2008 MEETING THE FUTURE CHALLENGES OF THE URANIUM INDUSTRY

By

J Carr, N Zontov and S Yamin

Clean TeQ Ltd Australia Mining Division

Presented by

John Carr

jcarr@cleanteq.com

1 INTRODUCTION

Processing uranium for supply over the next decades will undergo change bought about through reserves, economics and environmental regulation. Technology advances will be rapid and those not adapting will find that the cost structures of conventional technology will place them at a competitive disadvantage.

All uranium processing requires the uranium to be leached from the crushed or ground ore. Leaching is usually conducted using acid or alkali depending on the mineralogy of the ore. The resulting uranium is a soluble uranyl salt and is then processed via solid – liquid separation, soluble uranium concentration and purification routes. Processes historically have not been based on simple separation technologies with emphasis on down stream refining steps such as ion exchange and solvent extraction providing concentration and purification.

1.1 FILTRATION

Filtration is the most conventional way to remove soluble uranium. Typically it involves horizontal belt or disk filters with washing to separate the soluble uranium phase from the solids. The recovery rates can be up to 98-99% but the capital and maintenance costs can be extremely high to achieve adequate separation of liquids from solids. Filtration is only an effective method when the pulp consists of larger particle sizes as pegging of the filter cloth due to small particle fractions or slimes can greatly reduce the efficiency of separation.

1.2 COUNTERCURRENT DECANTATION (CCD)

Counter current decantation is widely used in the uranium processing industry as a method for solid / liquid separation. Its main purpose is the washing of solids and removal of soluble uranium from the solids phase of the pulp. This is achieved through counter currently running wash water against pulp through a series of CCDs. The overflow stream from the first CCD is then sent to ion exchange or solvent extraction for further uranium concentration. The stripped waste from IX/SX can be recycled for CCD wash water.

While this technology can provide effective separation, soluble uranium in the pulp is diluted during the process. In some processes this dilution can be up to a factor of 3. The dilution is detrimental in a processing sense as it increases the hydraulic flows down stream, increasing the capital and operating costs of these down stream processes. The practical loss of uranium to tails is also limiting and dependant on the number of washing stages and the amount of soluble uranium in the incoming wash water. CCDs have a limit to their ability to separate solids and liquids and the operating costs increase when fine particles are present in the pulp, which require the addition of coagulants to assist with settling rates.

Both filtration and countercurrent decantation only act as solid-liquid separation process steps and therefore still require a concentration step before precipitation. Both unit processes also require the input of water to ensure that there is sufficient recovery of soluble uranium.

1.3 CONVENTIONAL ION EXCHANGE & SOLVENT EXTRACTION

The original processes of ion exchange (IX) as a method for uranium extraction used strong base anionic resins. While the uranium recoveries were high, the selectivity towards uranium was low and impurities in the product streams could be high. This problem led to the development of more specific solvent extraction processes. These extraction processes using weak base tertiary amines reduced the impurities in the uranium stream. Solvent extraction also offered the benefit of selective stripping to remove impurities, the combination of which provided a cheaper and higher purity uranium extraction system then conventional IX. Further developments optimised both IX with solvent extraction to have high recoveries and low impurities. This combination of processes (Bufflex or Eluex) optimised the recovery and purity of uranium. The majority of the uranium processing plants commissioned in the last 40 years in the western world have used solvent extraction alone.

Both conventional IX and solvent extraction work on a clear solution and so require the complete removal of the solid phase. This extra process unit increases capital and operating cost for uranium extraction.

The chemicals required in solvent extraction are highly volatile and create a safety risk. There are several recorded incidents of SX fires (e.g. ODX, Stepnogorsk) which have led to an increase in insurance premiums for mine sites with the SX process unit.

The development of moving bed IX systems able to handle up to 60% solids in pulps as well as developments in the loading and selectivity of SBA resins has provided an opportunity to revolutionise hydrometallurgical flow sheets.

1.4 IMPROVING PROCESS FLOW SHEETS FOR URANIUM EXTACTION

Continuous countercurrent ion exchange (CCIX) has been developed to extract uranium from the liquid stream with reduced or no solid separation step that has traditionally been required. Developments in continuous countercurrent Resin-In-Pulp (cRIP) technology means that slurries with up to 60% solids can be processed to recover up to 99% of soluble uranium. The ability to directly process pulps using cRIP leads to a reduction in fixed plant leading to substantial capital cost savings. A range of ion exchange resins are now available that offer selectivity and high loading capacity that again improves the economics of resin processes leading to lower operating costs. The flexibility of the flow sheets means that processes can be designed to deal with a wide range of mineralogy and process conditions.



Figure 1: Conventional process selection for uranium extraction and precipitation

Continuous countercurrent ion exchange allows for the partial or complete removal of the solidliquid separation step and reduces the complexity of the flow sheet:



Figure 2: Process selection for uranium extraction utilising CCIX technology

For leached pulps with solids content of ca. 10 - 60%, a Resin-In-Pulp system is the process choice. With cRIP, the best economy is obtained when solids are maintained at the higher levels providing the lowest hydraulic flow and highest uranium tenor. Low hydraulic flows result in smaller equipment

and lower capital costs. Higher uranium tenor results in higher uranium resin loading capacity, lower resin inventory and lower operating costs.

Direct extraction of uranium from pulps means there is no dilution of the uranium stream as in CCDs. Where reagent recovery is required CCDs or thickeners or tails return can be used.

When the pulps can be economically separated into sand and slimes, there is the opportunity to treat the uranium containing low solids slimes (less than ca. 10% solids) using a continuous resinin-fluidised column (cFLX). For heap leaching and ISL applications or where CCDs are currently used, and where solids are less than ca. 100mg/L, a continuous resin-in-packed bed column (cLX) can be used. Both these systems offer considerable capital cost advantages over the cRIP process.

Ultimately operating at higher percent solids and higher tenors reduces the capital and operating costs of the plant and greatly simplifies the flow sheet for uranium extraction plants. This opens the door way for smaller uranium ore bodies to be potentially economic operations and increases the ability to supply the increasing market demand for uranium.

2 URANIUM EXTRACTION UTILISING CONTINUOUS COUNTERCURRENT ION EXCHANGE

2.1 PROCESS DESIGN CRITERIA FOR RESIN PROCESSES

The main principles that govern the use of ion exchange resin in a process are the sorption isotherm and the kinetics of sorption and desorption. The isotherm is the relationship between the loading capacity of the resin at a particular concentration of uranium in the leach solution. The construction of the isotherm is done through laboratory experiments. While the isotherm represents the equilibrium loading capacity of the resin and the amount of resin required in the system, it does not provide any information on the time taken to reach the equilibrium loading capacity, i.e. the kinetics of loading. The kinetics are determined by another set of experiments where resin is contacted with excess uranium in liquid for various times and the loading capacity of the resin is plotted against time. The process design then takes into account the residence time required for contact between resin and pulp for the resin to reach maximum loading capacity.

2.1.1 Kinetics

The kinetics of mass transfer in ion exchange is determined by two factors:

- The film diffusion rate of uranium from the bulk pulp or solution onto the surface of the resin
- The diffusion rate of uranium from the surface of the resin into the pores of the resin



Figure 3: Schematic diagram of a partially reacted ion-exchanger bead (Streat and Cloete 1987)

The first stage is dependent on the mass transfer through the liquid film layer and is assumed to be instantaneous. The rate limiting step is the diffusion of uranium within the resin which is a function of diffusion kinetics and steric forces. Taking both of these mass transfer steps into consideration, generally the initial loading rate is a magnitude of 2 to 5 times faster than the final loading rate. The time required for complete loading of uranium on the resin may be impractical for the process.

While initial loading is fast, the "tail" on the kinetics curve may increase the residence time of resin in the sorption circuit such that the system is uneconomical. Therefore the kinetics must be understood to determine the optimum loading for the process.



Uranium Sorption Time (hr)

Uranium Desorption Time (hr)

Figure 4: Resin kinetics graphs for resin sorption and desorption

The desorption process for removal of uranium is essentially the reverse of the sorption reaction. The resin is contacted with a desorption solution to strip the uranium until the concentration of uranium on the resin is low enough to not greatly effect the resin loading in the next sorption cycle. The desorption kinetics of uranium has the inverse relationship to that of sorption and this "tail" must also be taken into consideration when designing the resin system.

The most economical sorption and desorption loading capacities for the resin will give the "effective" loading capacity of the resin for the system. The kinetics of sorption onto the resin determines the residence time of resin in the sorption system, while the kinetics of desorption allows the residence time of resin in desorption to be determined.

2.1.2 Mixing and the Number of Contactors

The cRIP system reactor design is based on the "tanks in a series" model where a series of continuous stirred tank reactors (CSTRs) are used and non-ideal flow is assumed due to the mixing inefficiencies. The ideal reactor would be a plug flow reactor model where the residence time of all particles is the same throughout the reactor (See Figure 5 below). The process design for ion exchange process under these circumstances would be simple – a reactor would have to be designed such that all pulp and resin particles stayed in the reactor for the required time to reach equilibrium. The "tanks in a series" model, using a series of mixed tanks, deviates from this ideal case and these inefficiencies need to be taken into account with the design.



Figure 5: Concentration profile through an N-stage mixed flow reactor system compared with single flow reactors (Levenspiel 1999)

Using this model the three factors for mixing can be modelled:

• The residence time distribution of the resin and pulp where some of the particles stay in the reactor for longer than the required time and some do not stay long enough

- The earliness and lateness of mixing of particles in the reactor (i.e. areas in the reactor where mixing is high and areas where mixing is low)
- The level of aggregation of particles in each reactor, reducing the mass transfer efficiency

Empirically, continuous stirred tank reactor (CSTR) systems can be modelled based on the volume, flow rate and number of contactors. Changing each of these factors will change the level of deviation from the ideal system. Generally, one or a combination of the following will decrease the deviation from an ideal plug flow reactor:

- Increasing the number of reactors
- Decreasing the flow rate of particles through the reactors
- Increasing the volume of the reactors

It is important to understand the metallurgical and economic implications of each of these factors. It has been assumed that the flow rate is determined by process design criteria for the whole plant and is a constant. Increasing the number of contactors will increase the efficiency of the system but will also increase the capital cost of the plant. Increasing the reactor volume has implications on mixing efficiency in that the increasing tank size has the consequence of increasing the time for "complete mixing". This relationship can be linear or exponential depending on the quality of mixing (Tatterson 2003).



Figure 6: Average mixing times (θ_m) as a linear and exponential function of tank volume (respectively) for effective and ineffective mixing geometries (Tatterson, 2003)

Above a critical reactor volume the time for complete mixing increases at a rate higher than the volume increase. Under these conditions there is no benefit gained from increasing the reactor volume and increased extraction performance will only be achieved through increasing the number of contactors. Figure 6 also demonstrates that proper tank and mixing orientation (conditions E to H) compared to poorly designed orientations (conditions A to D) can also greatly influence ability to scale up.

The residence time of the pulp in the sorption circuit is therefore governed by the efficiency of mixing. The time required for complete mixing for each tank multiplied by the number of tanks determines the time the pulp should remain in the sorption circuit. Understanding this relationship is a key when determining the optimum balance between reactor volume and number of reactors.

In fixed bed (cLX) and fluidised (cFLX) systems, complete mixing is instantaneous and residence time is not a design factor. In these systems the physical constraints such as pressure drop and superficial velocity in column are more important factors for the process design.

2.1.3 System Design

From the equilibrium loading of uranium on resin, the number of theoretical mass transfer steps can be determined. Figure 7 shows the McCabe-Thiele method for determination of the number of theoretical transfer steps required to extract uranium. The working line used in this diagram is the line connecting the feed and tail concentrations of uranium in the liquid phase.

In Figure 7 two different working lines were constructed in the same isotherm. Case A results in a lower resin loading capacity and a lower number of theoretical transfer steps or in practice less number of contactors. Case B results in a higher resin loading capacity and greater number of transfer steps and contactors. While Case A may appear to provide a simple and more economic process, other variables such as system robustness, co-loading impurities, desorption costs and resin inventory will also require analysis before the best working line is chosen.



Figure 7: Uranium isotherm and working line for (A) lower resin loading; and (B) higher resin loading

For RIP systems, determination of the theoretical transfer steps for mass transfer is used to determine the number of contactors required for the process. As the isotherm is fixed, it is the construction of the working line that the theoretical transfer steps to be calculated (as seen in Figure 7 above). In general, the working line is constructed at 80% of the loading capacity at the feed concentration to a point that represents the practical tails concentration.

Section 2.1.2 discussed the issues around reactor volume and mixing times and that there is a critical volume reached before more contactors are required to maintain process performance. Generally as a rule of thumb for large scale cRIP contactors (500m³), the mixing efficiency is ca. 70% is assumed. Therefore to achieve 97% mixing efficiency (where at least 97% of the particles have been in the contactors long enough to reach equilibrium for a theoretical transfer step) requires between 2 and 3 contactors. So depending on contactor size, the number of contactors required equals the number of theoretical transfer steps times an efficiency constant, where this constant ranges from 1 to 4.



Figure 8: Relationship between mass transfer equilibrium and number of contactors

The total volume of sorption circuit is governed by the flow rate of pulp, and the mixing efficiency (the residence time required to achieve complete mixing, generally 10-30 minutes of each tank and the number of contactors.

When designing fixed bed systems (cLX), contact with the resin is intimate and therefore uranium extraction from solution is achieved at a much faster rate than in RIP systems. The process design in cLX systems is based on loading capacity, kinetics to equilibrium and the physical constraints of pressure drop over the column. Similarly for fluidised bed (cFLX) systems, uranium extraction from the feed stream is again very fast and therefore process design becomes a function of resin bed volume expansion and flow distribution of the suspensions in the column.

2.2 METHODS OF MODELLING AND EXPERIMENTATION

In IX, the thermodynamic and kinetic properties are the fundamental bases for cRIP plant design. These parameters are determined in the laboratory using the proposed resin and real or simulated solutions.

2.2.1 Isotherm Data Collection

In order to establish the isotherm for a specific leach, resin and liquid or pulp at different ratios are mixed using a bottle roll technique. The equilibrium time is set to a number that ensures equilibrium is established among constituents in solid and liquid phases. The compositions of each phase is determined and plotted, typically as the resin uranium concentration versus the liquid uranium concentration. The isotherm in many cases is strongly influenced by the pH and composition, including uranium and other competing ions.

2.2.2 Kinetic Data Collection

Kinetic data is established by measuring the time taken to reach a maximum equilibrium loading capacity. Fresh resin contacted with an excess of liquid or pulp and at set time intervals, the resin is analysed for uranium content. The data collected is then plotted as the uranium concentration on resin versus time. Similarly resin is contacted with desorption solution (in excess) at different time intervals to determine the kinetics for desorption. Varying strengths of desorption solution can be also tested to determine the most economical option. Kinetic data is influenced by the concentration of constituents, species, temperature, resin type, ionic form, and pH. Therefore, all these variables are to be closely monitored to determine their affects on the kinetics of sorption and desorption.

2.2.3 Mini pilot plant

The mini pilot plant is a laboratory scale working model of the main process units of the system. This MPP plant includes 8 to 10 sorption reactors, generally 300 to 1,000ml in volume and the desorption and regeneration system. The purpose of the mini pilot plant is to validate the resin inventory per reactor, the number of reactors, resin flow rate and the kinetics and process conditions of desorption. The mini pilot plant also identifies issues that may affect the performance of the system, allowing the overall process design criteria for a full scale plant to be established.



Figure 9: Sorption and Desorption Mini pilot plant for uranium

Because of the small size of the reactors, mini pilot plant experimentation cannot be used for determination of mixing efficiency in full scale RIP contactors.

2.2.4 Modelling

Mathematic modelling of the sorption and desorption processes are established and validated using the isotherm, kinetic data, and the data collected from the mini pilot plant. A process flow diagram is then proposed for the system and a model is built using a software package such as SysCad or MetSim. The model has all the component of the proposed process.





Figure 10: SysCAD models of sorption and desorption process units for CCIX

Simulation of dynamic systems has been growing in complexity over the last few decades. Historically, bench and pilot scale test work was the benchmark for process design, but today, computational fluid dynamics (CFD) models now have the power to reveal much more information. While there has been discrete development in different process variables in cRIP processing (mass transfer, film diffusion, particle suspension) CFD brings these areas together to give complete modelling of the complex, unsteady, multiphase, non-Newtonian flows that can occur in these applications. (Koh and Xantidis 1999). CFD also allows for comparison of different systems, such as air and mechanical agitation, to be carried out to improve process selection.

While CFD offers a more in-depth technique for process design, it is fundamentally built on conservation equations (momentum, continuity, etc) that are empirically determined and are only as accurate as the data used. Therefore CFD should only be used in conjunction with experimentation or pilot plant studies for process validation. CFD does reduce scale up problems because the models are based on fundamental physics and therefore are scale independent (Paul et al 2004).

2.2.5 Demonstration Plant

Demonstration plants, with a design flow rate of 5-10% of the full scale plant provide detailed information on resin performance and the operability of the process to be validated. While the process performance is generally well understood through lab and mini pilot plant work, operability issues around the sorption and desorption unit processes generally require a demonstration size plant. At this size parameters such as flux rates over screens, mixing efficiency and resin attrition can be verified.

2.3 CONTINUOUS RESIN-IN-PULP / LEACH (cRIP/cRIL)

Resin-in-pulp (RIP) as a method for uranium processing has been used in such varying geographic locations as Russia, South Africa, USA, China and France (Anon, 1993). The major development of this technology was carried out in the former USSR and was driven by the Russian uranium industry over the last 50 years. The success is mainly due to the parallel development of ion exchange resins for uranium extraction (Section 4) and process. The use of resin processes for uranium extraction from leachates in the 1970's delivered a large reduction in the capital and operating costs. Compared to conventional filtration technology, energy costs were reduced by a factor of 2-3, labour productivity was increased by a factor of 2-2.5 and there was a reduction in capital cost (Shatalov, V.V., et al, 1999).

Continuous resin-in-pulp (cRIP) technology for uranium extraction is proving to be a cost effective alternative to conventional extraction routes. The cRIP process, by directly extracting the uranium from pulp, eliminates the need for the solid-liquid separation step. In addition, by concentrating the uranium tenor in the pregnant liquor, the hydraulic flow downstream of the process is also reduced significantly. These changes significantly reduce capital and operating costs as well as reducing the overall process plant footprint.

The design parameters that are most important for the cRIP sorption process are

- the method of mixing resins and pulps and
- the method of separating resin and pulp for transportation between contactors and columns

Mixing efficiency directly impacts the rate of mass transfer of uranium from the liquid phase onto the resin. The method of separation is critical to the ability to maintain resin flows and hence the resin to pulp ratios in process. These parameters must be maintained without excessive resin attrition or resin replacement costs and lost uranium values will adversely affect the economics.

2.3.1 Method of Agitation

The method of mixing resin and pulps has been the subject of many investigations. In general, mixing has been by air or mechanical means. The designs and configurations of equipment in both these areas have changed considerably with time.

The use of air as a method of pulp agitation has been widely used for many decades in the aluminium, copper, gold and uranium leaching, bacterial oxidation of pyrite industries as well as others. The slurry motion in an air agitated tank is established by injection of air through a central or multiple draft tubes. The airlift orientation is an important consideration for design with the full centre draft tube being more efficient than either the stub column or free air injection.



Figure 11: Air Lift Designs (G.G. Roy, R. Shekar, and S.P. Mehrotra, 1996)

The process parameters of the system are determined by a mixer of forces such as buoyancy, inertia, friction and hydrostatic pressure, all which form complex fluid system. (Rodriguez et al 2007). While air does apply some force to the resin and pulp, its main function is to change the bulk density of the pulp such that it rises while normal "more dense" pulp falls, creating the mixing pattern. This by nature is a much more gentle method of mixing compared to mechanical agitation, which in the process of rotation creates high localised shear forces.

The use of air mixing becomes more important when the rheological properties of the pulp are problematic. In these cases, the conventional approach is to dilute the pulp to a point where the rheology is controllable. Dilution however is counterproductive in the RIP application where the pulp solids and solution tenor is a major economic driver. Pulps with thixotropic nature or shear thickening behaviour under mechanical agitation can be efficiently mixed using air mixing.

The design of the draft tube is the key design parameter. In general, for large diameter tanks the minimum diameter of the airlift is one tenth that of the tank diameter to achieve particle suspension for typical slurries. Test work has also found that the critical velocity for particle suspension decreases as the tank increases, suggesting that air agitated tanks become more efficient at suspending solids in scale-up.

One of the notable differences in air agitation design is the tank orientation. While traditionally tanks are normally designed for H/D ratio of 1:1, air agitated tanks typically have H/D ratios of 3:1 to 4:1. The design ratio is necessary to reduce the critical velocity required to suspend particles and the overall air requirements of the system. By increasing tank height, the potential energy of the particles increases and this reduces the requirements of air for suspension and air lift. Experimental data shows that tank diameter has little effect on the air requirements for mixing. (Roy et al 1998) Therefore the use of air agitated systems for RIP processes is only constrained by the capital cost of tall tanks and the power requirements for air pumping.

Mechanically mixed systems for pulps have also been widely used in the metallurgical industry. Mechanically stirred tanks have been used in the gold industry for CIL and CIP as well as several other leaching applications. There has been a large amount of work done on the mixer design and power requirements for mixing multi-component systems however little published work has been done on the use of mechanical mixers for resin and pulp slurries, especially pulps with high solids and/or difficult rheology. The power requirements for mechanical agitation should be carefully considered. Increasing the power used for mixing increases the shear forces on components of the mixture, in this case resin. Increased shear will generally result in increased resin attrition. More emphasis needs to be placed on tank orientation and impeller design to compensate for higher shear and to avoid higher operating costs due to increased resin attrition.

One approach when faced with problems in rheology in mixing is to operate with lower pulp solids (e.g. reduce from 50% to 30%). The mixer under these circumstances can operate with lower shear requirements for complete mixing. While this approach lowers the resin attrition rate, it also results in lower resin loading (higher resin inventory) and higher hydraulic rate requirements (larger tanks), both detrimental to the process economics.

Mechanically agitated tanks typically are designed with a 1:1 to 1:2 aspect ratio, which reduces the capital cost requirements compared to the higher tanks required for air agitation.

2.3.2 Transport of Resin Slurries

The transport and separation of resin and pulp is a critical design factor. cRIP has been compared to carbon-in-pulp (CIP) technology in the gold industry. In gold CIP, the carbon and pulp is separated in-vessel by an inter-stage screen. The pulp is pumped from inside of the screen and the carbon is transported intermittently together with pulp by gravity between contactors. This type of countercurrent flow arrangement works well when the sorbent is a very small percentage of the pulp and the kinetics are slow. In the uranium cRIP systems, this CIP approach is difficult as the resin concentration in the process is higher and the loading kinetics are faster than the gold case.

The best efficiency in the uranium cRIP process is obtained when resin and pulp are continuously separated and transported counter currently thereby optimising the loading capacity of the resin and minimising the problems associated with back-mixing. While there are several different ways to transport the resin and pulp, it is important to understand the process implications of each. With resin prices generally 5 to 10 times higher than carbon and resin inventory in uranium processing significantly higher than in gold, the resin attrition becomes an important operating cost factor in uranium RIP applications

Transport of the resin between contactors is normally carried out by two processes. The first method is through the use of airlifts. Airlifts have been around for several decades and all RIP plants in the former Soviet Union use this method. The use of air as a method for resin transport is a gentle system that minimises resin attrition. The pumping power requirements for airlifts can be empirically determined and it has been shown that approximately $3m^3$ of air is required to move $1m^3$ of pulp at 50% solids. While the air requirement is dependent on the density of the pulp and the hydraulic throughput of the plant, the power requirement is dependent on the size and orientation of the contactors as this will directly impact the head pressure requirements of the air compressor.

The second method is mechanical pumping and the development of this process for RIP was first established in South Africa, using Wemco recessed impeller pumps. (Cloete, 1984) The benefit of using this type of pump is that the centrifugal force of the liquid stream is used to transport the slurry reducing the contact with the impeller and consequently the attrition of the resin.

Clean TeQ has compared the two methods on a pilot plant scale operation. Operating two tanks, one with airlift and the other with mechanical pumping, and transporting a resin-in-pulp slurry found that the annualised resin attrition utilising a recessed impeller pump was twice that for the air lift. In the economic evaluation, the additional operating cost of air in an air lift system must be compared with the increased resin attrition when using impellor pumps.

2.3.3 Separation of Resin and Pulp

Resin and pulp are generally separated using screening devices. Several versions of screening processes have been used over the years. The main issue in resin and pulp separation is the size difference between the resin particles and the pulp particles. When separating particles with similar particle sizes, the flux rate over screens becomes limiting. This has become one of the major process design issues for cRIP plants.

Pilot plant test work has been done in the past to develop a screen-less process, whereby the resin overflows into the next reactor (Carman 1960), but this was unsuccessful due to the low mass transfer characteristics observed and poor recoveries due to a lack of control of resin transport. Submerged screens had also grown in popularity. Widely used in South African plants was the Dutch State Mines (DSM) wire mesh and Laxen et al (1979) suggested using a cloth screen bubbling air to transport pulp tangentially to the screen achieving high flux rates.

Another method which is becoming used in RIP carrousel operations is the mineral processing separating screen (MPS) and the mineral processing separating pumping screen (MPS(P)) (Kemix Pty Ltd, 2005). Both of these utilise cylindrical wedge wire baskets, which use a rotating wiper to keep the screen free of resin and pulp. A pumping impeller is also utilised to create a pressure difference to transport pulp, while keeping resin within the tank.

Unsubmerged static screening is the other alternative for resin and pulp separation. Commercially there are three methods currently available for this application. The first are sieve bend screens which were first investigated by Mintek and were used in operation at the Golden Jubilee Mine in South Africa in conjunction with external airlifts. The second method the use of wedge wire screen decks, however the construction and layout of wedge wire decks means that its rigid structure lends itself to high levels of pegging. Without any vibration of the screen through the kinetic energy exchange of the slurry stream landing on the decks, there is not enough energy to effectively separate the resin and pulp streams.

The third system is the screening system used by Clean TeQ and is a woven wire static screen system. The screen decks for the resin separation module are located above the tank and the resin and pulp is airlifted onto the screen deck. Experimentally this configuration has been found to provide the highest flux rates and the best operational performance. The system uses the pulsing action of the airlift to induce vibration in the woven wire screen to efficiently separate resin and pulp. Unlike wedge wire screens, which are rigid, the flexible design of the woven wire mesh screen reduces the amount of pegging. An independent validation of a woven wire mesh screen used in an cRIP application found that after several months of operation, low wear and no pegging was observed on the screen (Figure 12).



Figure 12: Images of New woven wire mesh and worn woven wire mesh after several months of operation on nickel laterite pulp. It can be seen that there is little difference in the screen after use.

2.3.4 Clean-iX[®] cRIP Flow Sheet

Typically a Clean TeQ Clean-iX® cRIP flow sheet would include the sorption circuit and a Clean-iX[®] elution circuit.



Figure 13: Typical cRIP flow sheet in series

After leaching, the pulp is pumped into the first contactor and exits the Nth contactor to tails. The resin enters the Nth contactor and is transported counter currently to the pulp flow. The loaded resin is transported to the elution circuit for separation and purification,. All water and reagent streams are captured in the Clean TeQ circuit and are either re-used in the process or are recycled to the leach circuit. The elution circuit is a patented process (discussed in Section 2.6) and the sorption circuit operates with either air or mechanically agitated contactors.

2.3.5 Air Agitated Contactors (Clean-iX® Air)

The Clean-iX[®] Air mixing technology uses a specifically designed draft tube to induce mixing in the contactor. This system differs from traditional draft tube design where is injected air into the bottom of the tank through a diffuser (free air system) or a short stub tube. Diffuser and short stub air systems are prone to clogging on power outages and restart can be difficult. To overcome this problem, a "pachuca valve", i.e. a heavy-duty non-return valve, was developed. This development then prevented pulp travelling up and blocking the feed air line. However this approach also increased the compressor duty required to counter these higher head pressures adding additional mechanical and operating cost to the system.

Clean TeQ uses a special draft tube design that has been developed to ensure the air bubble size and velocity allows for optimum mass transfer. This draft tube design is not prone to blockage on power outages. The concentric design of the draft tube means that it is also used to transport the resin and pulp to the resin separation module and into adjacent contactors.



Figure 14: General Arrangement of Clean TeQ Air system

2.3.6 Mechanically Agitated Contactors (Clean-iX® Mech)

Clean-iX® Mech, the mechanically agitated system, uses a low shear, two-stage mechanical agitator to mix the resin and pulp. The system is designed to ensure that resin and pulp is well mixed and mass transfer is maintained. The system uses an airlift system, similar to that of the air agitated system, to lift both resin and pulp to the separation screen for transportation. Mechanically agitated systems offer a different alternative for RIP and should be included in economic evaluations of the optimum process flow sheet.

The transportation and separation methods for the mechanical agitation system is the same as the air system, utilising draft tubes for airlifting and woven wire mesh screens for resin and pulp separation. Because these mechanically mixed tanks tend to have lower aspect ratios, the height required for air lift is lower and therefore the compressor requirements are reduced compared to that of air agitated systems.



Figure 15: General Arrangement of Clean TeQ Mech system

2.3.7 Comparison

Typically, the main operating parameters that are compared with mechanical and air agitated systems are the power and resin replacement rate. The operating cost for power in air agitation tends to be higher than that of mechanical agitation. However the higher capital and operating costs of the mechanical agitators should be included in the overall cost equation.

In low resin inventories, such as in gold applications where the percentage of resin the contactors can be as low as 1%, the costs associated with resin attrition are quite low compared to the power costs. In uranium cRIP the resin inventories can be 10-15% and in nickel/cobalt they can be up to 30%. In these systems the affect of resin attrition on operating cost can be substantially. One issue to note is that the addition of energy into each of the systems is different.

Typically the power costs increase only marginally with increasing resin percent to create homogeneous mixtures. Therefore the following relationship is possible:





As Figure 16 demonstrates, there is a break even point whereby the cost of resin attrition exceeds the additional power requirements for the system. This is the fundamental relationship that needs to be understood when comparing air and mechanical agitated systems. While air agitation has a higher operating cost, it has lower resin attrition rates. Mechanical agitation has lower operating cost but has higher resin attrition rates. Performing this cost analysis is a key for optimal process selection.

2.3.8 Carousel RIP

The other main process that is available for this application is the Carousel mode of RIP, a semicontinuous countercurrent operation. The pulp is moved through the sorption plant, while the resin remains in each contactor. The lead contactor is intermittently rotated using a valving system until the resin is fully loaded. Once this has occurred, the contents of that contactor is emptied over a screen with the pulp going back to the feed and the loaded resin being sent to the elution circuit. The contactors are mechanically stirred with an interstage screen that keeps the resin within the contactor and the pulp pumped through the contactors.

The benefits of this process are stated as optimum resin inventories can be controlled with discrete batches of resin in each contactor. The main drawbacks of this system are the additional contactors needed for comparative operation and the subsequent additional resin inventory. The carousel system was originally designed to avoid the issue of back mixing as was apparent in gold CIP plants when carbon and pulp were pumped together to transport the carbon upstream. This misplaced pulp would dilute the gold concentration in the pulp and therefore reduce the efficiency of the system. Keeping the carbon within the tank and just transporting the pulp eliminated this effect. However extra tanks were required for emptying and loading in order to keep the system online all the time. Where Clean TeQ may require N contactors for operation, a Carousel system generally requires N+2 cells. The other drawback is that due to the "recycling" of pulp upon emptying of the contactor, as so each contactor must be larger to account for this recycle stream to achieve the same throughput as the Clean TeQ system.

2.3.9 Resin-in-Leach (RIL)

The resin-in-leach (RIL) process can be used to obtain additional uranium recovery from the solid phase. Typically, leaching is limited by the diffusion restriction of the leaching kinetics or the leached uranium can be sorbed by competing sites. The presence of the resin in the leach minimises the negative influence of re-precipitation, co-precipitation, occlusion and sorption of uranium by the solid phase (Zontov 2006). Removal of uranium from the leachate by the resin ensures that the driving force further leaching remains and the amount leaching chemicals can be reduced, uranium recovery increased and capital reduced. Generally the leaching chemistry is governed by similar diffusion layers as adsorption as seen in Figure 17.



Figure 17: Matrix mineral fragment illustrating reaction zone and reacted and un-reacted regions. (Wadsworth 1987)

The RIL process is similar to RIP except that the number of contactors is increased to include the additional time for leaching.



Figure 18: Typical cRIL flow sheet in series with leach reagent recovery

Figure 18 shows a typical Clean TeQ cRIL system, whereby M contactors are the additional contactors required to allow for the kinetics of leaching. RIL is the obvious progression for RIP technology and can be used in conjunction with any one of Clean TeQ's resin technology platforms to improve the economics of an ore body. The RIL platform is used where atmospheric leaching is the most economical option and test work has shown that there can be significant increases in uranium recovery by using the RIL flow sheet.

2.4 CONTINUOUS FLUIDISED LIQUID EXTRACTION (cFLX)

Like most ion exchange technologies, the use of fluidised beds of resin to contact fluids has been around for a long time. The advantage with a fluidised bed is that it allows fine particulates to pass through the bed without blockages and so streams with up to 10% solids can be used in this application for uranium extraction.

One of the first utilisations of fluidised beds in resin was the Dorrco softener, where the resin sat on a series of trays and liquid continuously flowed upward while the resin travelled downwards through the use of a liquid ejector. Further developments relied on the addition of trays within the system. This meant that when feed was periodically shut off, the resin could settle onto these trays and the whole system could then flow by gravity to move the resin counter currently to the flow of liquid.

2.4.1 NIMCIX Columns

The NIMCIX fluidised column system for continuous ion exchange was developed by Mintek. To date this technology has been implemented in s projects including Vaal River, Chemwes and Blyvooruitzicht (Kotze et al 2006). The benefit of the unit was that it could operated with up to 300mg/L suspended solids. The liquid is pumped upwards through perforated distribution plates fluidising a series of resin beds. At the end of normal operation, there is a settling period, where the resin falls through the distribution plate and into the empty stage below. The loaded resin at the bottom is transferred by a pump into the desorption circuit.

2.4.2 Himsley Columns

Himsley fluidised bed are similar to that of NIMCIX or USBM columns in that liquid is pumped up vertically through different stages of fluidised beds of resin. The batches of resin contained in each stage are sequentially transferred downward by reversing the flow of liquid downward to displace the resin into the vacant stage below it. Resin is transferred to the desorption section using the same method. Screens are required at the top of each stage to avoid any resin being removed by the pump. This system use a large number of valves and has requirement for a second pump to operate as the transfer pump.

2.4.3 Porter Tanks

The limitations with the previous fluidised contactors are that stages are created on top of each other. Large flow rates mean the columns have to be quite substantial and tall to allow for the resin inventories. Porter and Robert (US Patent 3, 879,287 (1975)) designed a system for large flow rates through a series of open tanks in a cascade arrangement. Liquid is pumped into the first tank at a low level through a pipe distributor and is continuously transferred to successive tanks through gravity, using overflow weirs at the top of each tank. Screens are used to avoid resin transfer with the liquid. Resin is transferred through the use of airlifts. The largest application of the Porter IX system is in Rössing Uranium Mine in Namibia.

2.4.4 Clean TeQ cFLX

Clean TeQ's continuous fluidised liquid extraction (cFLX) system utilises expanding the bed of resin to allow good contact and mixing with solutions, while allowing particulates to pass through into tails. Each contactor is designed to allow bed expansions of up to 200% to avoid issues with channelling and blockages, which can be an issue in traditional fluidised bed columns where the bed is only slightly expanded. Solid concentrations of up to 10% can be processed through the system. Resin transportation is from the bottom of the columns using airlifts similar to the Porter system. The cFLX system uses a series of columns with each column representing a transfer stage. No screens are needed as the columns are designed to account for the height of expansion for the smallest resin particles and a resin disengagement section to allow resin to settle prior to transport.

Typically the process flow sheet for cFLX will involve a series of fluidised columns, with resin and solution moving continuously and counter currently. The fully loaded resin is airlifted from the first contactor to Clean TeQ's desorption circuit for uranium extraction and concentration. The regenerated resin is transferred into the last fluidised column, closing the loop. Between each column there is an intermediate tank and pump, which eliminates the need to use a cascade arrangement. Avoiding a cascade arrangement reduces the overall height of the sorption system and increased operability, which can be beneficial in large scale operations. The inclusion of an intermediate tank and pump means that the plant is able to cope with fluctuations in feed conditions and improves its operational performance maintenance requirements overall. A typical cFLX flow sheet can be seen in Figure 20.



Figure 19: Column/Tank Arrangement for cFLX



Figure 20: Typical cFLX Flow sheet

The attrition rates associated with this system are low as the resin is only transported through the use of airlifts, a more gentle option than pumping. These cFLX systems can also be used in conjunction classification and filtration when the uranium fraction is able to be separated into a low solids slimes feed. An example of this flow sheet can be seen in Figure 21 below.



Figure 21: Typical cFLX Flow sheet with Classification and Filtration

2.5 CONTINUOUS LIQUID EXTRACTION (cLX)

Apart from fixed bed ion exchange, moving bed ion exchange has formed the basis of continuous counter current ion exchange in hydrometallurgy, resource recovery and water treatment throughout the world. Moving discrete amounts of resin throughout the system, creating a semi-continuous process has the ability to increase the process performance and overall footprint of the IX processing plant.

2.5.1 Batch Ion Exchange

Batch ion exchange has been widely used in the uranium industry for uranium extraction. While this system was used to meet the early demands of the nuclear industry, the developments in continuous ion exchange utilising fluidised and RIP contactors has reduced the competitiveness of this platform.

The design of batch contactors for uranium extraction are based on developments in the water industry. Typically both the sorption and desorption of the resin is performed in the same contactor. With this system there is an absolute requirement to have clear solutions with no suspended solids as the presence of these greatly affect the performance of the system and the pre-filtration equipment can cost as much as the ion exchange system. Process streams with a percentage of fine solids present operational problems to batch ion exchange and there is difficulty in economically removing this size fraction.

2.5.2 SepTor (ISEP Process)

The Outokumpu SepTor and Calgon ISEP processes combine a series of fixed beds in a cascading carrousel arrangement to load and strip the resin. The feeds into each of these contactors could be changed through a system utilising rotating columns and multiport distributor valves. The resin and solution are moved countercurrent to each other to ensure the maximum efficiency of recovery. The elution and regeneration steps happen on the same train, which minimise the overall footprint of the process. A number of economies can be achieved due to this design such as recycling of process and water streams as well as the ability to accurately optimise loading on the resin.

There is still the requirement for a clarification step, as the SepTor process is essentially a series of fixed bed columns, and is therefore subject to the same process issues as batch IX. All of the columns in the SepTor system are also exactly the same size and dimensions. For optimum performance of each of the process steps (adsorption, elution, washing) each column must be individually designed.

2.5.3 Clean TeQ cLX

Clean TeQ's continuous liquid extraction (cLX) system is a continuous countercurrent ion exchange system with built in robustness and flexibility to handle conditions where conventional systems cannot. The sorption contactor is a packed bed column where the liquid flows upwards and resin is moved downwards to optimise the mass transfer driving force. Continuous movement of the resin counter currently ensures the resin is loaded to its maximum potential and reduces the resin inventory required in the system. Adding regenerated resin to the top of the column intermittently drastically reduces the risk of uranium breakthrough into the waste stream.

Once the resin is fully loaded with uranium, it is transferred via airlift into a fluidised wash column. In this column, wash water is used to remove any particulates that may have been in the feed stream, reducing the risk of contaminating the pregnant liquor stream. As packed resin beds act as a filter, the fluidised wash column ensures the resin is washed, allowing the feed stream to have up to 100ppm solids without affecting performance. The cLX system has less of a reliance on upstream solids separation / filtration unit processes than other technologies of this type.

2.6 CLEAN-iX[®] ELUTION CIRCUIT

Clean TeQ's patented elution circuit utilises countercurrent operation with concentration desorption to ensure high concentration and purity pregnant liquors with minimum resin inventory. This circuit can be designed to fit with all the different types of Clean-iX[®] sorption circuits described above. Also each column is individually designed for its application, allowing for the optimum fluidised washing, desorption and washing possible.

In the elution circuit the first column is generally a fluidised wash column. This column washes any particulates off the resin to protect the purity of the pregnant liquor stream. In RIP applications, a screen with wash water is used upstream to assist in the washing process.

The resin is airlifted from the bottom of the fluidised wash column into the concentration desorption, or "U", column for uranium stripping. Resin and desorption solution are passed counter currently to each other to maximise the driving force for desorption of uranium from the resin. The concentration desorption process is dependent on two factors: the process flow characteristics (flow rate of pregnant liquor versus flow rate to waste); and the selectivity of the resin towards uranium.



Figure 22: Typical Arrangement of Concentration "U" Column and Wash Column used in Clean TeQ's elution process

As the desorption solution contacts the resin, uranium is stripped. The tenor of the stripped uranium builds and at a point close to the bottom of the U column, there exists a zone where uranium on the resin is in equilibrium with a very high uranium tenor in solution. The liquid phase is removed at this point, as it is the maximum concentration of uranium. The high uranium loading at this point has caused other loaded components to be chromatographically pushed into the upward leg of the U column and eventually to waste or recycle.

Following stripping the resin is transported to the wash column where the resin is washed with water and excess desorption reagent is captured for desorption reagent makeup.

Clean TeQ's elution circuit has the ability to produce high concentration, low flow, and high purity uranium streams. This ability opens the way for a single process step to uranium recovery, without the need for solvent extraction in many cases.

3 APPLICATIONS

3.1 ATMOSPHERIC AND PRESSURE LEACHING

The leaching of uranium using acid or alkaline leach at atmosphere or under pressure provides a feed stream for uranium processing. The use of resin technology as a method for extracting uranium from these feeds will become the method of choice in the future. The system chosen (cRIP, cFLX, cLX) will be dependent on the physical nature of the pulp, the economics of solid – liquid separation and the water balance of the system. If cRIP is chosen, the use of air or mechanical system will rely on the pulp solids, viscosity and particle size distribution.

Typically a leach solution containing 500ppm uranium can be extracted and purified to provide a 10-15g/L feed to uranium precipitation circuit.

3.2 IN-SITU LEACHING (ISL)

In-situ leaching will continue to be a part of the uranium world. The recovery of uranium and return of the leachate using cLX technology offers an economic and operational advantage over batch processing due to its ability to deal with particulates in feed.

Typically a leach solution containing 50-100ppm uranium can be extracted and purified to provide a 5-10g/L feed to uranium precipitation circuit.

3.3 HEAP LEACHING

Heap leaching of uranium will be a part of the majority of future uranium processing plants. Where there is a possibility of recovering uranium using this low cost route, both cLX and cFLX technologies can be integrated to provide a high tenor uranium output.

Typically a heap leach solution containing 100-200ppm uranium can be extracted and purified to provide a 5-10g/L feed to uranium precipitation circuit.

3.4 URANIUM CONTAMINATION IN GROUND WATER

Uranium can be found in ground water and sometimes in a range that can be detrimental to health. The use of cLX circuits for the extraction and recovery of uranium is a solution. The chemistry of ground water uranium treatment is generally different to processed uranium liquors with different resins and processing conditions being applied.

3.5 TAILINGS RECOVERY

As these new technologies develop and uranium process stabilise at new levels, the economic equation for uranium recovery will be challenged. The Clean TeQ cRIP, cFLX and cLX circuits provide a new processing regime that will provide business opportunities.

4 RESINS

Uranium can be extracted from two main leach types, namely acid and carbonate leaches. In sulphuric acid leach solutions the uranium can be present as $UO_2^{2^+}$ cations or $[UO_2(SO_4)_2]^{2^-}$ and $[UO_2(SO_4)_3]^{4^-}$ anions. In carbonate leaches, the uranium is present as the complex anion $[UO_2(CO_3)_3]^{4^-}$. In acid leaches the uranium can be extracted in both the cationic and anionic form while only in the anionic form in carbonate leaches. A range of resins can therefore be used to extract uranium depending on the characteristics of the uranium.

4.1 STRONG BASE ANIONIC (SBA) EXCHANGERS

In sulphuric acid leached solutions typically the uranium is present and adsorbed onto the resin as $[UO_2(SO_4)_3]^{4-}$ at ph < 2. The sorption process is also highly affected by the presence of HSO_4^{-} ions and therefore the pH of the leach can greatly influence the level of uranium extracted. Decreasing

this HSO_4^- concentration (or increasing pH) noticeably increases the uranium loading capacity. Increasing pH also changes the form of the uranium to $[UO_2(SO_4)_2]^{2^-}$, which increases the loading capacity for uranium (based on equivalency). Hydrolysis of this complex also occurs, forming another complex, which further increases the loading capacity of the resin.

Typically the impurities that load onto the resin are $SO4^{2-}$, $Fe(SO_4)^{2-}$, $Fe(SO_4)^{3-}$, CI^- , NO_3^- and some anionic forms of V, P, As and Mo. The presence of impurities can have a large impact on the loading capacity of the resin and therefore need to be considered when selecting resin as they have the potential to decrease the loading capacity and poison the resin.

Carbonate leaches tend to make up a small minority of economic ore bodies. Carbonate leached solutions are only present as the complex anion $[UO_2(CO_3)_3]^{4-}$ and therefore only strong base anionites can be used for uranium extraction.

Developments in resin chemistry and synthesis mean that SBA resins are now more selective towards uranium and have higher loadings, increasing their suitability over solvent extraction as the optimum ion exchanger for uranium extraction.

4.2 WEAK BASE ANIONIC (WBA) EXCHANGERS

Weak base anionic resins have primary, secondary and tertiary sites for exchange and therefore acidic conditions can protonate these sites and have less of a response for changing leach conditions. These resins tend to be more selective towards uranium, and less affected by the presence of impurities. Higher acidic conditions means the resin will no longer load the impurity complexes, whilst still maintaining a high loading capacity for uranium. This relationship is not true for caustic conditions, where the presence of carbonate and bicarbonate (through oxidation) drastically reduces the loading capacity of uranium. Therefore only strong base anionic resins are suitable for alkaline leaches.

Weak base exchangers directly compete with SX exchangers for uranium extraction. While liquid exchangers in SX have faster kinetics than resin based WBAs, the ability to use resins in a wide range of applications with the various Clean TeQ platforms makes WBA resins an economical option.

4.3 STRONG ACID CATION (SAC) EXCHANGERS

Strong acid cation resins generally have very fast sorption and desorption kinetics and a very high affinity towards uranium ions. The loading capacity for uranium increases as the pH increases and is typically desorbed using ammonium nitrate solution. While there may be some applications were SAC exchangers can be used, they have a low selectivity towards uranium, which typically makes them unsuitable.

4.4 WEAK ACID CATION (WAC) EXCHANGERS

Weak acid cationic resins contain a carboxylic acid functional group and sorption is based on the formation of complex compounds between uranyl and carboxyl ions. While the effect of salts on the loading capacity of WAC is less than SAC, it is still highly influenced by pH. There is only a narrow band of pH (2.8-3.5) where loading is good and the resin is highly selective towards uranium. Therefore this pH correction step is WAC resin's major disadvantage. Sulphuric acid can be used at small bed volumes to strip the uranium.

5 OVERALL PROCESS SELECTION

Overall process selection will be based on:

- Ore type
 - hard or soft rock
 - o alkaline / acid consuming
- Leach
 - o Acid / alkaline
- Pulp
 - Particle size sands or slimes
 - \circ Solids content 10 60%
 - Viscosity
- Tenor of in-situ or heap leach

Purity of product

As technical develops continue there are opportunities to reassess the economics of uranium extraction. The environmental impacts of mining can be managed through improved plant design with size and scale being reduced, water utilisation minimised, values maximised leading to a low environmental footprint. As the demand for uranium increases, the need to develop sustainable, economic mining operations for lower grade ore bodies will become paramount. Ion exchange is the technology platform for the paradigm shift occurring in the uranium industry.

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