.4 SECONDARY AMINES

The manufacture of tertiary amines inevitably leaves a small concentration of secondary amine in the final product. This may be between 1 and 5% depending on the quality of the tertiary amine.

Secondary amines do load and strip uranium under the conditions used to load and strip tertiary amines and, for this reason, the presence of secondary amines in a circuit organic, either as a result of the amine manufacturing process or due to degradation of tertiary amine to secondary amine, is not readily detected by monitoring plant performance or by carrying out loading tests on samples of plant organic.

Secondary amines have lower loading characteristics than tertiary amines and are also less selective for uranium over ferric iron than the tertiary amines.

# 4. GENERAL CONCEPTS OF TERTIARYAMINE URANIUM EXTRACTION CIRCUITS

## 4.1 GENERAL CIRCUIT LAYOUT

The general circuit layout of a typical uranium SX circuit using tertiary amines is shown in Figure 5. As with all SX circuits, PLS clarification prior to SX is vital. For uranium leach circuits, this problem can be more complicated than for copper heap leach solutions since uranium leaching is normally an intensive process carried out at elevated temperatures. This can result in high concentrations, 500-1500 ppm, of soluble silica being present in the PLS. If this silica is allowed to remain in the PLS then during extraction it can nucleate and precipitate at the organic-aqueous interface. The reasons for this nucleation are not clear but may result from hydrogen bonding of the silica to OH groups on the isodecanol commonly used as a third phase modifier. Also, the positive charge on the amine at the interface may electrostatically attract anionic silica to the interface concentrating these species at the interface to such a degree that they precipitate as solids.

Precipitation of soluble silica and removal of the precipitate during the clarification stage is attempted by most plants. High molecular weight polyethylene oxide based flocculants, such as Union Carbide's Polyox reagents, have been used to assist in precipitation of the soluble silica. Hydrogen bonding of the ethylene oxide groups on Polyox and the silica may provide the mechanism for silica precipitation.

Agitation leach systems involve extensive solid-liquid separation stages, usually involving CCD or belt filters.

Considerable quantities of polymers flocculants, typically polyacrylamides or guar are added to the pulp during this separation and these polymer can lead to phase separation problems in SX. Guar flocculants have been reported to produce less problems than polyacrylamide flocculants.

Uranium SX plants usually employ 3 - 4 stages of extraction. The throughput O/A may be 1:1 for high grade ores or as high as 80:1 for low grade ores.

## 4.2 LOADED ORGANIC SCRUBBING

The loaded organic is usually scrubbed in a multi-stage scrub circuit to remove anionic contaminants. Typical scrub aqueous solutions are:

a. Water

b. Dilute sulphuric acid (10%)

c. $(NH_4)_2SO_4$ at pH 2-2.5

The scrub aqueous exiting the circuit is usually returned to E1. Use of $(NH_4)_2SO_4$ as a scrub aqueous together with pH control can be effective in removing silica and anionic species such as zirconates, which strip at a lower pH than $U_3O_8$, or at the same pH and, if left on the loaded organic entering strip, will report to the strip aqueous either as a soluble contaminant or as a crud forming precipitate.

The use of dilute sulphuric acid is effective in scrubbing of iron from the organic.

## 4.3 STRIPPING

This is normally done using $NH_4OH$ over four stages with a pH profile which approximates:

| | pH |
|---|---|
| S1 | 3.5 |
| S2 | 3.8 |
| S3 | 4.2 |
| S4 | 5.0 |

The pH of S1-S3 is controlled by $NH_4OH$ or $NH_3$ gas addition. The pH of S4 normally is not controlled but allowed to float at the pH produced by return of the ADU thickener overflow.

Strip pH controllers require accurate pH measurement of the mixer emulsion.

Since the mixers are often run organic continuous, measurement of pH using a probe in the mixer box is not always effective and a small side mounted pot (Al Ross pH Pot) may be used or the pH may be measured in the settler. The latter involves a time delay.

### ADU Precipitation

The strip aqueous is precipitated using ammonia either as gas or $NH_4OH$. The pH is maintained at 7 - 7.5. The solution must be maintained at about 30°C during precipitation. If it is hotter or colder the sulphate content and the physical size of the ADU particles can be adversely affected.

## 4.4 REGENERATION OR SCRUBBING OF THE STRIPPED ORGANIC

The stripped organic may still retain loaded anionic species other than $U_3O_8$.

In addition, tar and humates present in the PLS may also be loaded onto the organic. In order to remove these species the organic is scrubbed at pH 10 - 10.5 using a sodium hydroxide/sodium carbonate solution. This deprotonates the amine allowing adsorbed anions to be scrubbed off. The alkali also saponifies any fatty acid groups and removes these into the aqueous.

Tertiary saturated amines are stable in alkali at pH 9-11. However, some plant operators are concerned that the tertiary amine may degrade along the lines of the Hofmann elimination whereby quaternary amines in the presence of heat (125°C or higher) or strong alkali decompose to a tertiary amine, an alkene and water. This reaction applies only to quaternary amines and not to tertiary amines.

In some cases an alkaline methanol or ethanol scrub may be used to remove organics, particularly polar organics from the stripped organic.

# 5. ASPECTS OF EQUIPMENT SELECTION AND PLANT DESIGN FOR TERTIARY AMINE URANIUM SX CIRCUITS

The fast extraction kinetics of uranium recovery by tertiary amines mean that the mixer residence times in extraction can be as low as 45 seconds to 1 minute. This compares with the 2 minutes typically used for Cu extraction.

These short residence times in turn result in a range of contactors being used in uranium extraction. The include:

- Conventional mixer settlers
- Davy CMS contactors
- Pulsed columns

By far the great majority of plants use conventional mixer settlers with extraction mixer settlers of 1 minute residence time and specific flow of mixed phase through the settler of 4.5 - 5.0 $m^3/m^2/hr$. Because many uranium orebodies yield a PLS of less than 5 gpl $U_3O_8$, sometimes less than 1.0 gpl, a 5% V/V tertiary amine extractant is widely used together with organic recycle to maintain an O/A in the mixers of 1:1. The use of 5 - 8% V/V tertiary amine and a small throughput flow of organic on low grade $U_3O_8$ leach solutions means that the loaded organic scrub and strip mixer settlers are relatively small compared with the extraction units.

# 6. SPECIAL PROBLEMS DUE TO ORGANIC CONTAMINANTS AND CRUD

There are two commonly occurring special problems in uranium SX recovery circuits using tertiary amines. These are:-

## 1. Poor phase separation due to soluble silica and polymeric silica - flocculant species

Most ores will generate some soluble silica during a $H_2SO_4$ uranium leach. The longer and more intensive the leach the greater the soluble silica content of the PLS. Typical values of soluble silica are 300 - 700 ppm but some ores and leaches generate up to 5000 ppm. Any value greater than 500 ppm has the potential to create a problem. Dissolved silica, especially in the polymeric form, has hydrogen bonding capability and can interact with OH groups on the organic. They can also interact with polyacrylamide flocculants used in solid-liquid separation.

The exact mechanisms of the interference are unclear but the following model fits many operations:

a. The soluble silica, a silica-polyacrylamide complex or possibly just the polyacrylamide concentrates at the positively charged organic water interface of the emulsion.

b. In this locally high concentration some precipitation occurs - perhaps as a monomolecular layer.

c. As an aqueous continuous emulsion breaks the area of the organic water interface decreases by many orders of magnitude. This squeezes the monolayer of precipitate into a multi-layer and the multi-layer (usually visible) interferes with further phase disengagement.

d. Because the precipitate is aqueous wetted, the interference is much greater for aqueous continuous emulsions than for organic continuous emulsions. For an aqueous continuous emulsion an aqueous film has to thin to produce coalescence. Organic continuous operation can significantly reduce the effect of silica on phase separation. Figure 6.

## 2. Problems due to humates and tars

Organic matter in the ore can, under leaching conditions, form soluble species such as carboxylic acids and organic sulphates which are extracted or solubilised in the organic. They then:-

a. Interfere with phase disengagement. They are normally surfactant species.

b. Can, by association with the amine, form anionic-cationic complexes that reduce amine loading capacity.

c. Can extract other metals.

Scrubbing with an alkali methanol or ethanol water solution can remove these organic contaminants.

## 7. REFERENCES


1. C. Phillips. Operating Experience of the Solvent Extraction Processes in Thermal Oxide Reprocessing Plant ISEC. Value Adding Through Solvent Extraction. University of Melbourne, 1995 p. 783
2. C. Phillips. Development of Thorp Chemical Separation Plant Atom 394. August 1989
3. J.P. McDonald, P.L. Mattison and J.M.W. Mackenzie. Problems in the Hydrometallurgical Extraction of Uranium in the USA and South Africa. Journal S.A.I.M.M. October 1981 p. 303


## ACKNOWLEDGMENT


The author acknowledges the permission of Henkel KGaA to publish this paper.

**TABLE 1.**
**COMMONLY INTERFERING ANIONS IN TERTIARY AMINE EXTRACTION OF URANIUM**

| | |
|---|---|
| $HSO_4^-$ | Can compete with uranyl sulphate in ion exchange. Reduces the extraction kinetics of uranium. Particularly noticeable in the treatment of IX conc eluates (Bufflex circuits) where 100 - 120 gpl $H_2SO_4$ is used for elution. Extra extraction stages and/or longer mixer residence times may be required.<br><br>Transfer of $HSO_4^-$ to strip can make pH control in the ammonia strip difficult. A loaded organic scrub stage may be required. |
| $MbO_4^{2-}$ | Common ingredient of some uranium ores (USA particularly). Extraction by Trilaurylamine with an acid chloride strip for uranium followed by a $Na_2CO_3$ strip for molybdenum is used. |
| $VO_3^-$ | V(4) does not extract and is the predominant anion in the emf range 400 - 500 mv (with reference to saturated calomel electrode).<br><br>V(5) does extract and occurs at emf values above 600 mv. |
| $Th(SO_4)_3^{2-}$ | Not strongly extracted by $C_8$-$C_{10}$ tertiary amines but may be extracted by primary and secondary amines. |
| $Cl^-$ | Can be present in process waters. Can interfere with stripping of uranium by ammonia. Can compete with uranyl sulphate in extraction and can form anion complexes with other metals. These anion complexes can then extract on $C_8$-$C_{10}$ tertiary amines. Figure 1 shows some of the more common metals extracted by this mechanism. |
| $NO_3^-$ | Can be present in leach solutions due to the nitrate content of explosives. Under certain highly oxidising conditions can react with tertiary amines to form carcinogenic nitrosamines. This has been observed at two uranium SX plants and results in loss of extractant and potential health problems. |
| Thiocyanates ($SCN^-$) and thionates $S_2O_3^-$ | Can co-extract with uranium and does not strip in ammonia. Can be scrubbed off with an alkali scrub. |

**TABLE 2.**
**CHEMISTRY OF URANIUM RECOVERY USING TERTIARY AMINES**

## EXTRACTION

$$[2R_3N]_{org} + H_2SO_4 \_ [(R_3NH^+)_2\, SO_4^{2-}]_{org}$$

pKa 9.02

$$[2(R_3NH^+)_2SO_4^{2-}]_{org} + UO_2(SO_4)_3^{4-} \_ [(R_3NH^+)_4UO_2(SO_4)_3^{4-}]_{org} + 2SO_4^{2-}$$

**OR**

$$[(R_3NH^+)_2SO_4^{2-}]_{org} + UO_2(SO_4)_2^{2-} \_ [(R_3NH^+)_2UO_2(SO_4)_2^{2-}]_{org} + SO_4^{2-}$$

## STRIPPING

### AMMONIA STRIP

$$[(R_3NH^+)_4\, UO_2(SO_4)_3^{4-}]_{org} + 4NH_4OH \_ (4R_3N)_{org} + (NH_4)_2SO_4 + (NH_4)_2[UO_2(SO_4)_2] + 4H_2O$$

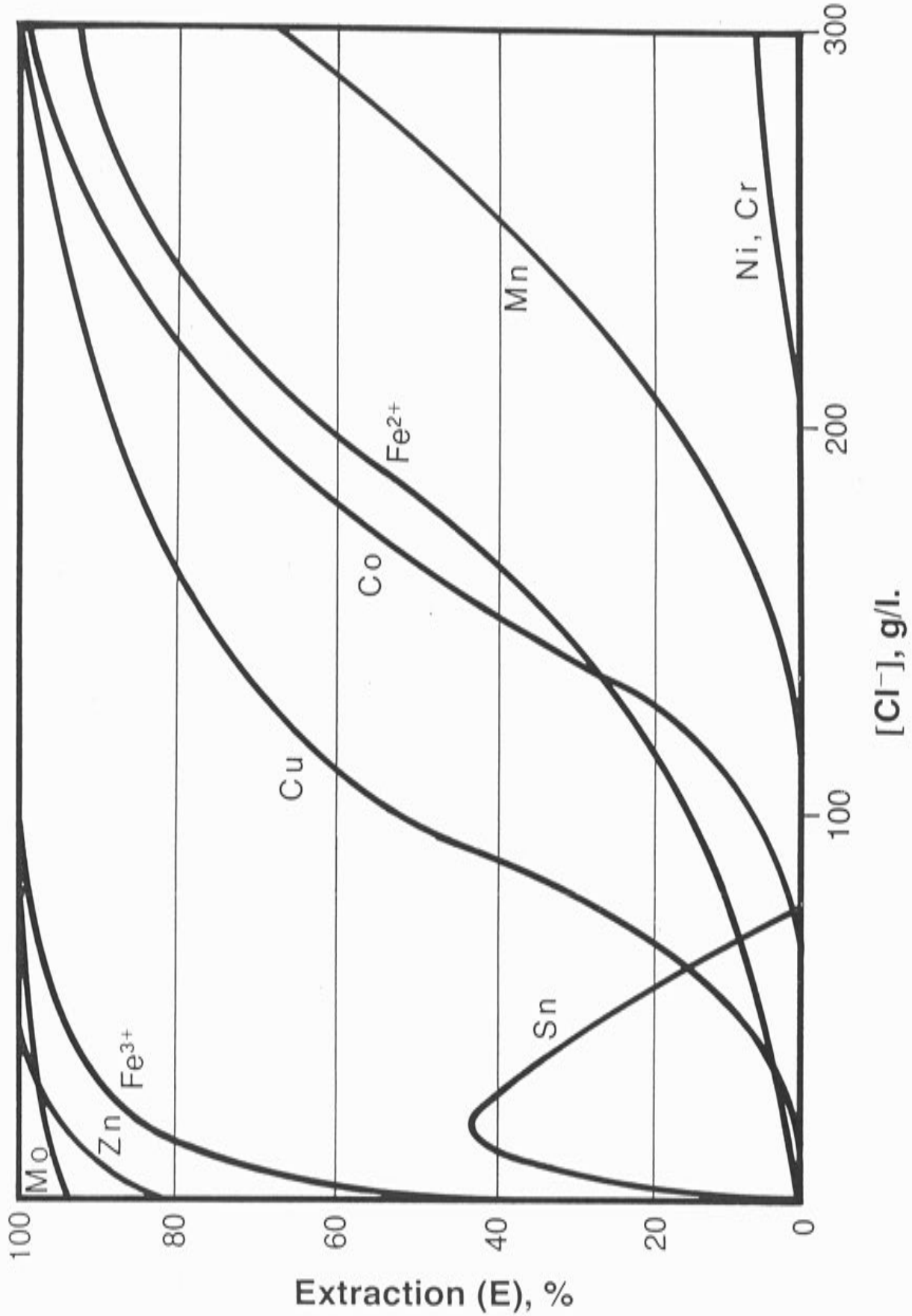
### CARBONATE STRIP

$$[(R_3NH^+)_4\, UO_2(SO_4)_3^{4-}]_{org} + 5Na_2CO_3 \rightarrow (4R_3N)_{org} + Na_4UO_2(CO_3)_3 + 2H_2O + 2CO_2 + 3Na_2SO_4$$

### ACID CHLORIDE STRIP

$$[(R_3NH^+)_4\, UO_2(SO_4)_3^{4-}]_{org} + 4HCL \rightarrow (4R_3NHCL)_{org} + UO_2SO_4 + 2H_2SO_4$$

Figure 1. **Alamine® 336 Extraction Isotherms from Chloride Solutions at 40°C and pH = 2**



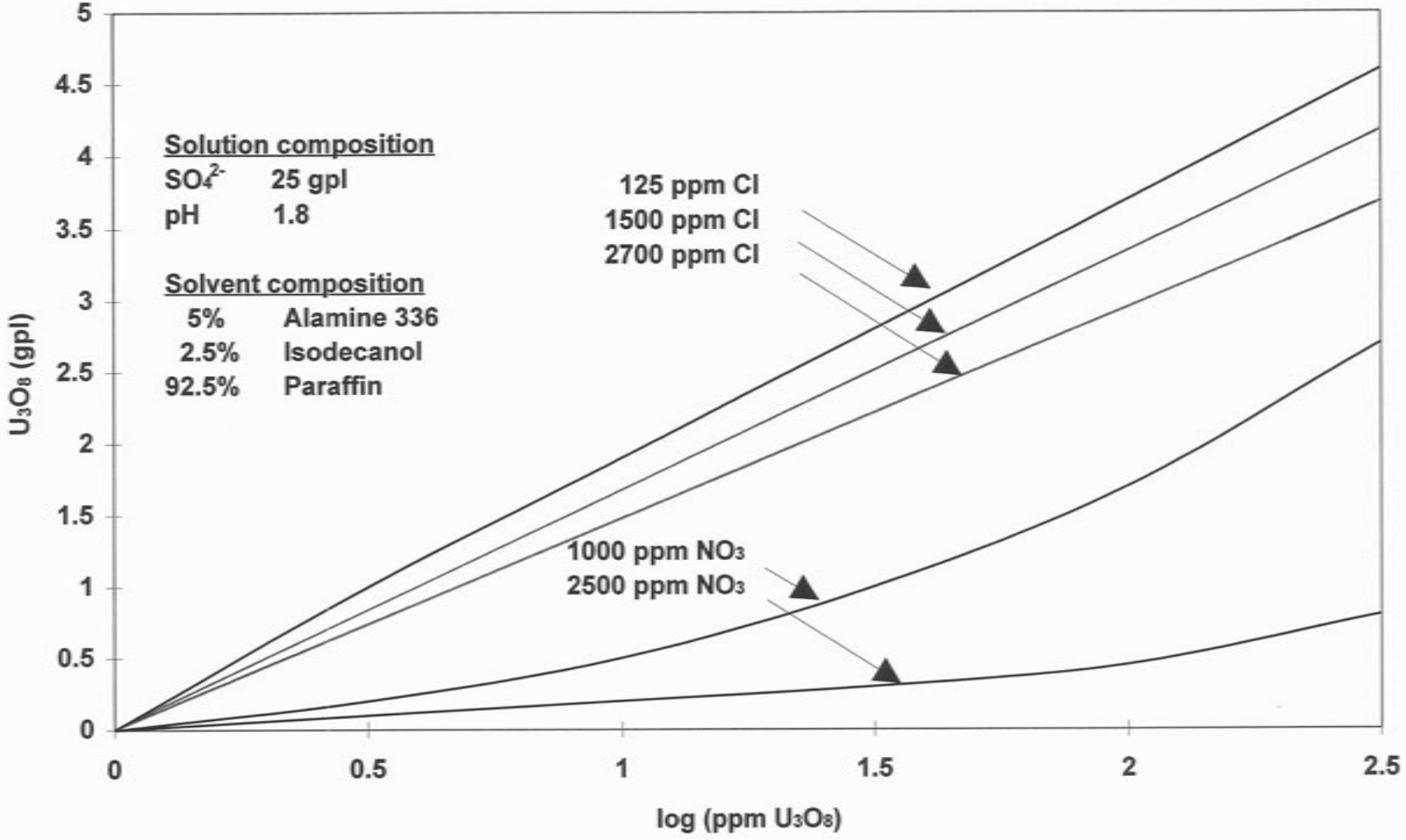



**Figure 2. The Effect of $Cl^-$ & $NO_3^-$ on the Loading of $U_3O_8$ on Solvent**

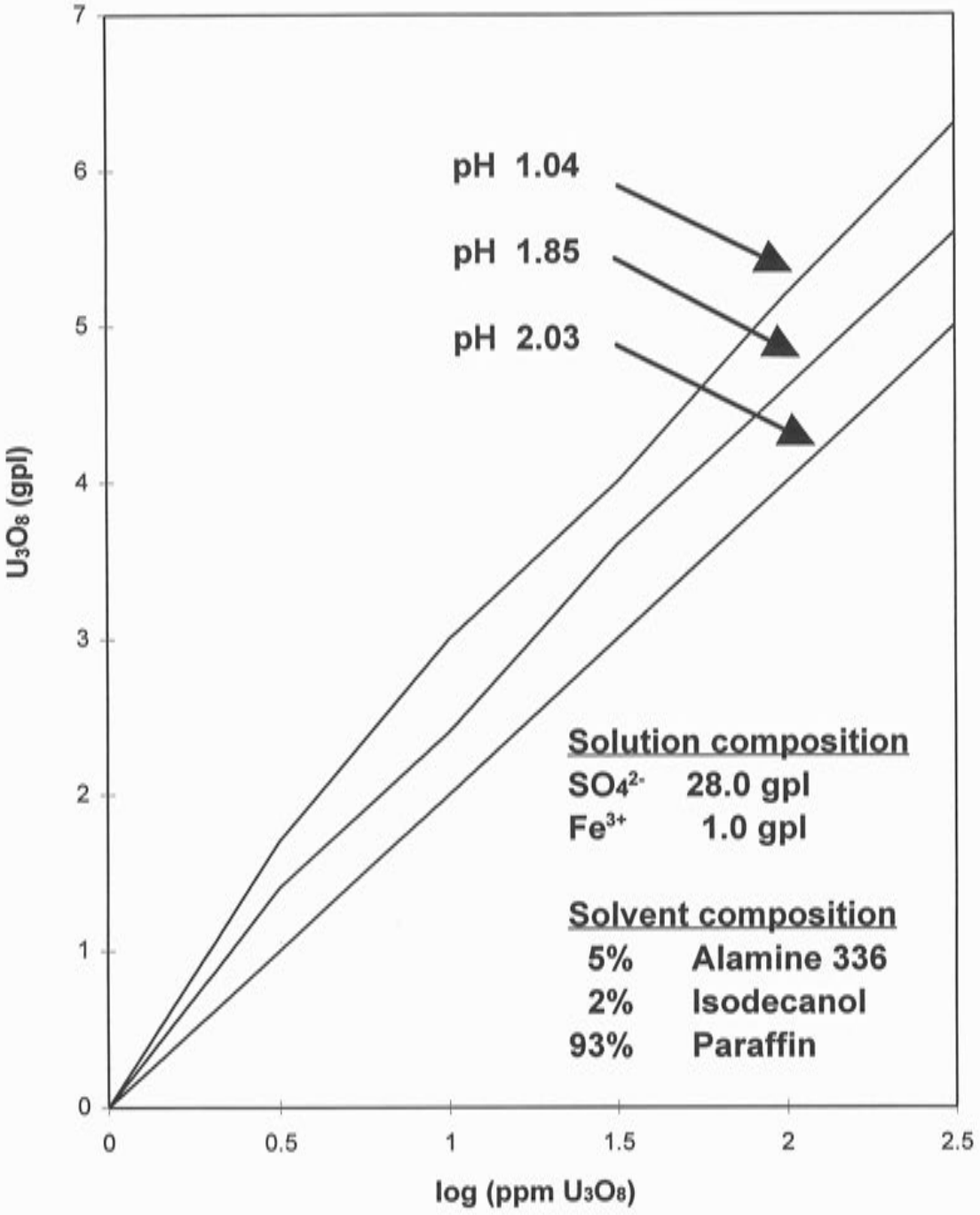



**Figure 3. The Effect of pH on the Loading of $U_3O_8$ on Tertiary Amine Solvent**

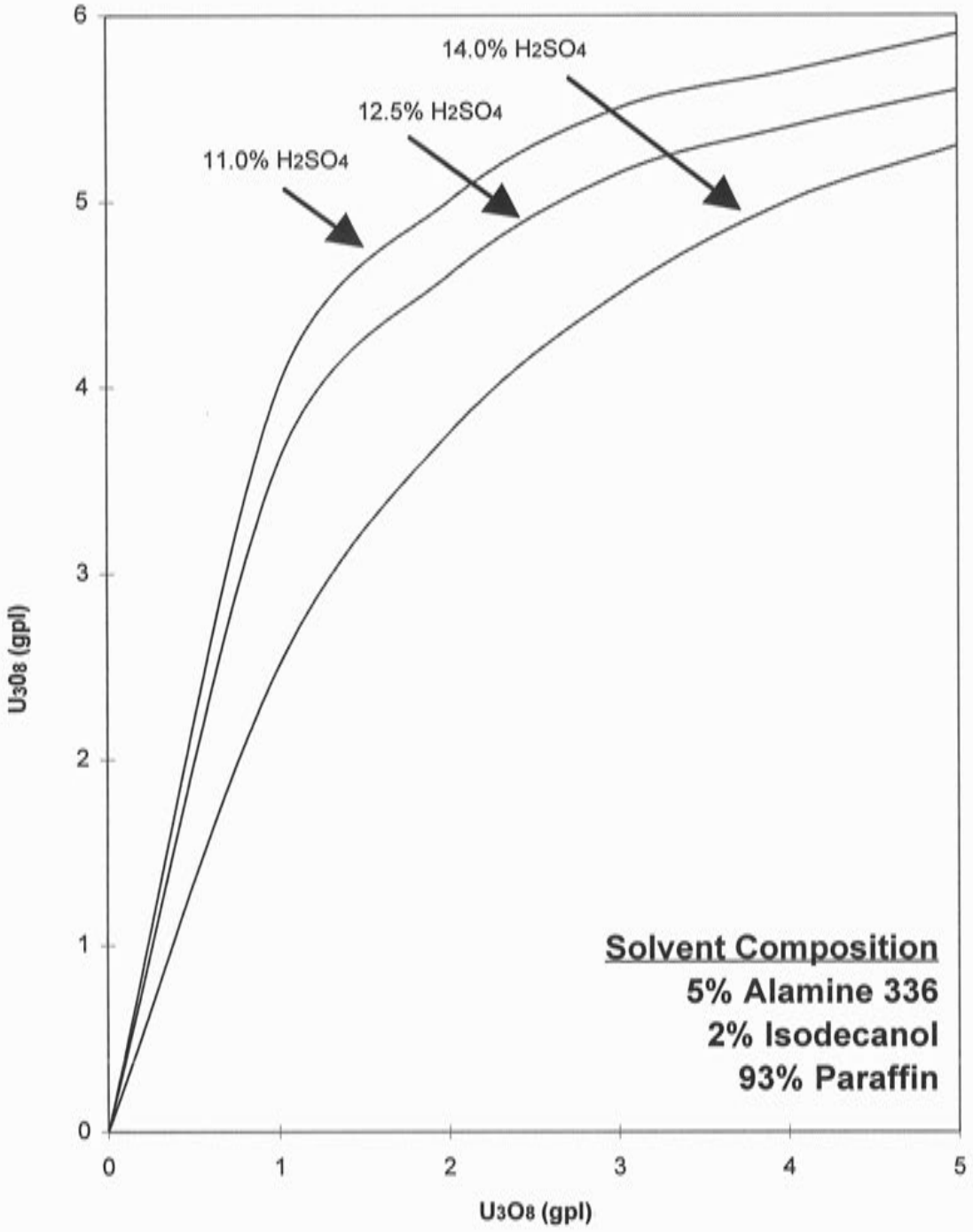



**Figure 4. The Extraction of $U_3O_8$ from $H_2SO_4$ Solution**

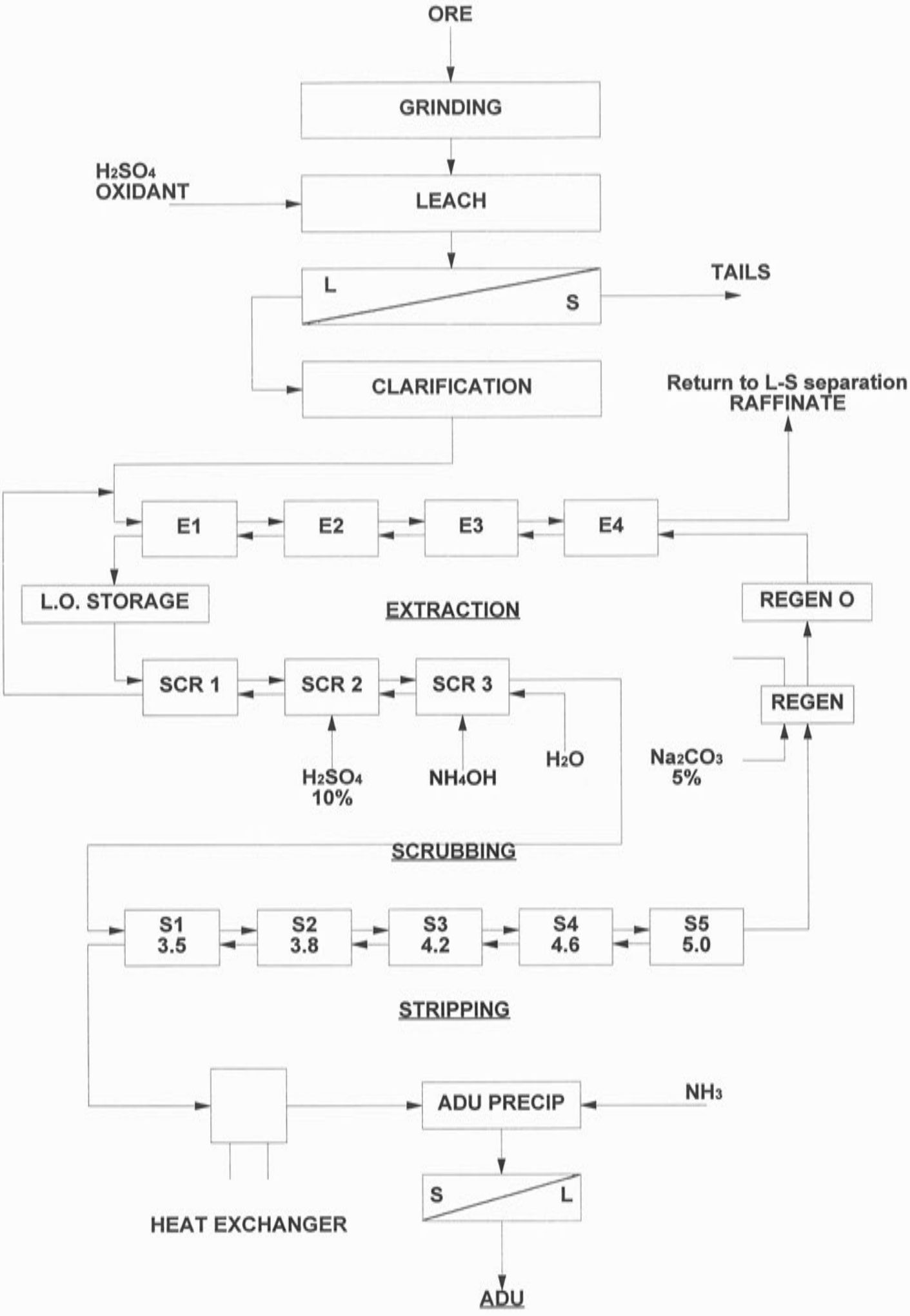
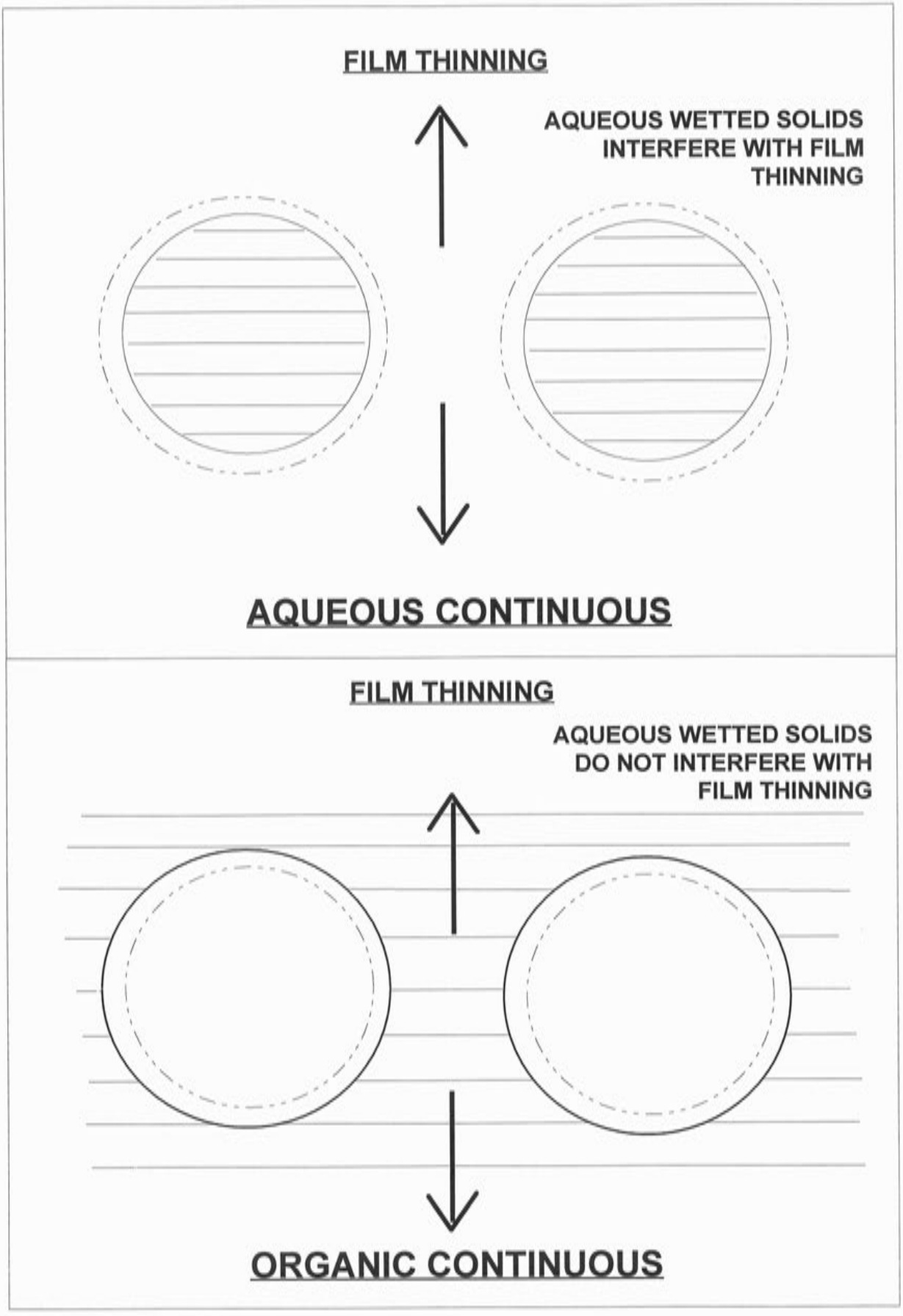



**Figure 5. Typical Acid Leach - SX Uranium Circuit**

Figure 6. Effect of Phase Continuity



# USE OF HYDROGEN PEROXIDE AND CARO'S ACID IN URANIUM ORE PROCESSING

by
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# 1. INTRODUCTION

Hydrogen peroxide and its analogues have been used in a variety of processing options for uranium for many years. These include acid and alkaline leaching, precipitation (both direct and from SX strip) as well as in water & effluent treatment.

In the late 1970's, early 1980's, development of improved leaching applications for peroxygens was undertaken to increase the use of peroxygens in mineral processing. This included applications for both primary and secondary hydrometallurgical processes (1). The outcome of these efforts was to show the viability of Caro's acid as an alternative leach oxidant to the traditionally applied pyrolusite or chlorate for acid leaching uranium ores (2,3, &4).

Due to the to the events in subsequent years which have affected the development of the uranium industry, expansion on this initial work did not occur. However opportunities in environmental treatment and paper industries provide the impetus for employment of these technologies. The recent changes in the political and economic character of the uranium industry as well as the increased interest in producing higher value added mineral and metal products in Australia have warranted a review of potential for applying peroxygens in mineral processing (5). This review is confined to the area of conventional acid leaching.

## 2. CHARACTERISTICS OF PEROXYGENS

Hydrogen peroxide is an effective oxidant in both acid and alkali media. It does however, tend to decompose in the presence of suitable catalysts. These catalysts are common metal ions such as iron and copper (see Table 1). Ions which normally occur in acid leaching of uranium ores. Caro's acid $H_2$ S $O_5$ - Peroxymonosulphuric acid) on the other hand, exhibits superior stability in the presence of these decomposition agents (6). Caro's acid is generally more cost effective in leaching applications from a variable cost perspective than hydrogen peroxide.

**TABLE 1.**
**PEROXYGEN CHEMISTRY:**

| | | | |
|---|---|---|---|
| $H_2O_2 + H_2SO_4$ | → | $H_2SO_5 + H_2O$ | (Formation) |
| $2H_2O_2$ | → | $2H_2O + O_2$ | (Decomposition) |
| $2H_2SO_5$ | → | $2H_2SO_4 + O_2$ | (Decomposition) |

Commercially, Caro's acid is made by reacting hydrogen peroxide and sulphuric acid. In order to ensure high yields of Caro's acid, high reagent concentrations are necessary e.g. greater than 50% $H_2O_2$ and greater than 94% $H_2SO_4$. The smaller the quantity of water presence during the synthesis of Caro's acid, the greater the conversion of hydrogen peroxide. The reaction is exothermic in nature and this aspect was in the first instance dealt with by provision of a cooling system.

The table 2 illustrates that the peroxygens are strong oxidants and appropriate for oxidising the primary leaching agent in acid conditions, namely iron.

**TABLE 2**

| | |
|---|---|
| $HSO_5^- + 2H^+ + 2e^- \rightarrow HSO_4^- + H_2O$ | $E_o$ = 1810 mV |
| $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ | $E_o$ = 1780 mV |
| $ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$ | $E_o$ = 1450 mV |
| $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ | $E_o$ = 1210 mV |
| $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$ (sulphate) | $E_o$ = 640 mV |

**TABLE 3**
**PEROXYGEN - URANIUM CHEMISTRY**

| | | |
|---|---|---|
| $UO_2 + 2Fe^{+3}$ | $\rightarrow$ | $UO_2^{+2} + 2Fe^{+2}$ |
| $2Fe^{+2} + H_2O_2 + H_2SO_4$ | $\rightarrow$ | $2Fe^{+3} + 2H_2O + SO_4^{-2}$ |
| $2Fe^{+2} + H_2SO_5$ | $\rightarrow$ | $2Fe^{+3} + SO_4^{-2} + H_2O$ |
| $UO_2^{+2} + H_2O_2$ | $\rightarrow$ | $UO_4 + 2H^+$ |

# 3. ACID LEACHING APPLICATIONS

Peroxygens are highly reactive in nature. As mentioned above this has the disadvantage of potentially increasing the consumption of these reagents when used in environments hostile to their stability. Use of Caro's acid maximises the stability of their oxidation capacity in acid slurry environments (6). This reactive nature also provides the leach circuit with very rapid response times with respect to Oxidation Reduction Potential (ORP) control and the capacity to control to very narrow operating parameters if required. Perturbations in leach characteristics such throughput, head grade and mineralisation variation can be effectively managed quickly.

Application of these reagents requires that close attention be paid to the method of introduction and dispersion of the reagent in the slurry. Being liquids, storage, handling and metering are simplified when compared to solid oxidants.

From an environmental perspective, peroxygens do not add to the ionic load of the mill water circuit i.e. neither anionic or cationic residuals occur from the application of peroxygens in acid leach circuits. Overall reagent consumptions can be minimised with peroxygen use.

## 3.1 ENGINEERING ASPECTS.

For all applications of peroxygens, some form of storage facility will be required for hydrogen peroxide. These are generally tanks constructed of stainless steel, varying in size according to consumption rate and site location. Piping and valving is also in stainless steel. Maintenance costs for this plant are low.

The first applications of Caro's acid incorporated reagent generation, storage and cooling as well as dosing (7). This created a plant of significant complexity and cost. These characteristics were an impediment to broadening the adoption of the reagent in a variety of applications. By the mid '80's, improvements in generation technology had been made and verified by field application. Cooling has been dispensed with and the reagent is made adiabatically.

The adiabatic method affords a number of advantages, including (a) minimising the amount of Caro's acid present at any instant (b) allows the reagent to made on a demand basis only, thus eliminating the need to store any quantity of Caro's acid (c) the temperature output of a generator can be used to assist, control and optimise the reagent flows of hydrogen peroxide and sulphuric acid, reducing significantly the level of complexity and cost for instrumentation for the plant involved.

The capital cost for Caro's acid plants has been reduced by an order of magnitude for equivalent capacities by using the adiabatic approach. Thus, retrofitting such plant is less inhibited by the risk of capital exposure. The major capital expenditure component for such applications is in peroxide storage. Figures1and 2 illustrate the difference in the two manufacturing routes.

# 4. HYDROGEN PEROXIDE AND URANIUM PRECIPITATION

## 4.1 INTRODUCTION:

Traditionally hydrogen peroxide precipitation of uranium has been undertaken where interference can occur, resulting in the contamination of the final product. Ores where significant amount of molybdenum, zirconium or vanadium are found are cases in point. Here, the peroxide provides a product free of contamination of these metals, by forming soluble peroxy species with the metal whilst also precipitating the uranium under acid conditions (8).

In the past, due to the higher unit cost of peroxide relative to the conventional precipitation reagents, such as ammonia and magnesia, peroxide has not been employed for the more conventional SX liquors.

## 4.2 CHEMISTRY:

There are two potential options for using $H_2O_2$ for producing an acceptable uranium product. One via direct precipitation from pregnant liquor, the other from SX strip liquor. In both cases the initial precipitant is uranium peroxide or $UO_4 . xH_2O$ . This material can be marketed as such or further processed to produce $U_3O_8$ , which is considered to be the more conventional product.

As mentioned above, the production of uranium peroxide follows the reaction:

$$UO_2^{+2} + H_2O_2 \rightarrow UO_4 + 2\,H^+$$

Precipitation by hydrogen peroxide occurs at acid pH's and is acid generating by nature. pH control is an essential aspect of the process. There are a number of parameters which impact on the performance of the peroxide precipitation, including: pH, impurity concentrations, anion type and concentration, and uranium concentration (9,10,13). The consumption of peroxide will vary according to solution chemistry, but is usually in the range 0.15 - 0.25 Kg/Kg $U_3O_8$.

## 4.3 DIRECT PRECIPITATION:

In this case, there is a requirement for pregnant liquor uranium concentrations to be high to ensure high efficiencies in both reagent consumption and precipitation. This necessitates leaching of high grade ores or some form of beneficiation to provide high head grade material as leach feed and the pretreatment of the pregnant liquor to remove impurities prior to $UO_4$ formation. The performance of the solid/liquid separation unit operation becomes a key mill performance parameter as even small variations in efficiency at this point will involve significant losses in leached uranium due to the high tenor nature of the leach solutions. Pregnant liquor conditioning is a crucial unit operation to ensuring efficient peroxide utilisation in the subsequent precipitation stage. The advantage of the direct approach is to remove the requirement for solvent extraction from processing with a view to reducing both capital and operating costs for the mill.

## 4.4 SX STRIP LIQUOR PRECIPITATION:

Historically, peroxide could not, in general, compete with ammonia or magnesia on cost criteria. More recently, the competitive position of the reagent has improved. This is particularly the case with respect to greenfields projects where environmental constraints on development are becoming tighter and the operational attractions of $UO_4$ production become clearer.

Strip liquors from SX are produced by treating the loaded organic with acid or ammonium sulphate. The latter is commonly used where ammonia precipitation is employed. For peroxide precipitation route, it is common to use acid stripping of the organic. The principles behind the precipitation process are as for the direct method. Here however the size of the solution flows is significantly smaller, and thus the equipment also. Simple flowsheets (see Figures 3 & 4) below illustrate a conventional ammonium precipitation/ calcination approach and that for peroxide.

## 5. $UO_4$ OPERATIONAL CHARACTERISTICS

It is worthwhile highlighting a number of product and processing characteristics associated with the peroxide approach to uranium recovery from solution. The nature of $UO_4$ is such that it is easy to handle (e.g. thickening and dewatering). Tables 4 and 5 illustrate a comparision of uranium peroxide and ammonium diuranate. Equipment involved can be smaller and more efficient in producing a higher solids density feed stream to a calciner or drier (10,11). The requirement to calcine the final product becomes debatable as $UO_4$ is an acceptable feed stock for uranium enrichment, subject to purity requirements (12). Elimination of calcining has numerous advantages including energy savings, maintenance as well as reduced capital cost for a drier instead of a calciner.

TABLE 4
**COMPARISON OF YELLOWCAKE ASSAYS**
**(TYPICAL RANGES)**

**DRYING TEMPERATURE: 150 - 170°C**

| | Uranyl Peroxide | Ammonium Diuranate |
|---|---|---|
| % $U_3O_8$ | 90-95 | 85-89 |
| % $V_2O_5$ | 0.05-0.75 | 0.30-1.50 |
| % Na | 0.10-0.20 | 1.00-2.00 |
| % Ca | 0.03-0.08 | 0.25-0.80 |
| % Mo | 0.01-0.08 | 0.22-1.00 |
| % Fe | 0.06-0.25 | 0.50-0.75 |
| % $PO_4^{-3}$ | 0.04-0.10 | 0.08-0.20 |
| % $Cl^-$ | 0.03-0.15 | 0.08-0.25 |
| % $SO_4^{-2}$ | 0.40-0.60 | 1.00-2.00 |
| % Mg | 0.05-0.30 | 1.00-2.00 |

Ref. Brown, R.A., Aime ,1982

TABLE 5
COMPARISON OF PHYSICAL PROPERTIES

| | Uranyl Peroxide | Ammonium Diuranate |
|---|---|---|
| Effective Particle Size | 12-15u | 10-12u |
| Slurry Settling Rate | 4-6 cc/min | 2-4 cm/min |
| Settling Density (% Solids) | 40-50% | 20% |
| Specific Gravity, Solids | 5.7 g/mL | 2.8g/mL |
| Kg $U_3O_8$ /Liter Settled Slurry | 2.42 | 0.48 |
| Filter Cake Density (% Solids) | 59-70% | 28-38% |

Ref. Brown, R.A, Aime, 1982

Environmentally, employing a drier rather than calciner, enhances the quality of emissions from final product manufacture. Thus the scrubber requirements can be expected to be reduced for comparative performance and emissions of ammonia would be eliminated. Calciners can after a period of operating time, require re-lining. Driers would significantly reduce the potential for exposure to radiation which is possible undertaking re-lining operations.

Should calcination be used, $UO_4$ as a feedstock has the potential to increase the capacity of an existing calciner, and decrease the operating costs of production for $U_3O_8$. As the level of entrained sulphate and /or chloride is low, there is usually the opportunity to operate at lower calcining temperatures (550-600 $^{o}$C).

# 6. CONCLUSIONS

Hydrogen peroxide applicability to uranium processing operations has been well established for many years. Developments in the past decade have been to improve the commercial viability with respect to alternative technologies. Additionally, the unit cost for hydrogen peroxide over the past 15 years has reduced significantly in real terms. Figure 5 shows the trend in hydrogen peroxide pricing 1981 to 1996.

These factors, coupled with the ongoing and increasing environmental pressures on industry in general and uranium in particular will ensure that peroxygen based options are kept firmly on the agenda.

# 7. REFERENCES


1. Caro's Acid - A New Oxidant for Uranium Ore Processing - R.J. Ring, B.G. Charlton and M. Yamine, 3rd AINSE Engineering Conf., Lucas Heights (1981).
2. Queensland Mines Plant Trials with Caro's Acid. G Lucas, E. Fulton, R.J. Ring, F.E. Vautier and D.J. Waters - Proc. Aus I.M.M., No. 287, p. 27-34 (1983).
3. Caro's Acid - A Non-Polluting Oxidant for the Leaching of Uranium Ores - R.J. Ring and D.J. Waters - Proc. Scientific Workshop on Environmental Protection of the Alligators Rivers Region, Jabiru (1983).
4. Caro's Acid - An Oxidant for Acid Leaching of Uranium Ores. R.J. Ring, D.J. Waters and M.Yamine - can. Inst. Min. Met. Bull., Vol77 (862), p. 27-34 (1984).
5. Commercial Implementation of Caro's Acid as an Oxidant for Australian Uranium Ores. A.Nugent and R.J. Ring - 4th *AINSE Engineering Conf.*, 16-17 May (1985).
6. Catalytic Decomposition of Peroxygen Compounds in Uranium Leaching Circuits. R.J. Secomb, R.J. Ring and A.T. Nugent - *Proc. Chemeca '85*, p.139, Perth (1985).
7. Performance of Caro's Acid as an Oxidant at the Nabarlek Mill. R.J. Ring, F.E. Vautier, G. Lucas, E. Fulton and D.J. Walters - *Proc. IAEA Tech. Committee Meeting on Advances in Uranium Ore Processing and Recovery from Non-Conventional Resources,* Vienna, Sept. 1998 (1985)
8. Merrit, R.C., The Extractive Metallurgy of Uranium, Colorado School of Mines Institute, 1971.
9. Hopkins J.S. et al; Critical Factors influencing Uranium Precipitation by Hydrogen Peroxide: The use of Experimental Design Techniques, Hydrometallurgy, 17 (1987) p. 315-334.
10. Brown, R.A., Uranium Precipitation with Hydrogen Peroxide, Presented at AIME Annual Meeting, Las Vegas, Nevada - February 24-28. 1982, Preprint Number 80-63.
11. Shabbir, M. and Tame, K.G., Hydrogen Peroxide Precipitation of Uranium, USBM 7931, 1974.
12. Mattus, A.J. and Lopez, M.F., Hydrogen Peroxide Precipitation of Uranium Eliminates Silica Problems Associated with a Magnesia Process, Metallurgical Society of AIME, Warrendale, PA., Paper No. A83-28, 1983.
13. W. Berry, Recovery of Uranium from Phosphoric Acid, American Journal of Chemical Engineering 1981. p. 76-83.

FIGURE 1. CONVENTIONAL CARO'S ACID MANUFACTURE

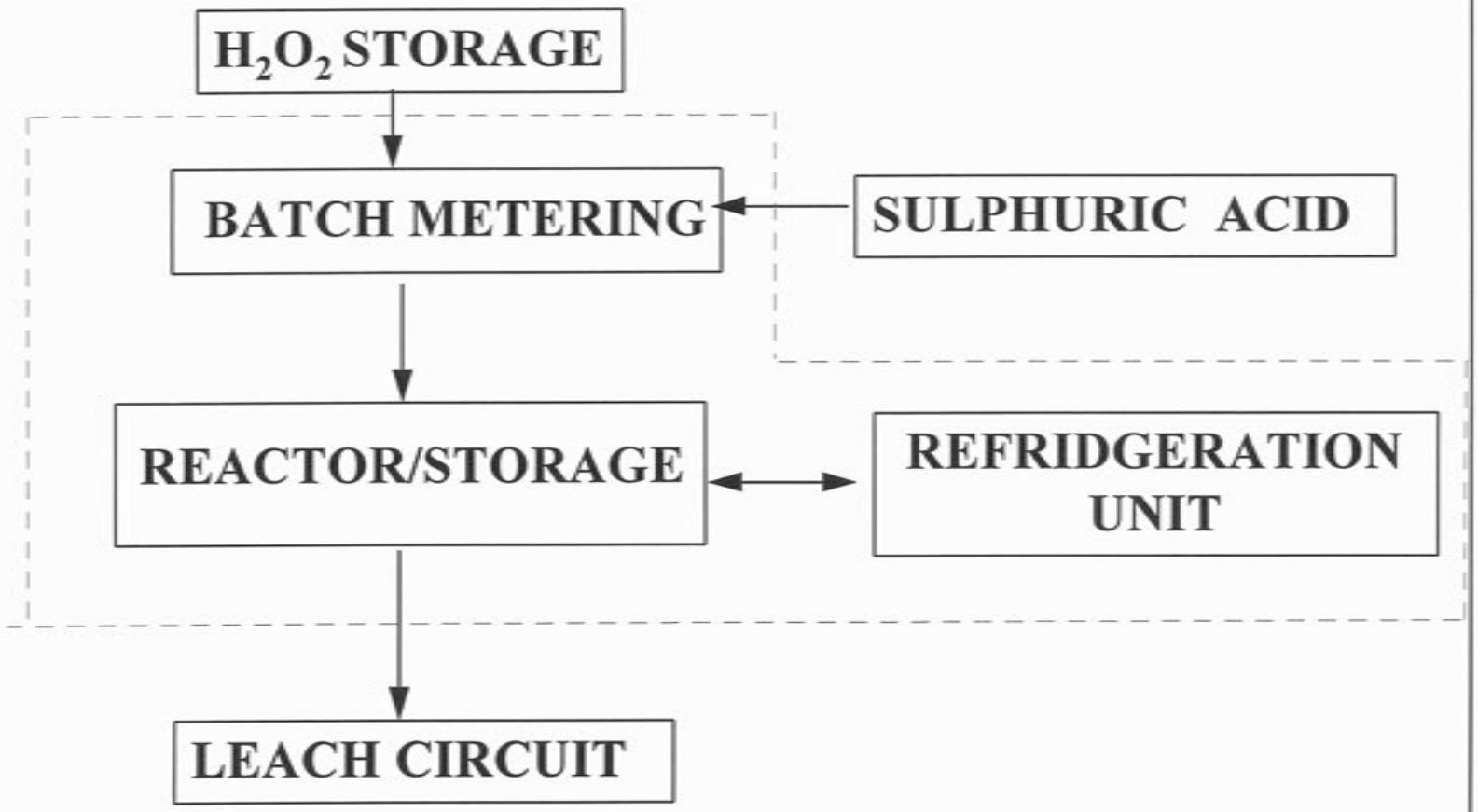


FIGURE 2. ADIABATIC CARO'S ACID MANUFACTURE

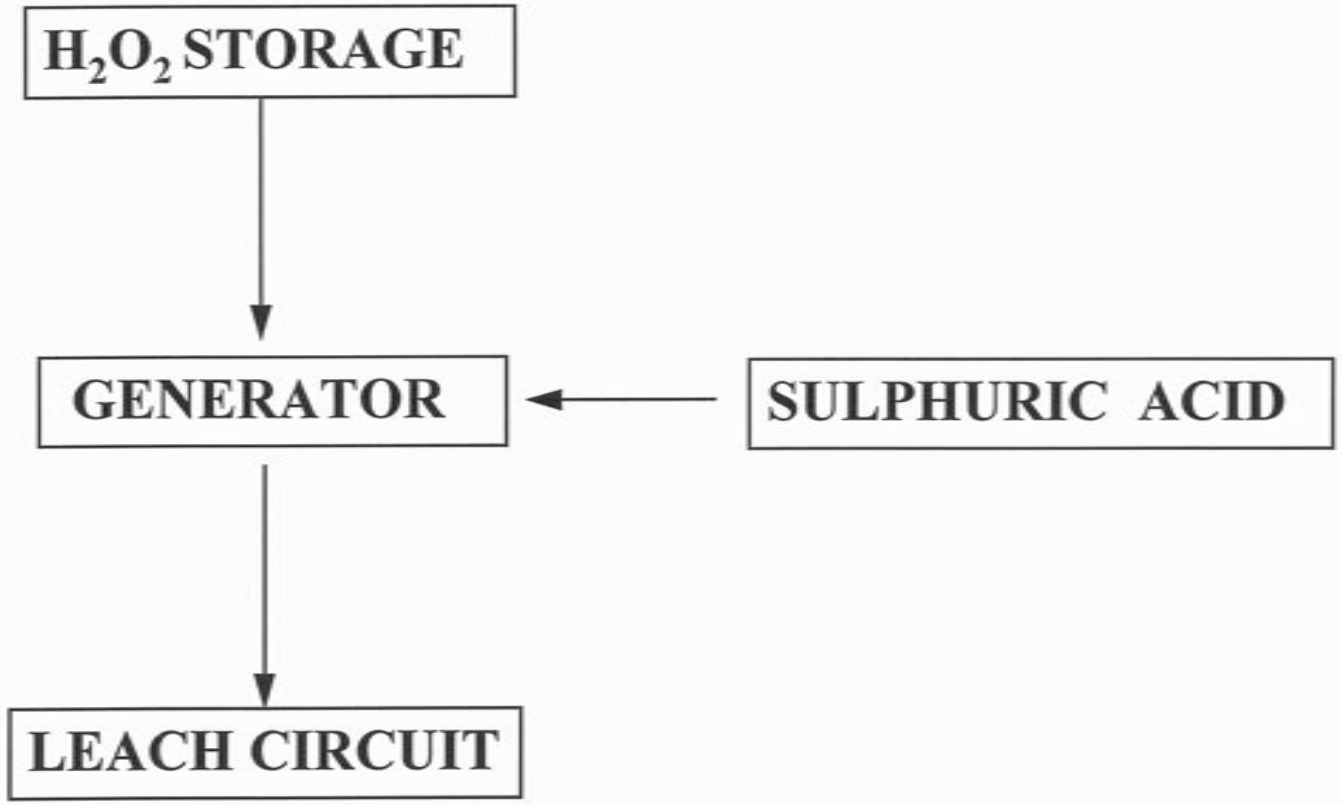


FIGURE 3. ADU PRECIPITATION

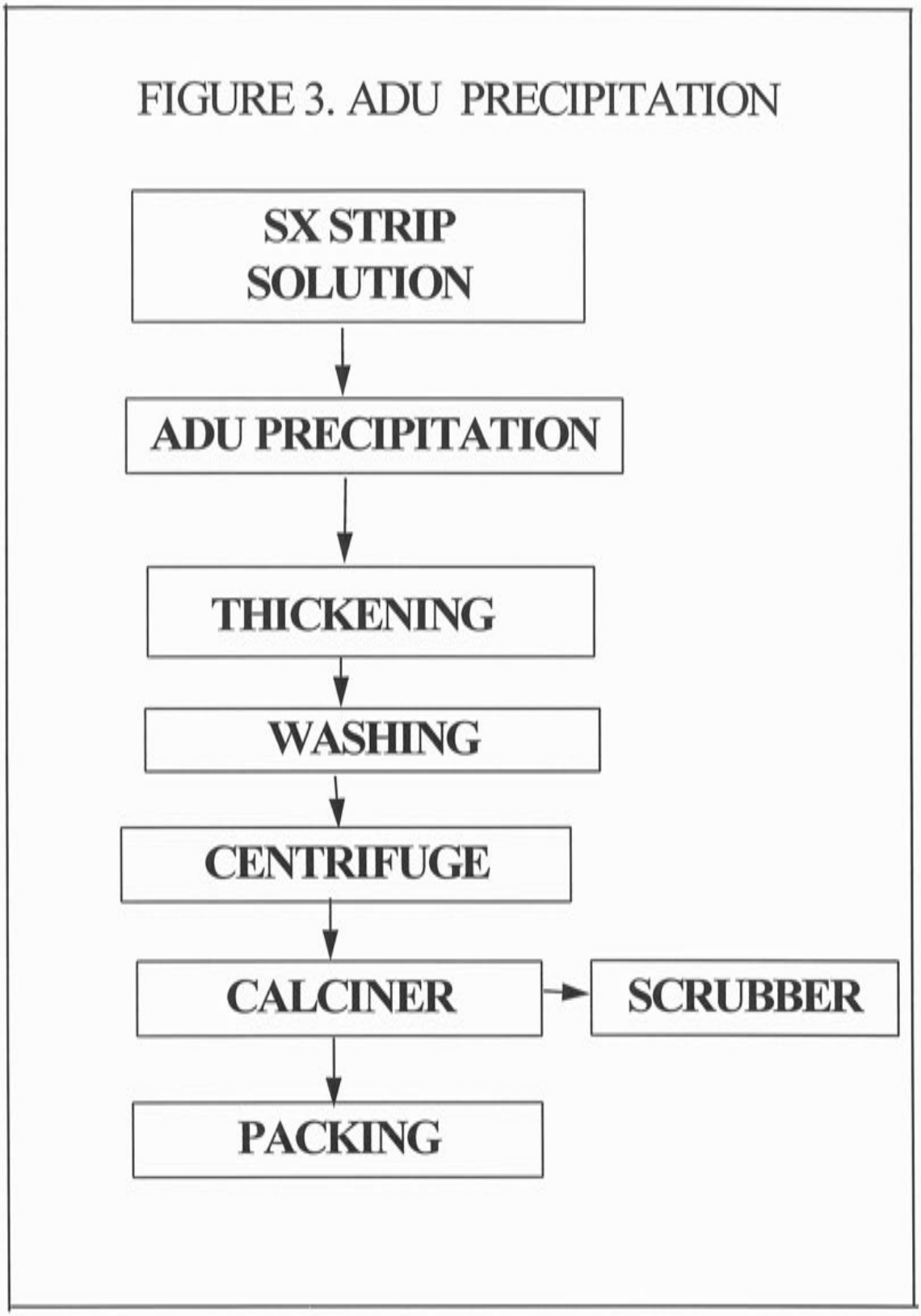
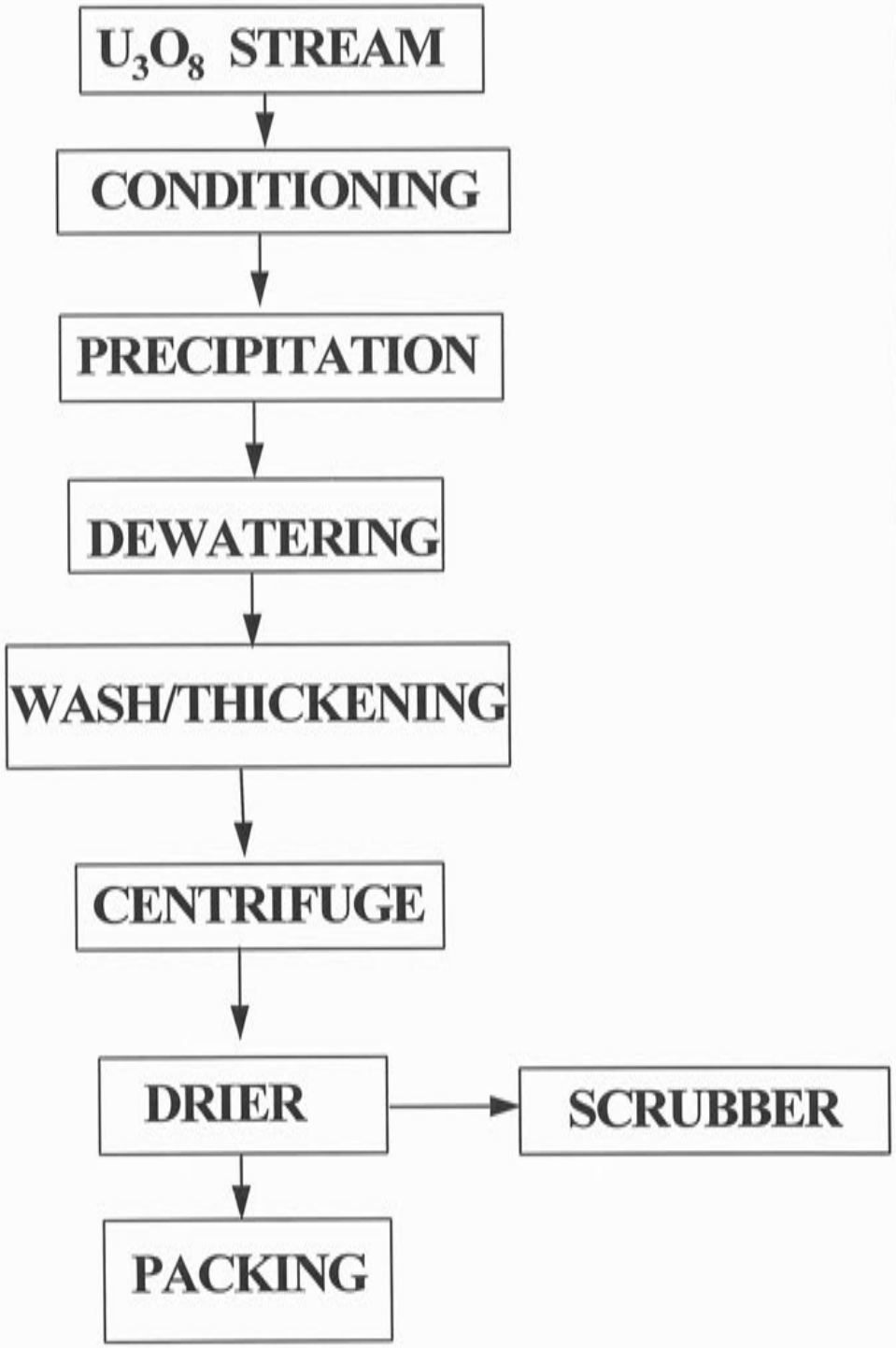
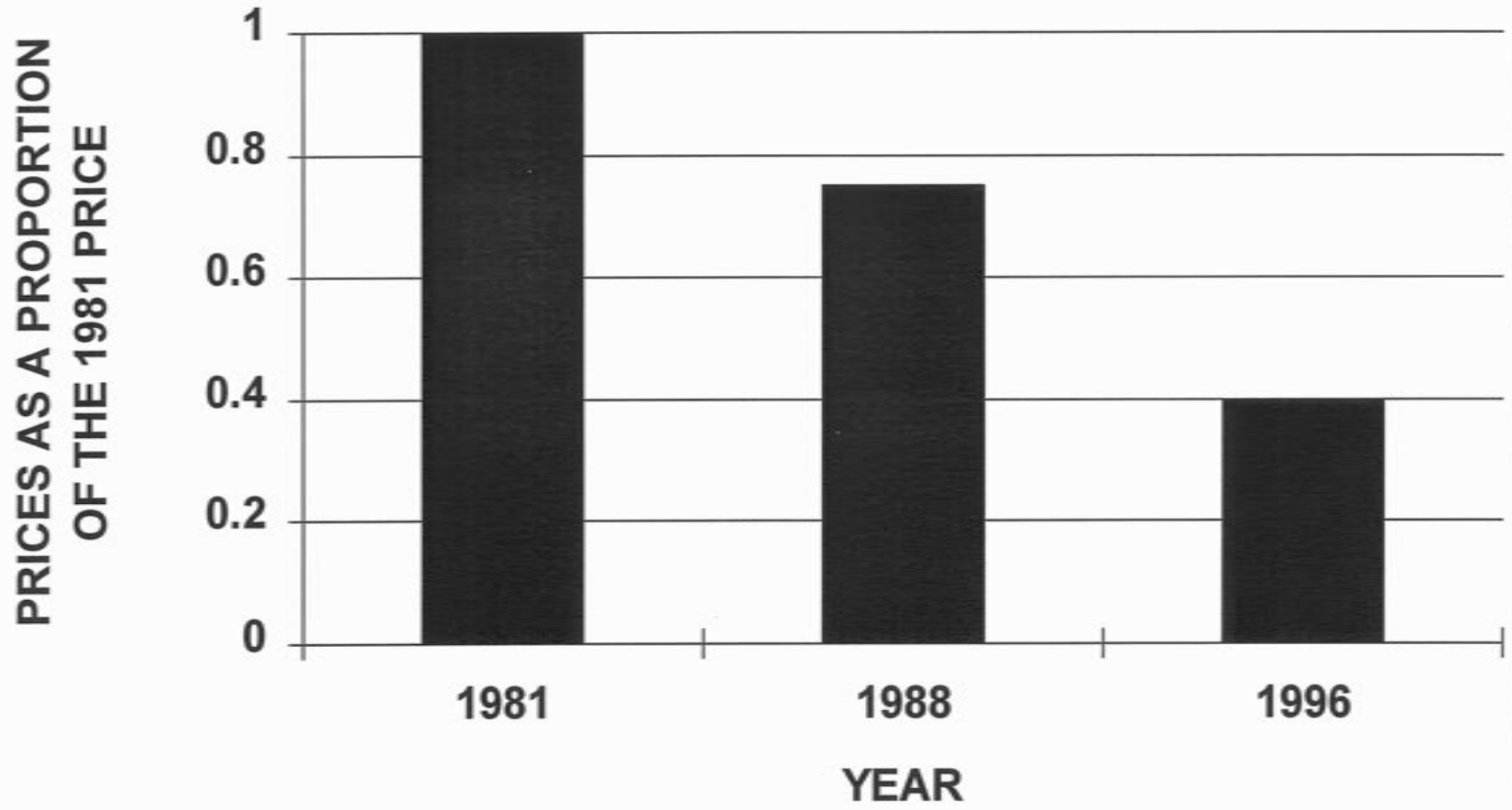


FIGURE 4. $UO_4$ PRODUCTION



## FIGURE 5. HYDROGEN PEROXIDE PRICING (RELATIVE TO 1981)



# ATOMAER'S FILBLAST PROCESS FOR FERROUS SULPHATE OXIDATION AND URANIUM LEACHING

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## ABSTRACT

Although oxidation property of ferric sulphate over uranium bearing minerals has been well known its commercial application has not been feasible mainly due to its high cost compared to other oxidants.

Recently Atomaer has been involved in developing an economic process for conversion of ferrous sulphate to the ferric state using the company's proprietary Filblast Gas Shear Reactor and oxygen. The process is economically and technically attractive as it involves a rather simple installation and employs neither bacteria nor pressure autoclave resulting in a trouble free operation, low capital investment and operating costs. A patent has been applied and a proposal has been submitted for installation of a commercial scale ferrous-ferric conversion operation for uranium leaching at a major global uranium mine.

A feasibility study has been conducted at the client site using a pilot plant of 150 L capacity. Ferrous oxidation rates in excess of 20 g/LH have been achieved during the first 15 minutes at an initial ferrous concentration as low as 20 g/L. However, the oxidation slows down as the oxidation approaches equilibrium and ferrous concentration is depleted. Final conversions of 60+% have been achieved after a residence time of one and a half hours.

The oxidation process is very efficient with an oxygen utilisation of approximately 80+% depending on initial ferrous concentration and oxygen injection rate resulting in an oxygen consumption to ferric production weight ratio of approximately 1 to 5. At the current PSA/VSA oxygen generation cost as low as 15 cents/kg, such a process is very economic.

Leaching tests revealed that the resulting ferric sulphate is suitable for leaching of uranium. The reduced iron in the raffinate after the uranium solvent extraction stage can be recycled. Simultaneous ferrous oxidation and uranium leaching has been recommended for maximum efficiency.

# 1. INTRODUCTION

While the hexavalent uranium is readily soluble in sulphuric acid, other forms of uranium minerals particularly those in the tetravalent oxidation state are only sparingly soluble. In order to attain economic recovery of uranium from ores, strong oxidants such as peroxide or chlorates are often utilised.

Ferric sulphate has also been known as useful for the leaching process because of its excellent oxidising power over tetravalent uranium (Dwivedy & Mathur, 1995).

$UO_2 + 2Fe^{3+} \longrightarrow UO_2^{2+} + 2Fe^{2+}$
Uraninite + Ferric ion ------> Uranyl ion + Ferrous ion

However, in commercial practice, the use of ferric sulphate for uranium extraction has been largely overlooked due to the reagent's high cost and the lack of an economic process for production/regeneration of ferric sulphate in leach solutions. While aqueous ferrous sulphate can be oxidised to the ferric state by oxygen in a sulphuric acid medium with the presence of copper catalyst (Matthews & Robins, 1972), the required high solution temperature and oxygen pressure for effective operation rendered the process uneconomic.

$2FeSO_4 + 0.5\ O_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O$
Ferrous sulphate + Oxygen + sulphuric acid -------> Ferric sulphate + Water

Atomaer Pty Ltd has developed an economic process for oxidation of ferrous sulphate to the ferric state with the aid of the company Filblast Gas Shear Reactor (GSR). A patent has been applied for the process which can be employed for leaching of uranium and base metals.

The major advantage of Atomaer's Filblast process is that constant application of high oxygen pressure over the bulk ferrous solution is not required. Instead, the acidic ferrous sulphate solution is recirculated through a Fiblast GSR which is injected with oxygen. In this manner, gas-liquid mass transfer is improved and effective and efficient oxidation can be achieved within a short residence time.

Feasibility of the process has been confirmed through a pilot study conducted at a major global uranium operation and commercial scale operation has been proposed.

## 2. EXPERIMENTAL

The oxidation tests were conducted using a pilot Filblast process evaluation unit (PEU) of 150 L capacity equipped with a pilot Filblast Gas Shear Reactor (see Figure 1). A pressure of 100 KPa was applied over the solution in order to eliminate pump cavitation caused by high water vapour at elevated solution temperature. The 100 KPa pressure essentially simulates the pressure exerted on the pump inlet by the solution in a 10 metre height vessel.

Ferrous sulphate / sulphuric acid solution in the reaction vessel was heated with steam and recirculated through the Filblast reactor which was injected with oxygen at a pre-determined rate. Unless otherwise stated, ferrous concentrations within the range of 20-25 g/L were employed for the tests. Samples of solution were taken at various time intervals for analysis of residual ferrous sulphate by titration with a standard potassium dichromate solution. The ferric concentration of the solution was derived from the decrease in ferrous concentration.

The resultant ferric sulphate solution was then used for uranium leaching tests the results of which confirmed the ferric sulphate's effectiveness for uranium dissolution. These leach results shall be published in due course.

# 3. RESULTS AND DISCUSSION

The test work revealed that the Filblast ferrous oxidation was influenced by:

- concentration of copper catalyst,
- solution temperature,
- oxygen overpressure,
- acid concentration,
- oxygen injection rate,
- residence time,
- ferrous concentration.

## 3.1 EFFECT OF COPPER CONCENTRATION ON FILBLASTFERROUS OXIDATION

Oxidation of ferrous sulphate occurred at a relatively slow rate and after 90 minutes, approximately 40% was achieved at a relatively high temperature (90°C) and excess of oxygen. However, as shown in Figure 2, tests conducted with addition of copper (as sulphate) at concentrations ranging from 0.18 g/L to 1g/L, and a liquor temperature of 90°C, revealed that the oxidation rate was improved significantly. This is consistent with the findings by Matthews and Robins (1972) that the oxidation rate was significantly improved in the presence of as little as 0.001 M (0.16 g/L) of copper sulphate.

However, increasing cupric concentration from 0.18 to 1 g/L caused inappreciable improvement in the ferrous oxidation during the Fiblast operation. The finding was not consistent with Matthews and Robins who found that the oxidation rate was proportional to power 0.28 of the copper concentration $[Cu2+]^{0.28}$ and the reaction's rate constant was doubled by increasing the cupric concentration from 0.001M (0.16g/L) to 0.01M (1.6g/L).

Unless otherwise stated, further tests were conducted using a copper concentration within the range of 0.15 - 1g/L. At this concentration range, the use of copper as a catalyst is economically feasible. It is not extracted during uranium SX operation and can be effectively recycled with the ferrous sulphate in the raffinate.

## 3.2 EFFECT OF SOLUTION TEMPERATURE ON FILBLAST FERROUS OXIDATION

Oxidation tests were conducted over the temperature range of 60 -100°C for the duration of 90 minutes. The results are presented diagrammatically in Figure 3.

It can be seen that the oxidation rate and hence the final ferric concentration after a fixed residence time of 90 minutes were significantly influenced by the solution temperature. In general the oxidation reaction was relatively slow at solution temperatures of 60 - 70°C but increased appreciably as the temperature increased to 80°C and 90°C. Final conversions in excess of 60% were achieved after 90 minutes operation within the latter temperature range. However, as the temperature increases to 100°C the oxidation slowed down possibly due to low oxygen's solubility in solution and reduced pump efficiency.

The final ferrous conversion varied only slightly within the operating temperature of 80 -90°C. This range of operating temperature would be recommended for fast and effective ferrous oxidation. The operating temperature can be reduced to temperatures as low as 70 - 75°C where a conversion rate of just under 50% would still be achieved. However, further reduction in operating temperature to 60°C would result in a significantly lower ferrous oxidation (less than 40%).

## 3.3 EFFECT OF FERROUS CONCENTRATION ON FILBLAST FERROUS OXIDATION

The concentration of ferrous iron was varied between 8 g/L and 40 g/L and it was observed that percentage wise the oxidation was not greatly influenced by variation in the initial ferrous concentration within the above optimal range of operating temperature.

Since the stoichiometric ferric - uraninite weight ratio required for the oxidation reaction is 1 : 2.27, the ferrous concentration required for each operation can be derived in accordance to uraninite concentration and the desired leaching temperature.

## 3.4 EFFECT OF OXYGEN OVERPRESSURE ON FILBLAST FERROUS OXIDATION

A test was conducted at an oxygen over pressure of 300 KPa in order to determine the effect of oxygen overpressure on Filblast ferrous oxidation. The results presented in Figure 4 indicate that the ferrous oxidation was improved considerably with increase in oxygen overpressure. However, the final conversion after a residence time of 90 minutes was only slightly better with 69 % ferrous - ferric conversion achieved. As the economic benefits from such an improvement would be unlikely to justify the capital and operation costs that would be required by a pressure autoclave, further tests were not attempted.

## 3.5 EFFECT OF SULPHURIC ACID CONCENTRATION ON FILBLAST FERROUS OXIDATION

As demonstrated in the Figure 5, decrease in sulphuric acid content from 39 g/L to 14g/L appeared to cause appreciable increase in the oxidation rate. This is consistent with the findings by Matthews and Robins (1972) who found that the rate of ferrous sulphate oxidation was:

- proportional to oxygen concentration and to square of ferrous concentration.
- inversely proportional to 1/4 power of the proton concentration $[H^+]^{1/4}$.

Such findings indicate that the rate of ferrous oxidation increases with decrease in acid concentration and the oxidation is most favourable at sulphuric concentrations below 1N (or 49g/L).

However it was observed that at sulphuric acid concentrations below 10 g/l, precipitation of jarosite occurred resulting in significant loss of ferric sulphate. Since the precipitation of jarosite is irreversible, initial sulphuric acid concentration of less than 30g/L should be avoided particularly when the ferrous concentration is higher than 30g/L in order to have sufficient allowance for the acid consumption during ferrous oxidation.

## 3.6 EFFECT OF OXYGEN FLOWRATE ON FILBLAST FERROUS OXIDATION

Effect of oxygen flowrate was investigated by running oxidation tests at 85°C and various oxygen injection rates (0.24 Nm3/H to 8 Nm3/H). The results as represented in Figure 6 indicate that the oxidation rate was only slightly influenced by excessive oxygen injection. In regard to efficiency the slower the oxygen injection rate the more efficient process would be achieved. The process efficiency was also influenced by the ferrous concentration. The higher the ferrous concentration, the higher the oxygen utilisation.

For efficient operation, the oxidation rate must be adjusted in accordance with the reaction demand, ie: the injection rate must be steadily reduced as the oxidation proceeds toward equilibrium.

For example, the most efficient operation at 40g/L of ferrous was achieved at an oxygen injection rate of approximately .72 $Nm^3/H$ for the first 15 minutes followed by .54 for the next 15 then .36 $Nm^3/H$ and .24 $Nm^3/H$ for the final two half hour periods. The resultant oxygen utilisation rates were 101%, 77%, 67%, 65% and 48% for the five periods respectively. The overall oxygen utilisation over 1.5 hour operation was 75%. Such high efficiencies were achieved without significant decrease in oxidation effectiveness and a final ferrous to ferric conversion in excess of 60% was still recorded after a residence time of 90 minutes (see Figure 6).

It can be seen that an oxygen utilisation in proximity of 80-100% is attainable if a high ferrous concentration is maintained (ie: equivalent to the first half hour of the reaction). This can be achieved in the presence of a ferric consumer such as uraninite which effectively reduces ferric to the ferrous state.

In summary the most efficient operation would be achieved by;

- maintaining relatively high ferrous concentration, and
- matching oxygen supply with the process demand.

## 3.7 STABILITY OF FERRIC SULPHATE PRODUCED BY THE FILBLAST OXIDATION

The ferric sulphate produced by the Filblast oxidation was very stable and no change in concentration was detected after more than four weeks storage. In practice, the ferric sulphate would be employed immediately after production.

## 3.8 OPTIMAL OPERATING CONDITIONS FOR FILBLAST FERROUS OXIDATION

It can be seen that the optimal operating conditions for ferrous oxidation consist of:

- a suitably arranged multiple stage oxidation circuit to reduce short circuiting of the liquor,
- a liquor residence time of approximately 1.5 hours in reaction vessels,
- a suitably scaled up Filblast operation to give sufficient residence time in the Filblast reactor through recirculation,

- a temperature in the range of 80 - 90°C,
- oxygen injection rate of just below the stoichiometric requirement of the reaction.

# 4. FERROUS OXIDATION & URANIUM LEACHING PROCESS

A multiple stage operation has been recommended for effective and efficient ferrous oxidation. In such an operation, short circuiting would be avoided while manipulation of oxygen injection rate to meet process demand would be feasible.

Because oxidation of ferrous is more favourable with increased ferrous concentration, simultaneous leaching of uranium and ferrous oxidation would be highly recommended. By doing so, the ferric iron is continuously consumed as soon as it is generated. Likewise, the ferrous iron resulting from the reduction of ferric iron by uranium bearing minerals would be continuously re-oxidised.

In other words the simultaneous leaching operation would favour maximum efficiency and effectiveness because of high ferrous concentration in the leach solution resulting in:

- maintenance of high rate of ferrous oxidation in excess of 20 g/L.H,
- high oxygen utilisation in excess of 80%.

A typical circuit design is presented in Figure 7. It can be seen that the Filblast process is technically simple, economically attractive and environmentally friendly because:

- neither bacteria nor autoclave would be required for ferrous oxidation stage,
- simultaneous oxidation and leaching mean that the Filblast process can be readily retro-fitted into existing operations,
- oxygen and sulphuric acid are the only major consumable chemicals. Ferrous sulphate and cupric sulphate can be effectively recycled depending on the ore's nature,
- oxygen cost would be very economic. At approximately 80% utilisation, one tonne of oxygen would be required for the production of 5.6 tonnes of ferric iron which can theoretically oxidise 12.7 tonnes of uraninite (the ferric demand of each individual uranium ore is dependent on its nature and the presence of ferric consuming minerals such as base metal sulphides).

# 5. CONCLUSIONS AND RECOMMENDATIONS

It has been demonstrated that ferrous sulphate can be effectively and efficiently oxidised to the ferric state using Atomaer's Filblast Gas Shear Reactor injected with oxygen. The installation and operation is simple without the need for an autoclave and would be useful for economic recovery of uranium.

The presence of copper in solution catalyses the reaction and oxidation is best performed in the temperature range of 80 - 90°C though slightly lower temperature would still be effective. While it appears that variation in the solution's acid content and concentration of copper catalyst have appreciable effects on the rate of the Filblast ferrous oxidation process, the extent of these effects are not as significant as those reported in the literature.

For efficient operation, it is desirable to:

- maintain a relatively high ferrous concentration in proximity of 40g/L,
- conduct simultaneous ferrous oxidation and uranium leaching in the same circuit.

## 6. REFERENCES

Dwivedy, K.K. & Mathur, A.K., (1995), Bioleaching, Our Experience, ***Hydrometallurgy,*** 38 (1), May, pp. 99 -109.

Matthews, C.T. and Robins, R.G. (1972), The Oxidation of Aqueous Ferrous Sulphate Solutions by Molecular Oxygen, ***Proceedings of the Australasian Institute of Mining and Metallurgy***, Nº 242, June, 1972, pp. 47-56.

## 7. ACKNOWLEDGMENTS

The authors wish to convey appreciation to the customer involved in the project for:

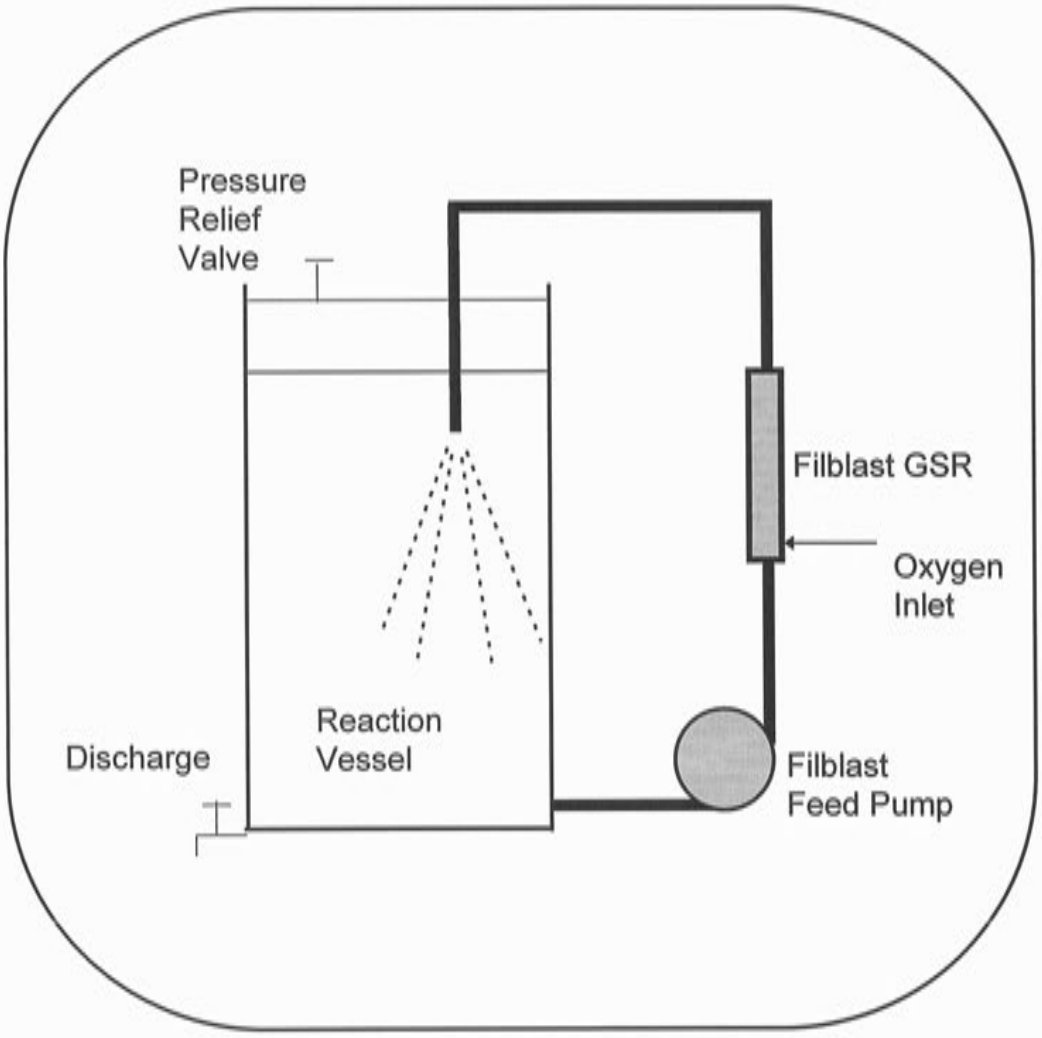
- granting Atomaer's access to site to conduct the pilot test work,
- providing analytical services for chemical analysis of samples,
- assistance in installation of the pilot test plant.

Unfortunately, due to the client's wish to remain anonymous at this stage, no public acknowledgment can be made.

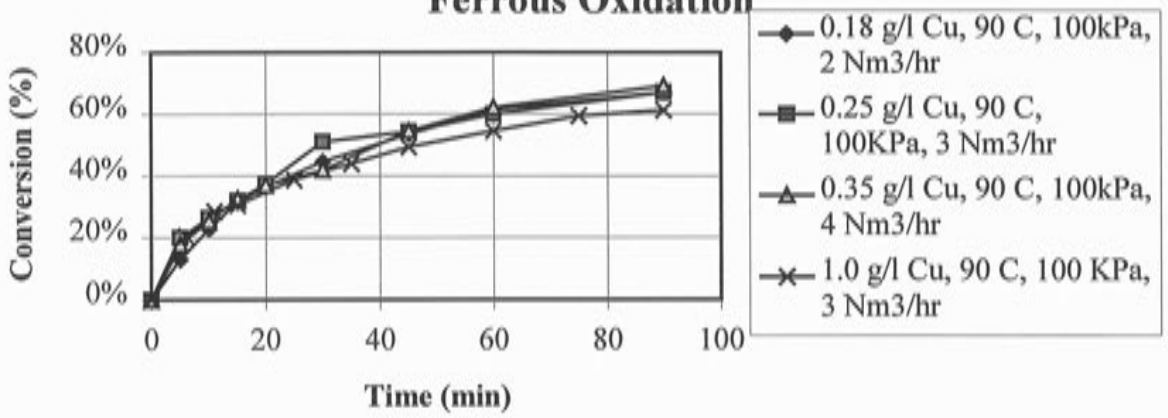
Furthermore, supports from Atomaer's Board of Directors, Management and staff particularly those from Managing Director Andrew Simpson and Metallurgical Director Bruno Sceresini are of vital importance to the project.

# 8. APPENDIX

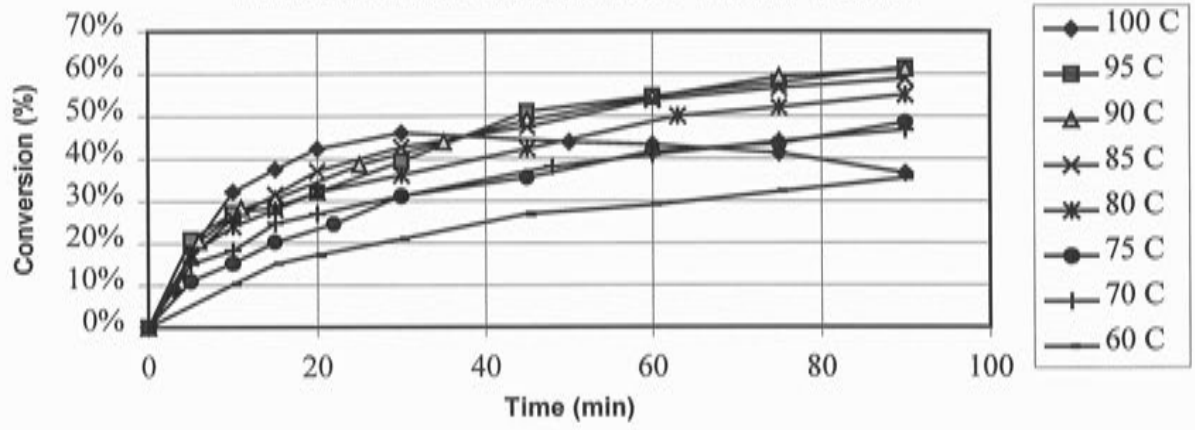
**Figure 1:** Schematic Diagram of the Pilot Filblast Process Evaluation Unit Employed for Ferrous Oxidation Tests



## Figure 2: Effect of Cupric Concentration on Filblast Ferrous Oxidation




## Figure 3: Effect of Solution Temperature on Filblast Ferrous Oxidation @ 3 Nm3/h, 100kPa




## Figure 4: Effect of Oxygen Over Pressure on Filblast Ferrous Oxidation @ 90 C

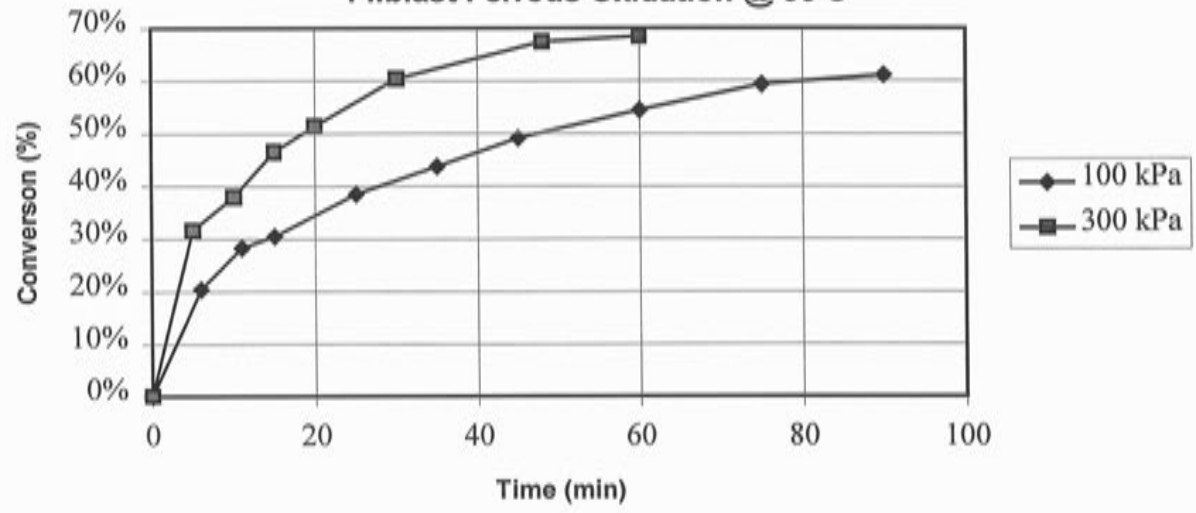


**Figure 5: Effect Sulphuric Acid Concentration on Filblast Ferrous Oxidation @ 90 C, 3 Nm3/h**

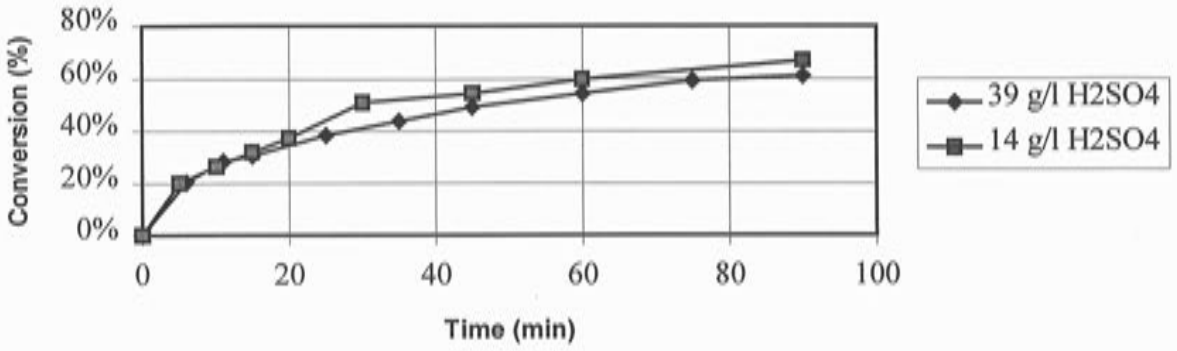



**Figure 6: Effect of Oxygen Flowrate on Filblast Ferrous Oxidation @ 85 C**

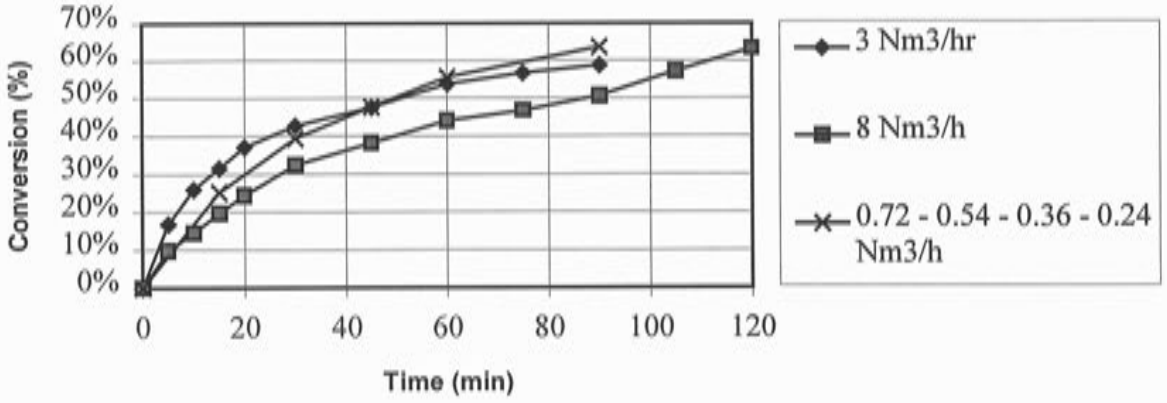


**Figure 7:** Schematic Diagram of a Typical Atomaer's Filblast Ferrous Oxidation - Uranium Leaching Circuit