2006 CONTINUOUS COUNTER CURRENT ION EXCHANGE IN URANIUM ORE PROCESSING

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1. ABSTRACT

Over the last few years Clean TeQ has been developing ion exchange technologies and process solutions for uranium recovery from leached pulps and solutions.

Conventional hydrometallurgical extraction systems generally rely heavily on physical separation processes. These processes typically have a very large footprint and tend to be inefficient in operation in respect to specificity and tenor of uranium. Targeted extraction processes, such as ion exchange, have the ability to simplify technology and reduce capital and operating costs. The benefits will become available when these processes can be used in the early stages of processing rather than in the refining steps. Recent advances in resin design coupled to improved process technology have made the application of Resin–in–Pulp (RIP) technology to the processing of uranium pulps a much closer reality.

The potential advantages of the direct uranium sorption from ore pulps became clear decades ago, but implementation of this process has been hindered by a lack of understanding and acceptance of the resin attrition rate and process equipment design.

The most important characteristics of the uranium sorption process, from both economical and technological points of view, are

- initial loading of the resin,
- resin consumption for 1 t of the processed ore,
- resin loading capacity,
- chemical consumption,
- plant footprint and
- volume and concentration of the eluates.

Most of these parameters depend upon the volume of the pulp produced from leaching 1 t of the ore, so it is preferable to minimize pulp volume and to maximize pulp density.

The RIP technology for direct uranium sorption from leached slurry may be conducted using a specially designed reactor with air used for mixing and for resin and pulp transfers. This type of reactor can be used for processing leached slurries containing up to 60% solids. The reactors can be designed to process hundreds of cubic meters of pulp in a fully automated state.

In addition, Clean TeQ designs other processes, such as the continuous counter current sorption process, which is effective for uranium recovery from solutions. Also a specific column for desorption concentration is available that dramatically increases uranium concentration in eluates.

2. INTRODUCTION

Conventional hydrometallurgical extraction systems generally rely heavily on physical separation processes. These processes typically have a very large footprint and tend to be inefficient in operation in respect to specificity and tenor of the targeted metals. Targeted extraction processes, such as ion exchange have the ability to simplify process flows and reduce capital and operational costs. These benefits will become available when these processes are able to be used in the early stages of processing rather than in the refining steps.

Already there are major applications for resin technology with several plants using resins for the recovery of high value metals, such as uranium and gold, from pulps and leachates. The advantages of the ion exchange processes include:

- High selectivity for target metals
- High separation capabilities
- Flexible processing regimes
- High concentration step
- Simple process design
- Small footprint of plant
- High level of automation

These advantages ultimately result in:

- Lower capital cost of equipment
- Lower operating cost
- Higher yield
- Best NPV

3. URANIUM SORPTION FROM SOLUTION

In sulphuric acid leached solutions uranium is present as UO_2^{2+} cations and $[UO_2(SO_4)_2]^{2-}$ and $[UO_2(SO_4)_3]^{4-}$ complex anions. The relative concentrations of these uranium forms depend on the pH of the solution and sulphate and uranium concentrations. Uranium can therefore be extracted using ion exchange resin from sulphuric acid solutions in both cation and anion forms.

The most important characteristics of the sorption process are

- maximum loading capacity and
- selectivity with
- good kinetic and
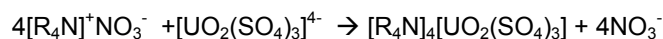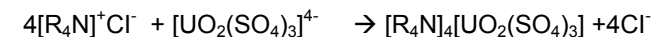- simple resin regeneration.

Usually the leach solution will contain high concentration of impurities such as SO_4^{2-}, HSO_4^-, CO_3^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, NO_3^-, Al^{3+} and lower concentrations of impurities such as Mo^{6+}, As^{5+}, Cu^{2+}, Ni^{2+}, Co^{2+}, P, F, Ti^{4+}, Th^{4+}, REE and natural radioactive elements. The complexity of the leachate means that the ion exchange resin must have a maximum selectivity to uranium to provide the most effective outcome.

3.1. USE OF ANIONIC ECHANGERS FOR URANIUM SORPTION FROM SULPHURIC ACID LEACHED SOLUTIONS

#### 3.1.1. Uranium sorption by strong base anion exchangers

In acidic solution (pH < 2) uranium is mainly present as $[UO_2(SO_4)_3]^{4-}$ ions and in this form uranium is sorbed by anion exchangers.

=The uranium exchange process can be expressed by the following reactions, where the anion exchanger is in either the chloride or nitrate form:

$$4[R_4N]^+Cl^- + [UO_2(SO_4)_3]^{4-} \rightarrow [R_4N]_4[UO_2(SO_4)_3] + 4Cl^-$$

$$4[R_4N]^+NO_3^- + [UO_2(SO_4)_3]^{4-} \rightarrow [R_4N]_4[UO_2(SO_4)_3] + 4NO_3^-$$

Just as uranium is exchanged, some of the other anions such as SO_4^{2-}, $Fe(SO_4)^{2-}$, $Fe(SO_4)^{3-}$, Cl^-, NO_3^- and some anionic forms of V, P, As and Mo can also be exchanged. The cations such as Fe^{2+}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Ti^{4+} are not exchanged by the anion exchanger.

This exchange process is dependant on the pH of the solution. At high concentration of sulphuric acid the exchange of HSO_4^- noticeably decreases the resin loading capacity for uranium. By raising the pH to greater than 2, and therefore depressing the concentration of HSO_4^-, the competition effect of HSO_4^- ions is reduced (Figure 1).

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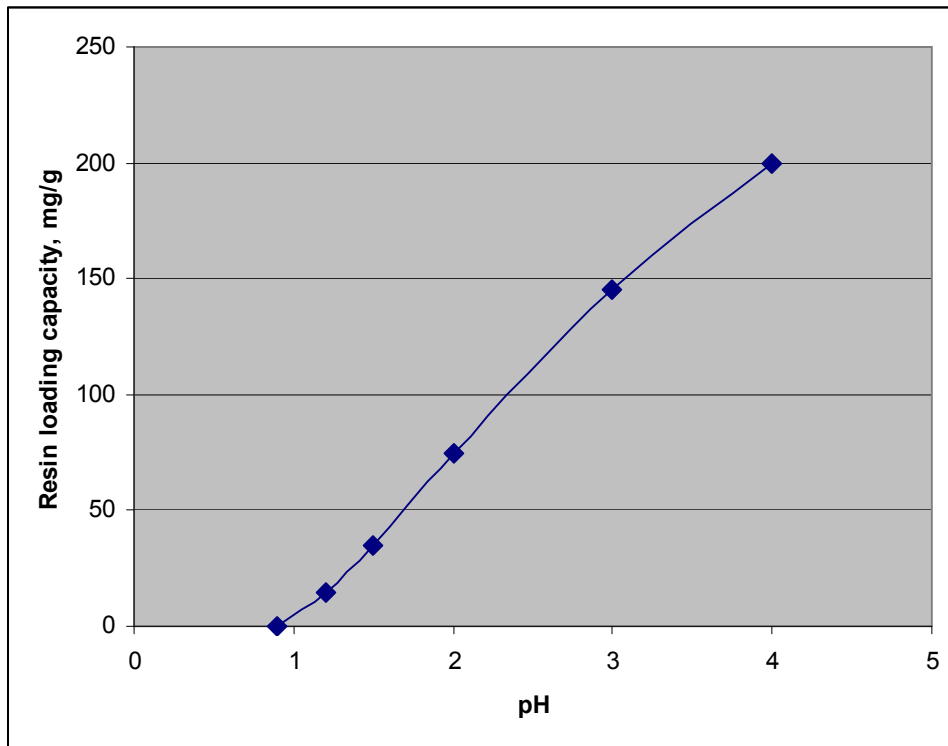
Figure 1. Influence of pH on resin loading capacity

As the acidity of the leach solution decreases, the concentrations of the various forms of the uranium anionic complexes change. $[UO_2(SO_4)_2]^{2-}$ ion concentration increases and $[UO_2(SO_4)_3]^{4-}$ decreases, which in turn leads to an increased resin loading capacity based on the equivalency.

If pH of the solution is ~2.5 uranium is usually presents as complex anions $[U_2O_5(SO_4)_3]^{4-}$ and $[U_2O_5(SO_4)_2]^{2-}$ and [as] a result of hydrolysis, this significantly increases resin loading capacity. Thus solution acidity has a strong influence on uranium sorption.

In spite of uranium being better exchanged than SO_4^{2-}, HSO_4^{-} and anionic complexes of iron, they depress uranium recovery by anion exchangers (Figure 2).
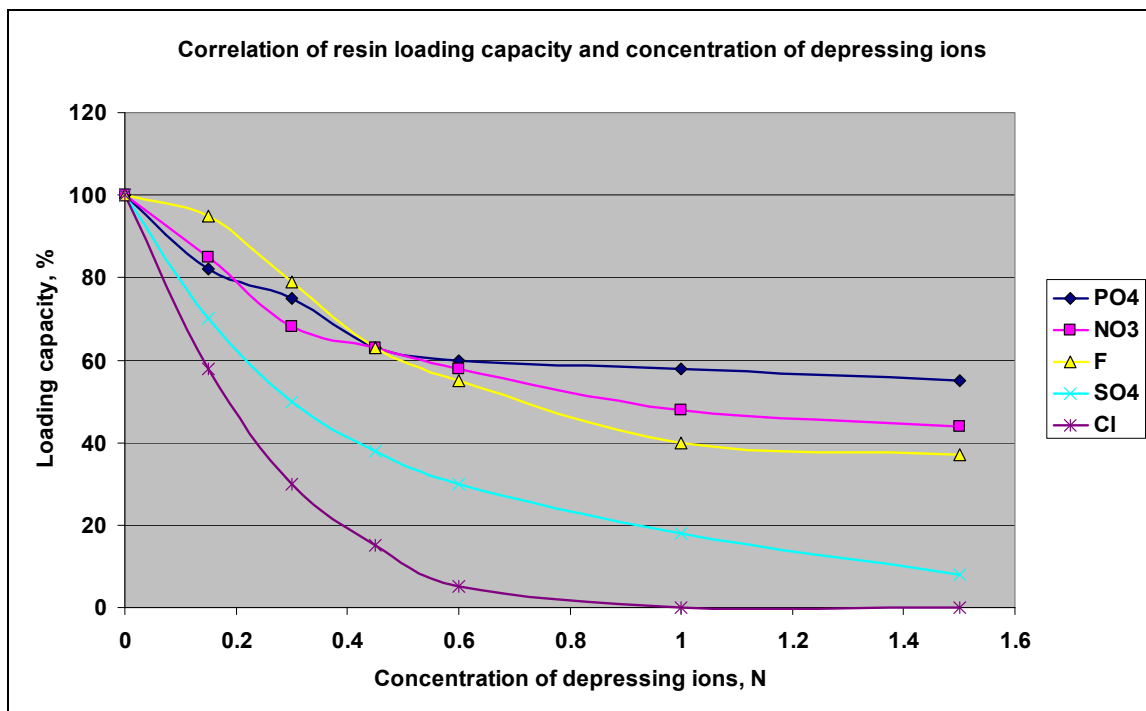
Figure 2. Correlation of uranium loading capacity and anions concentration

The uranium sorption depressing effect of some reagents is used in uranium desorption process. Nitric, hydrochloric and sulphuric acids are usually used for uranium desorption. Acidic nitrate solution is very effective for desorption, but for economical reasons a mix of sodium chloride and sulphuric acid is generally used.

Some substances have a very strong effect on the resin, to extent that the resin will be ultimately poisoned. Examples of these phenomena are:

1. Anions containing V^{5+} that are sorbed onto the resin cannot be desorbed with the commonly used desorption solutions. These compounds must be specifically washed from resin or the anionic V^{5+} must be transferred to the cationic V^{4+} form

2. Molybdate $[MoO_4]^{2-}$ ions are very strongly sorbed onto the resin and can be desorbed only using sodium hydroxide solution

3. Silica, present in solution as metasilicic acid or in colloidal form can be held very stably in resin pores as a result of silica sorption and coagulation. This colloid can only be removed by special treatment

4. Some leach solutions contain cyanide and thiocyanide ions. In this case poly-sulphide ions can be formed and elementary sulphur may be precipitated.

3.1.2. Uranium sorption by weak base anion exchangers

Weak base anion (WBA) exchangers containing primary, secondary and tertiary amino groups have good exchange properties when used in acid leach. These WBA exchangers are less dependant on the solution composition and more selective towards uranium.

An example of this effect is seen when comparing the loading capacity of the competing anionic complexes of uranium and iron at varying free acid concentrations. If the acidity of the leachate is increased from 10 g/L to 30 g/L, the uranium loading capacity of the WBA exchanger is not altered much, but the loading capacity for the iron complex is reduced by nearly six-fold (Figure 3).

**The correlation between loading capacity and sulphuric acid concentration**
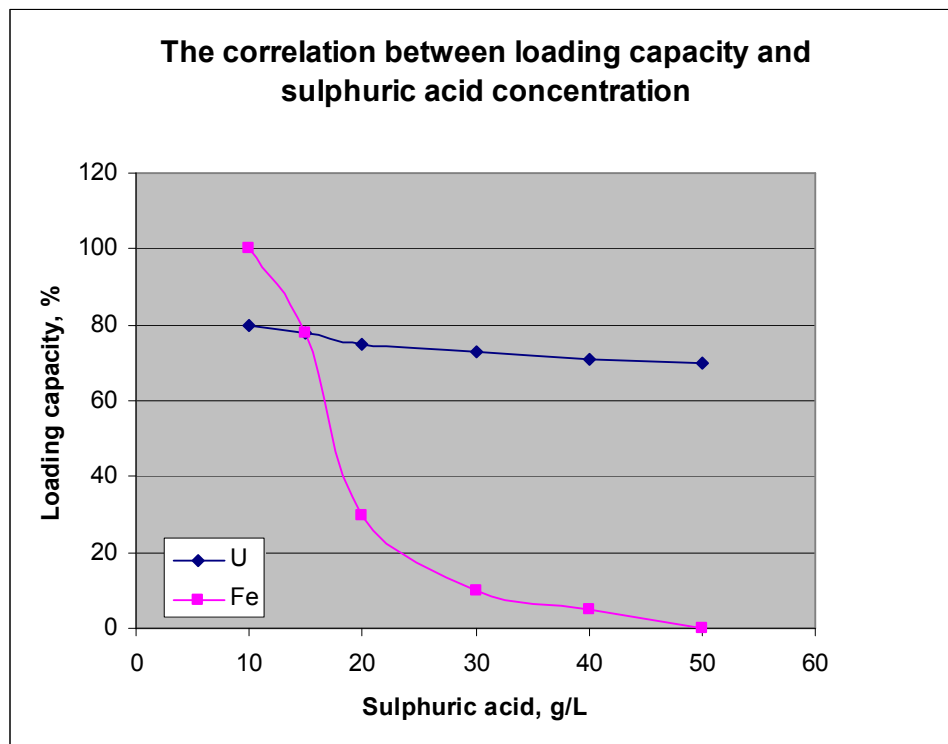
Figure 3. The correlation between loading capacity and sulphuric acid concentration

The solution composition has a weak influence on the sorption process. The washing of the loaded resin with 2% solution of sulphuric acid additionally removes iron from the loaded sorbent and increases resin selectivity to uranium. Impurities influence on sorption loading capacity for weak base anionits is a few times less then that for strong base anion exchangers. But strong base anionits only can be used for uranium recovery from carbonate solution. The presence of the carbonate, bicarbonate and sulphate ions, which may be formed during the oxidation of the sulphur substances under caustic conditions, influences negatively on uranium sorption.

3.2.   USE OF CATIONITS FOR URANIUM SORPTION FROM SULPHURIC ACID LEACHED SOLUTION

3.2.1.   Uranium sorption by strong acid cation exchangers

Strong acid cation (SAC) exchangers contain a sulphonic acid exchange group and generally have high affinity for uranium ions and good sorption and desorption kinetics with the equilibrium reached within 10 minutes.

$$2[RSO_3]^-H^+ + UO_2^{2+} \rightarrow [RSO_3]_2 UO_2 + 2 H^+$$
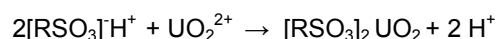
The resin loading capacity, at the same uranium concentration, increases as the pH of the solution is increased. The actual loading capacity may be higher than the theoretical full loading capacity because uranium is sorbed as polyions with structure $UO_2[OUO_2]n^{2+}$, where "n "varies from 0 to 1.2 depending on pH.

Uranium can be fully removed from the loaded resin using ammonium nitrate solution.

Strong acid cation exchangers are not used very often in the uranium industry because of they low selectivity. The selectivity coefficients in 0.5N sulphuric acid are: UO_2^{2+} - 30; Th^{4+} – 263; Mg^{2+}– 124; Fe^{3+} -255; Al – 540; Cu^{2+} - 128; Ce^{3+} - 1000.

3.2.2.   Uranium sorption by weak acid cation exchangers

Weak acid cation (WAC) exchangers contain carboxylic acid functional groups. The sorption is based on forming complex compounds between uranyl and carboxyl ions.

$$2[RCOO]^-H^+ + UO_2^{2+} \rightarrow [RCOO]_2 UO_2 + 2H^+$$

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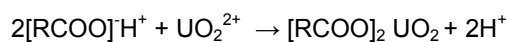
The loading capacity of weak acid cation exchangers is less dependent on the salt concentration in the leach solution than the strong acid cation exchangers (Figure 4).
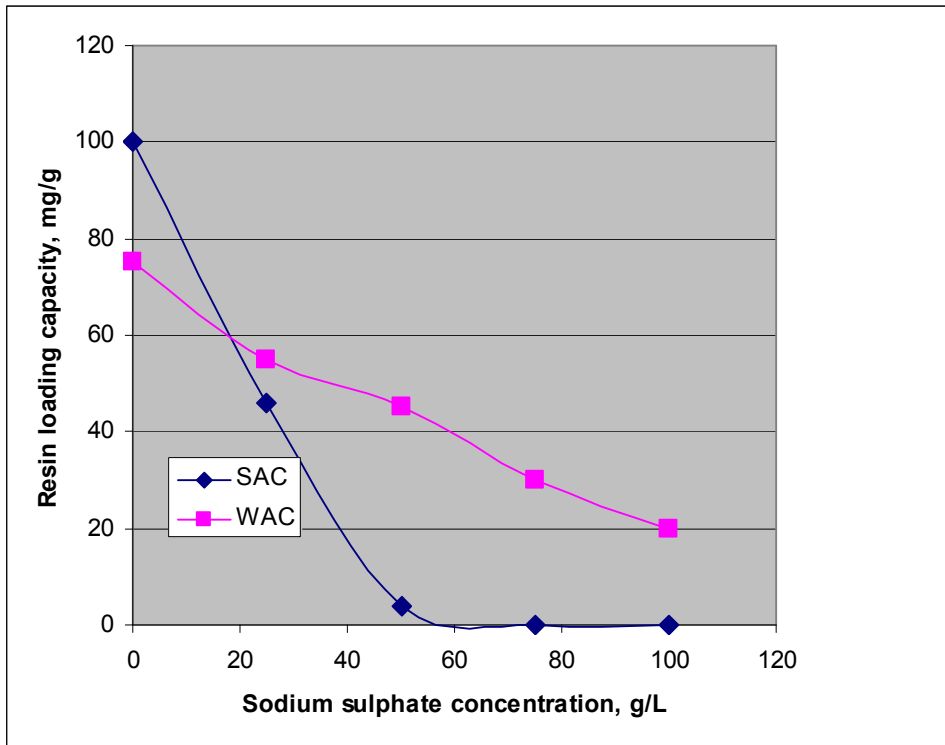
Figure 4. Correlation of uranium loading capacity and sodium sulphate concentration for strong and weak acid cation exchangers

The resin loading capacity for WAC exchangers is strongly correlated with pH of the solution. The WAC resin starts sorbing uranium only at a pH of 1.8-1.9. The loading capacity increases very quickly as the pH increases to a maximum at pH of 2.8 -3.5. The loading capacity results for some typical cations are shown in Graph 5.
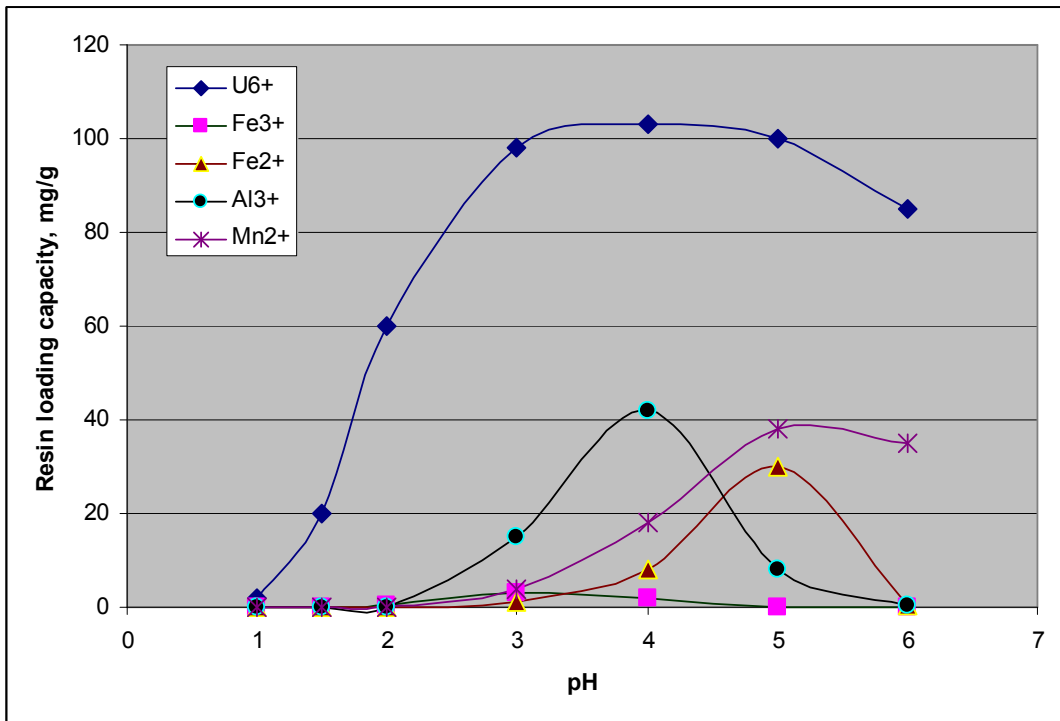
Figure 5. Influence of pH on loading capacity of weak acid cationits

Under a pH of 2.8-3.5, the WAC resin is characterized by good loading capacity and high selectivity for uranium. The acidic pH of the leachate is usually corrected by adding lime and under these rising pH conditions Fe^{3+}, Cu^{2+} and Mn^{4+} are precipitated as hydroxides with phosphorus, arsenic, antimony and other minor impurities being co-precipitated with iron hydroxide. At this pH the affinity of the resin to uranium is much higher than that to Al^{3+} so uranium replaces it on resin.

Nitrate and chloride ions do not have any influence on uranium sorption at concentrations up to 100 g/L.

Uranium is desorbed from the loaded resin using sulphuric acid solution with pH less than 1, and the desorption of the resin can be done with a small number of bed volumes. The desorption solution removes 95% of loaded uranium, and pure and concentrated pregnant solution is produced in this process.

The major disadvantage of using WAC exchangers for extraction of uranium from acid leachate is necessity of the pH correction step.

3.2.3.   Final comment on resin selection

The correct selection of the ion exchange resin for different types of the uranium ores can only be made after the determination of ore leaching conditions and an understanding of the leached solution composition.

4.   URANIUM SORPTION FROM ORE LEACHED PULPS

The highest effectiveness for uranium recovery from leached pulps is achieved under the following conditions:

- maximum uranium concentration in leached pulp
- minimum free acid concentration
- minimum impurities presence in liquid phase of the pulp

An essential distinction of direct uranium sorption from pulp is the additional uranium recovery from the solid phase of the pulp if the resin is added into the pulp during the leaching process, a process known as Resin-in-Leach (RIL).

This phenomenon is explained by an equilibrium shift between liquid and solid phases of the pulp by removal of the diffusion restriction of the leaching kinetics. The presence of the resin in the leach minimizes the negative influence of re-precipitation, co-precipitation, occlusion and sorption of uranium by the solid phase, and as a result the process uses less leaching chemical consumption, with a higher resin loading capacity, without the need for filtration. The sorption leaching effect is shown on the graphs below (Figure 6 and Figure 7).
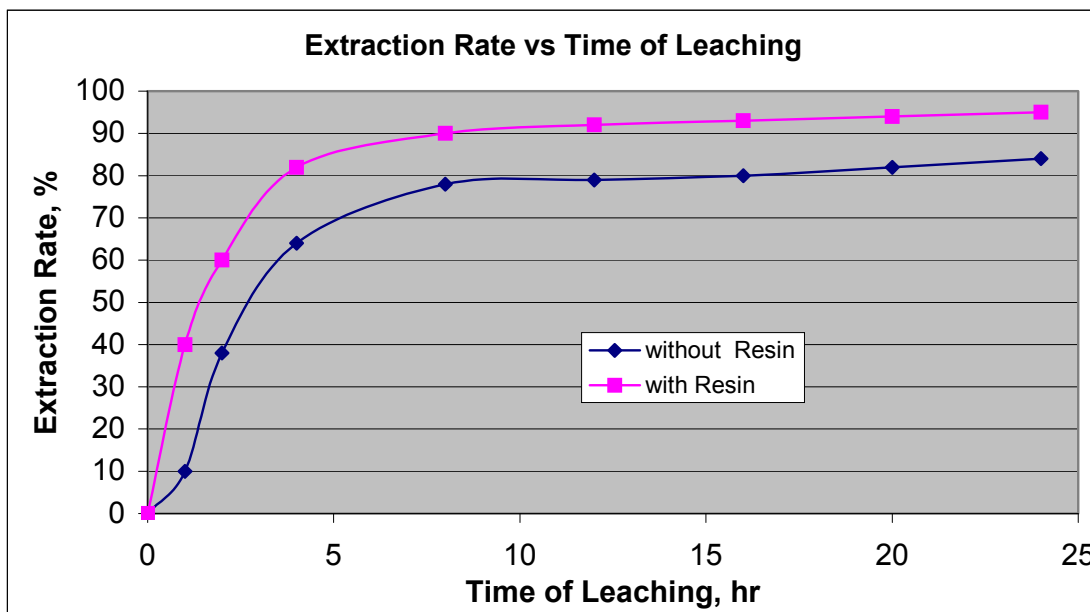

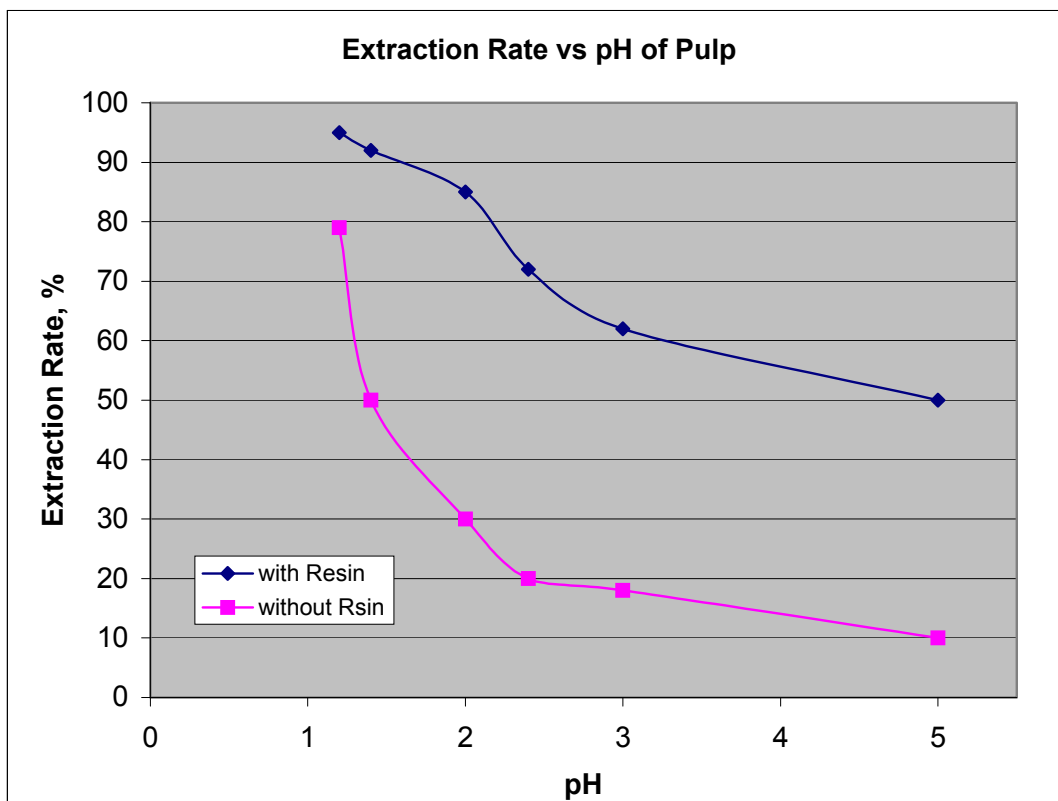
Figure 6. Extraction rate vs time of leaching

Figure 7 Extraction rate vs pH of pulp

The phenomena of sorption leaching effect was discovered and studied by the Russian scientist B N Laskorin in 1953, and since then has been in use in the Russian hydrometallurgical industry.

The potential advantages of the direct uranium sorption from ore pulps became clear a long time ago, but implementation of this process was linked to reluctance in accepting the process equipment design.

The most important characteristics of the uranium sorption process from both economical and technological points of view are:

- initial loading of the resin,

- resin consumption for 1 t of the processed ore,

- plant footprint,

- the eluate volume

- the eluate concentration and

- resin loading capacity.

It is clear that most of these parameters are related to the pulp volume produced from 1 t of the ore. It is therefore preferable to minimise pulp volume and to maximize the pulp density.
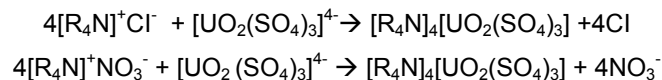
5. URANIUM RESIN-IN-PULP TECHNOLOGY

The most important operational parameters of industrial, continuous Resin-In-Pulp (cRIP) processes can be summarised as:

- Sorption time

- Number of sorption stages

- Pulp flow

- Resin flow

The process and equipment design for cRIP are based on these parameters which are interrelated and derived from fundamental physical/chemical laws of ion-exchange.

As stated previously, in acidic solution (pH<2) uranium is usually present as $[UO_2(SO_4)_3]^{4-}$ anionic complexes and the WBA or SBA anion exchanger sorbs uranium in this form. The reactions for the uranium ion exchange process for the sorption leaching process can be expressed as follows:

$$4[R_4N]^+Cl^- + [UO_2(SO_4)_3]^{4-} \rightarrow [R_4N]_4[UO_2(SO_4)_3] + 4Cl$$

$$4[R_4N]^+NO_3^- + [UO_2(SO_4)_3]^{4-} \rightarrow [R_4N]_4[UO_2(SO_4)_3] + 4NO_3^-$$

In this process, the most important parameter is the contact time between the pulp and resin. The contact time is controlled by varying the pulp residence time in sorption and the resin cycle rate. During the sorption process, as the concentration of the uranium in the liquid phase reduces, an additional amount of the uranium is leached from the solid phase into the liquid phase.

The residence time of the pulp is typically limited by the minimum required mixing duration with a single reactor. In industrial scale processes, this mixing time should not be less than 30 min.

The volume of the sorption circuit is dependent on the residence time of the pulp and the pulp flow rate, which can be expressed using the following equation:

$$Q_v = \tau_p \times q_p$$

Eq. 1

Where, Q_v is the volume of the sorption circuit, m3

τ_p is the mixing duration of the pulp, hr

q_p is pulp flow rate, m3/hr

In terms of a uranium mass balance, the resin cycle rate and the pulp flow rate can be related using the following equation:

$$q_p(C_i - C_o) = q_r(a_i - a_o)$$

Eq. 2

Where, q_r is resin cycle rate, m3/hr

a_i is the actual loading capacity of the resin, g/L

a_o is the loading capacity of the resin after desorption, g/L

C_i is the liquid phase uranium concentration of the feed pulp, g/L

C_o is the liquid phase uranium concentration of the barren pulp, g/L

Assuming that the resin absorbs all of the uranium, the equation above can be rearranged to give the resin circulation rate:

$$q_r = \frac{q_p(C_i - C_o)}{(a_i - a_o)}$$

Eq.3

In practice, the resin circulation rate is 10% higher than the theoretical value, particularly if two processes take place at the same time, i.e. sorption of the target species from the liquid phase of the pulp and sorption leaching from the solid phase.

Example 1 - Sorption process resin flow calculation

Given; - the pulp flow, q_p is 400 m^3/hr. (~50% solids; ~300 m3/hr liquor)

- resin loading capacity, a_i is 15 g/L

- desorbed resin loading capacity, a_o is 0.1 g/L

- liquid phase uranium concentration in the feed pulp, C_i is 0.05 g/L

- liquid phase uranium concentration in the barren pulp, C_o is <0.005 g/L

Using equation 3 from above, the theoretical resin circulation rate is:

$$q_r = \frac{q_p(C_i - C_o)}{(a_i - a_o)} = \frac{300(0.05 - 0.005)}{(15 - 0.1)} = 0.91 \, \text{m}^3/\text{hr}$$

The practical resin circulation rate will be 10% larger than theoretical resin flow, and should therefore be set at 1.0 m^3/hr.

The volume of the resin in the sorption circuit can be expressed in terms of the sorption cycle time:

$$Q_r = \tau_r \times q_r$$

Eq 4

Where, Q_r is the volume of resin, m3

τ_r is sorption cycle time, hr

In practice, the sorption cycle time is measured as time taken for the resin fed into the last Pachuca to exit as loaded resin from the first Pachuca. Similarly, the initial volume of the resin is typically expressed as a volume percentage of the total resin volume in the sorption Pachucas to the pulp volume into all Pachucas:

$$r_i = \sum_{1}^{N} \frac{Q_r}{Q_v} \times 100$$

Eq 5

Where r_i is the initial resin volume, %

Q_r is the total volume of resin, m3

Q_v is the total volume of pulp, m3

N is the total number of Pachucas

The efficiency of the sorption process depends primarily on the number of sorption stages and the transfer kinetics of the resin. The cRIP sorption process is carried out using a counter-current cascade of consecutively linked reactors. This counter-current cascade arrangement ensures maximum recovery of the target species from the pulp and provides a much greater efficiency than a single stage.

The number of theoretical sorption stages is calculated using a graphical method, similar to a McCabe-Thiele diagram (see figure below). The sorption isotherm, typically based on laboratory trials, is drawn as a correlation between resin loading capacity and equilibrium concentration of target species in the liquid phase of the pulp. The operating line (mass balance line) is drawn below the equilibrium curve and the sorption stages are stepped off between these two lines. The number of vertical lines on this graph represents the number of theoretical sorption stages (N^*_r).

In order to reach the equilibrium loading capacity (a^*_R), these theoretical sorption stages assume very long resin-pulp contact times. As this would not be practically feasible, a working loading capacity ($a_R = 0.8\ a^*_R$) is used for the operating line. Alternatively, the minimum number of process sorption stages or Pachucas in a real cascade (N_{min}) is 1.25 times the theoretical number (N^*).

The sorption effectiveness of every single sorption stage increases as the width of the gap between the equilibrium curve and the operating line increases. In other words, fewer sorption stages are required as the operating line shifts further away from the equilibrium curve (Figure 8).
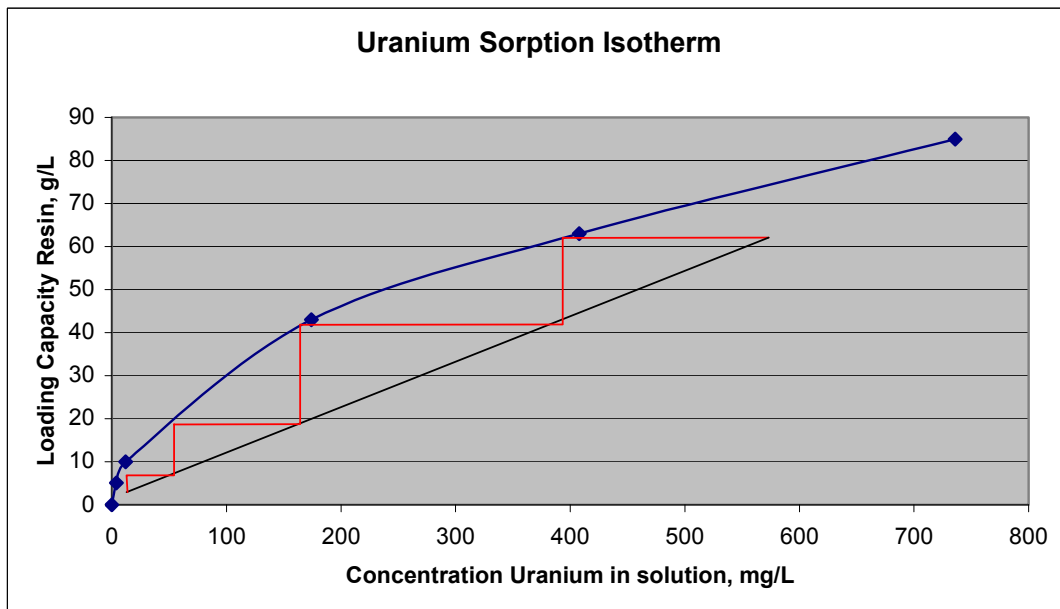

Figure 8. Uranium sorption isotherm

Once a plant is in operation, the volume of the sorption reactor can not be changed. Using the above equations, the contact time of the sorption leaching can only be regulated by changing the feed pulp flow rate or resin circulation rate. If the concentration of uranium in the liquid phase changes, either the pulp flow rate can be reduced or conversely the resin circulation rate can be increased to optimize the changed process.

For each resin particle, the time spent in a reactor will vary according to the probability of its transfer out of the reactor. This probability can be described by the following equation:

$$\alpha_r = 1 - \exp\left(\frac{q_r \tau_r}{Q_v}\right)$$

Eq. 6

Where α_r is the probability of a resin particle transfer

A percentage of resin particles will have insufficient contact time in the reactor to reach equilibrium before being transferred to the next reactor, so these resin particles will not have reached the equilibrium loading capacity.   Similarly, a percentage of resin particles will remain longer in the reactor than is necessary to reach equilibrium; these resin particles will have reached equilibrium and are not able to exceed this maximum loading capacity.

Due to this probability distribution, the average loaded resin concentration will be less than the theoretical loading capacity. To compensate for this, the contact time is typically increased beyond the theoretical, which typically results in an increase of the reactor volumes and total volume of resin in the system.

In practice, the contact time for all resin particles is standardized using a series of reactors. Each reactor has a theoretical mixing efficiency of ~ 70%; therefore the use of three reactors will provide 97% mixing efficiency calculated as follows:

Efficiency = 100% - (30%x30%x30%) = 100% - 2.7% = 97.3%

After calculation of the number of reactors, the volume of each reactor and the resin rate must be estimated. The time for the pulp in each reactor is limited by the required mixing duration. The volume of each individual Pachuca can then be optimized using the necessary residence time for resin-pulp contact.

6.   RESIN DESORPTION & REGENERATION

The desorption process removes the majority of the uranium that has been loaded onto the resin. The desorption process may regenerate the resin to the active sorption form or a separate regeneration step may be required. There are cases where either of the above are used in practice. For example, uranium is able to be removed from a sulphuric acid leached solution or pulp and the loaded resin is desorbed using sulphuric acid solution. But often the resin after desorption has to be regenerated to the active ionic form.

During the desorption process the concentration of sorbed components on the resin is gradually decreased until an equilibrium concentration of uranium on the resin is reached. This concentration must be low enough so as not to reduce the loading capacity of the ion exchanger in the next cycle. This concentration is named the residual loading capacity of the resin, and it should not be higher than 20% of the equilibrium loading capacity of the resin in the last reactor. Additionally, the residual acid from desorption that remains on the resin must also be low enough, so when contacted with the pulp, it does not increase the free acid concentration of the leach, a condition that may decrease the resin's uranium loading capacity.

6.1.   URANIUM DESORPTION TYPE 1

The first type of desorption is where the uranium is removed from the loaded resin by the same component as the leach. For example, uranium sorbed onto a WBA ion exchanger in the presence of a weak sulphuric acid is able to be eluted using a higher concentration of sulphuric acid. In this case, the eluted resin is regenerated to the SO_4^{2-} - form which is then used after a washing step for uranium sorption.

Normally 2–3N (10-15%) sulphuric acid solution is used for uranium elution from SBA exchangers, as the affinity coefficient is less then 1.

The kinetics of desorption of uranium elution from SBA exchangers varies at ambient temperature from 24 hr to 40 hr depending on resin type.

Temperature has a strong influence on desorption and so at a temperature of ~60^{0}C, the desorption time is halved.

6.2. URANIUM DESORPTION TYPE 2

Another type of desorption is where the uranium is replaced by the ions which have higher affinity for the resin. In this process the resin is transferred to desorption ions form and needs a special washing to move into working ionic form, which is acceptable for valuable component sorption

This method is widely used in the uranium industry, when uranyl sulphate complexes are exchanged and desorbed from the resin by either nitrate or chloride ions. In this case a solution containing 0.9 M NaCl and 0.1 M HCl is used. This process usually takes between 12 – 15 hours at ambient temperature.

The effectiveness of this process is dependant on the ionization potential of the salt that supplies the chloride ions. The best efficiency is obtained when ammonium chloride is used as desorption reagent. Sodium and magnesium chloride have typically 1.5 – 2 times lower efficiency.

The same results are achieved for nitrate desorption reagent, but because the affinity of nitrate ions to strong base anion exchangers is higher then that of chloride ion, a less concentrated solution should be used for uranium desorption. The volume of the eluate is smaller then that for chloride desorption.

6.3. URANIUM DESORPTION TYPE 3

The sorbed uranyl sulphate complex can be transferred to a chloride or nitrate complex by contacting the anion exchanger with 6 – 10% chloride or nitrate solutions with the weakly held chloride or nitrate complex being washed from the resin by water only.

For example, the uranyl sulphate complex is converted to the uranyl chloride complex by contact with a concentrated (10%) sodium chloride solution. The uranyl chloride complex is then readily desorbed using water to produce an eluent containing up to 60 g/l of uranium. During the transformation of the complex some uranium is desorbed. Generally this eluent is then returned to the process for subsequent retreatment.

This desorption method also provides an additional separation step to allow the separation of impurities that have been jointly sorbed with uranium such as Fe^{3+}, PO_4^{3-}, SO_4^{2-} ions.

The nitrate conversion of uranyl sulphate complex is similar but has the added advantage that the 6-8 M solution used for desorption does not desorb any uranium during the complex transformation.

7. EQUIPMENT DESIGN FOR URANIUM SORPTION FROM ORE LEACHED PULPS

According to the sorption isotherm, uranium recovery may be reached by shifting the equilibrium of the ion-exchange reaction to exchange resin counter-ions for metal ions from the liquid phase of the pulp. Reaction driving forces of the sorption process shift to achieve equilibrium. It is the difference between the target metal concentrations in the liquid phase relative to that of the resin. To achieve a maximum equilibrium driving force, the resin and pulp are cycled counter-currently.

The most suitable sorption reactor is the air mixed Pachuca. The Pachuca has a purpose-built separation device to allow resin and pulp to be continuously separated across a series of screens. The mass rate of the pulp through this type of ion-exchange equipment is mainly limited by the flux rates of the screening system. The screening rate depends on

- pulp particles size and
- physical properties of the ore

Screening rates in operating plants vary from 25 to 100 m^3/m^2/hr.

The sorption Pachuca comprises a mixing section, separation section, airlifts, and inlet and outlet pipes for transfer of pulp and resin and drainage section (Figure 9).
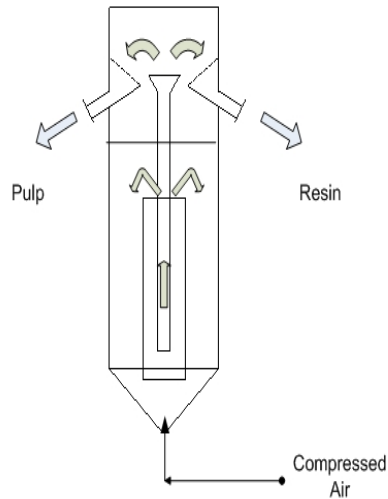
Figure 9. Sketch of the Pachuca

The Pachuca is shaped like a vertical cylindrical vessel with a conical bottom. Typically, access hatches and drain valves are located in the conical base to allow for maintenance works.

The diameter to liquid level height ratio of a Pachuca is typically 1:2 to 5.

Compressed air is used for mixing the resin and pulp within the vessel and for transporting the resin and pulp to the screening section. The air mixer runs continuously, agitating the pulp and resin in an axial motion. This type of mixing provides very efficient, non-destructive pulp and resin mixing in each Pachuca.

The airlift uses compressed air on a pulsing cycle to lift the resin and pulp up the inner airlift pipe and out into the screening section of the Pachuca. The pulp is separated from the resin by directing the airlifted resin and pulp over a distribution plate which then drains over an inclined screen. The distribution plate protects the drainage screen from excessive wear. With certain types of pulp that contain large amounts of particles with a size >0.16mm or high viscosity pulps, the screens may be prone to blockage. Under these operating conditions, the distribution plate may need to be removed and the pulp/resin mixture airlifted directly onto the separation screen. This type of operation causes the screen to vibrate, which in turn keeps the screen from blocking. The pulp cascades through the series of Pachucas using the hydraulic lift that the airlifts provide via interconnected pipe work.

The screened pulp travels to the next Pachuca. and the screened resin either returns to the mixing section of the Pachuca or is side streamed via an internally adjusted channel to the previous Pachuca. The angle of the channel regulates the amount of resin transferred between the Pachucas; when the channel is fully raised, all the resin is returned to the same Pachuca.

The screens require maintenance and are designed to be changed without taking the Pachuca off line. The screen typically consists of a metal frame with a tensioned stainless steel mesh. A mechanism for adjusting the tension of the screen is normally in the design to further reduce the likelihood of screen blockages.

The cRIP and cRIL process for the extraction of uranium from leached pulps using the air operated Pachuca is a good method for the treatment of slurries containing up to 60% solids having a particle size of less than 0.075 mm. The method also allows for an inclusion of 3-5% of particles with size +0.15 mm. The volume of the Pachuca in practice can be up to 500m^3. Higher volumes are quite possible as the cRIP technology becomes more accepted in the next few years.

The high productivity of the Pachuca allows the operator to minimise the number of process trains. The Pachuca itself does not have any moving parts and operates in a stable fashion over long time periods.

The airlift Pachuca provides the most cost effective method of extracting uranium from acid leached pulps. The process provides maximum uranium recovery and minimum resin attrition.

8. EQUIPMENT DESIGN FOR URANIUM SORPTION FROM SOLUTION

The continuous resin process consists of a number of unit processes. Each individual process has its own unique design parameters and resin circulates continuously through the complete process (Figure 10).
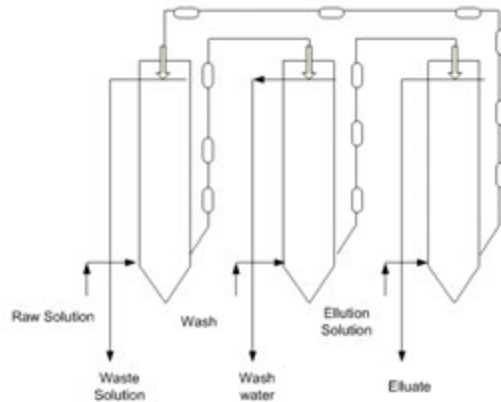
Figure 10. Sketch of the continuous counter current sorption process

In processes operating in a continuous mode, both the resin and liquid phases are transported continuously within the unit process and the resin between the processes.

In a continuous resin process all the resin participates in the absorption process. This is the most important distinction of continuous processes from those processes operating in batch mode.

The figure below illustrates the batch system:

- the layer of fresh resin (1)
- the layer of working resin (2)
- the layer of fully loaded resin (3)

Generally, layers 1 and 3 have larger volumes than layer 2. The resin inventory in the continuous process is between 2 -15 times less than that required if operating in batch mode (Figure 11).
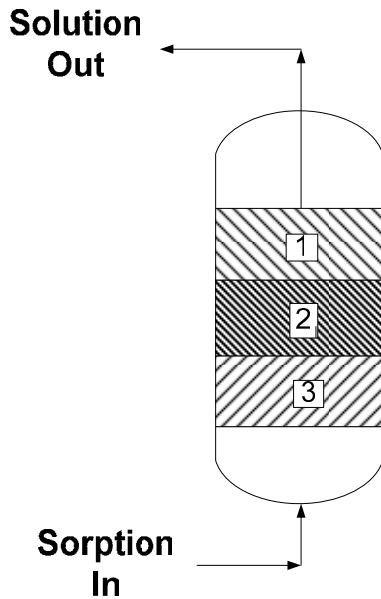
Figure 11. The sketch of the sorption batch process

Usually the continuous processes are operated in counter-current mode. The counter-current movement of resin and solution phases provides high concentration gradients that decrease by 2 -5 times the necessary contact time; maximize the loading of the resin and increases absorption effect.

The counter-current continuous operating mode also provides a stabilizing effect on the concentration of the uranium in the treated and elution solutions. The overall effect is a more effective use of the resin loading capacity and desorption reagents and a reduction in capital and operating costs.

Another important advantage of the counter-current sorption process is the design of the equipment that allows for varying specific volume of the resin in the various forms. The process operates at atmospheric pressure and there are no constrictions placed on the resin volume within a process. In comparison, the batch mode generally operates in a constricted vessel that limits the capacity of the resin to swell. In some instances, resin swelling can cause dramatic increases in pressure and vessel rupture.

Semi-continuous moving bed columns are widely used in the uranium industry. In this system, the resin and solution are moving through the column counter currently, with the resin moving from the top of the column to the bottom, and solution from the bottom to the top. These columns have a drainage system through which treated solution exits from the column located below the top of the resin layer, so a layer of dewatered resin is permanently present in the column. The resin layer becomes firmer because of the mass of the dewatered resin layer.

Transportation by water or airlifts is usually used for transferring the treated resin to the next process. Water transport uses liquid pressure to transfer the resin suspended in either water or feed solution. The resin transfer chamber is sealed from the column during resin transportation, and the pressure in the column must be regulated carefully or the integrity of the resin column will be interrupted severely.

The air lift transportation allows significant reductions the quantity of liquid that is transported with the resin. The air lift operation is simple, with the solution flow being stopped for short times as needed while the air lift operates by injection of compressed air for the resin transfer.

9. URANIUM DESORPTION / CONCENTRATION PROCESS

The loaded resin from the Pachuca circuit needs to be desorbed to recover the uranium. The resin is firstly passed though a rotary drum screen and then a wash circuit to remove any adhering pulp which may contaminate the final desorption liquor.

A specially designed desorption concentration column is used to desorb the uranium from the resin. The column is U shaped in configuration with resin entering at one end and desorption solution entering the other end. The resin progresses counter currently against the desorption solution as the two move around the column. Fully desorbed resin is removed from the opposing end of the U column and two liquor streams exit the column.

The first liquid stream, containing the concentrated uranium, exits at the base of the U column. This pregnant liquor can contain a very high concentration of the uranium, typically 10 - 60 g/L.

At the top of the U column, on the side where the pregnant resin enters the column, a waste liquor stream is produced that contains the impurities from the resin including such ions as iron and sulphate. The stream also has a small concentration of uranium which is recovered by recycling this stream back to the front end of the process.

The relative flow proportions between the uranium concentrate and waste stream are dependent upon the desired concentration of uranium required in the pregnant liquor and the concentration of the impurities (Figure 12).
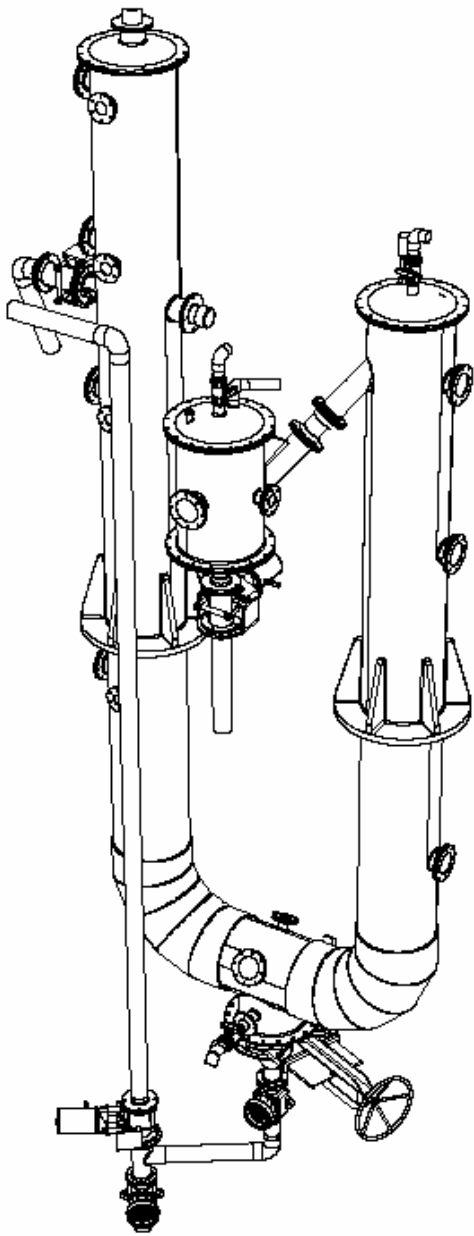

Figure 12. Sketch of desorption column

The key advantage of this type of column design is the ability to concentrate the uranium in the pregnant liquor stream while at the same time increasing the relative purity of the pregnant liquor. This is achieved by the desorption process within the U column acting as two integrated process steps.

Where the desorption solution enters the U column, only desorption by the acidic solution takes place. As desorption proceeds, an increasing uranium concentration gradient exists between the metal species loaded onto the resin, and the concentration of metal species in solution.

At a point, normally beyond the bottom extraction point, there is re-adsorption of uranium back onto the resin. This in effect allows the uranium to be carried further back up the column and effectively concentrates the uranium onto the resin. This consequentially concentrates the uranium in the desorption liquor until it is extracted from the bottom discharge point.

This system takes advantage of the high loading capacity characteristics of the uranium onto the resin. As the concentration of the metal species in the liquid phase increases, the loading capacity of the resin also increases. This in turn allows a desorption liquor concentration much higher than the initial loading capacity. In addition, the increased adsorption is at the expense of impurities present in the resin which are desorbed and displaced into the waste stream.

In terms of designing the U column, the volume capacity of the column is a function of the resin cycle rate which in turn is governed by the Pachuca sorption circuit and the required desorption residence time. These parameters are typically established by bench trials.

$$Q_U = \frac{q_r}{\tau_d}$$

Eq. 7

Where Q_U is the volume of desorption column, m3

q_r is resin flow rate, m3/hr

τ_r is the desorption time of the resin, hr

The desorption solution to resin ratio, and the split between pregnant liquor and waste desorption liquor, are determined during laboratory trials and adjusted during commissioning.

After desorption, the resin is washed with water and returned to the sorption (column or RIP) process. Water used in the wash circuit is recycled for dilution of the working desorption solution (10%) from the concentrated acid (98% or 70%).

10. CONCLUSION

Continuous counter-current sorption is an economically and technologically a very effective process for producing high quality uranium.

Advantages of continuous sorption processes:

High rate of uranium concentration, for example from 0.1 g/L to 15 -30 g/L, even to 30 – 60 g/L.

High selectivity of uranium recovery allows the production of rich and pure uranium concentrates.

Uranium is recovered directly from leached pulps with significant technological and economic efficiencies.

The method includes fewer technological stages.

The continuous sorption process is effective for uranium recovery even from poor and clayey ores.

11. ACKNOWLEDGEMENT

12. REFERENCES

1. Gromov, B.V. Introduction into Technology of Uranium, M.Atomizdat, (1978).

2. Uranium Mining In-Situ Leaching (V.A.Mamilov, Ed.), M.Atomizdat (1980).

3. Zakharov, E.L., Rjabchikov, B.E., Djakov, V.S., Ion-Exchange Equipment in Atomic Industries, Energoatomizdat (1987).

4. Zefirov, A.P., Laskorin, B.N., Nevski, B.V. Present State in Technology of Uranium Ores Processing, M.Atomnaja Energija 11 2 (1961).

5. Zontov, N. WO2004098776. Method and Apparatus for Desorbing Material.