2011 THE CLEAN TEQ U-HISAL™ PROCESS: EXTRACTION OF URANIUM FROM ACIDIC SALINE ENVIRONMENTS

By

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ABSTRACT

The U-HiSAL™ process extracts uranium from acidic saline solutions.

The past few years has seen a renaissance in uranium mining as the demand for nuclear power has increased. New mines have been developed to meet this demand; however the scarcity of fresh water means many uranium mines are having to source saline or hyper-saline water for the processing plants. Use of saline water (greater than 3g/L Cl) significantly reduces the performance of conventional uranium ion exchange and solvent extraction processes.

Currently, large-scale desalination plants producing potable water are being considered to allow the use of conventional ion exchange and solvent extraction processes. These desalination plants have exceptionally high capital (>$20M) and high operating costs (>$1/m^3).

Clean TeQ has developed the U-HiSAL™ process for extraction of uranium in acidic saline environments. The U-HiSAL™ process extracts 99% uranium in acidic saline solutions and slurries containing in excess of 20g/L Cl without the requirement for potable water. The U-HiSAL™ process is easily integrated with commercially available product recovery systems. Existing and future uranium plants without access to high quality water have the potential to significantly reduce their capital and operating costs using the U-HiSAL™ process.

INTRODUCTION

In the past five years there has been a significant increase in the demand of uranium for base load power generation, with new mines developed to meet this demand. Conventional processing requires leaching uranium bearing minerals in sulphuric acid or sodium carbonate under oxidising conditions to liberate the uranium as a soluble uranyl sulphate or uranyl carbonate complex.

For both in-situ leaching (ISL) and heap leaching, ion exchange (IX) is normally used to recover and concentrate uranium from solution. Solvent extraction (SX) can be used for recovery of uranium from ISL liquors. However, due to the low uranium concentration in solution it is normally proven to be uneconomical. In arid regions, the ground water is normally very saline and uranium recovery using IX is not possible. Therefore desalination water treatment or SX is required to allow mines to operate. In countries such as Namibia there are vast amounts of low grade uranium ore amenable to heap leaching. Large desalination plants have been built and more are proposed to exploit these deposits.

Hard rock uranium ore bodies usually use SX, IX or precipitation to recover uranium in solution. If high chloride levels are present in solution (either originating from the ore, chloride oxidant addition or water used in the process) then IX cannot be used. At elevated chloride levels only SX or direct precipitation has been available as a technically feasible option. Resin-in-Pulp (RIP) can also be employed where the resin is contacted directly with the leach discharge pulp, avoiding the requirement of a CCD wash circuit. Again RIP is only applicable when chloride concentrations are maintained below 3 g/L in the leach pulp.

The Present State of Uranium Extraction in High Saline Environments

Strong base anionic (SBA) resins have been widely adopted as the conventional approach for extraction of uranium from an acidic or alkaline PLS or pulp. An SBA resin has a quaternary amine functional group and chemically adsorbs uranyl sulphate or uranyl carbonate anionic complexes by electrostatic forces. Chloride is also a strong anion and when present in high concentrations it competes with the uranyl complexes. As the chloride concentration increases, loading of uranium onto SBA resins decreases. SBA resins preferentially load chloride. Once the chloride concentration typically exceeds 3.5 g/L, the loading capacity of the resin is significantly impacted.

For example, a strong base anionic (SBA) resin (Dowex 21K) has an equilibrium loading of 20 g U_3O_8/L_{wsr} loading when contacted with a solution containing 150 ppm U_3O_8 and 3.5 g/L chloride at pH 1.8. This loading decreases to 7 g U_3O_8/L_{wsr} at 7.5 g/L chloride and 4.3 g U_3O_8/L_{wsr} at 8.3g/L chloride (La Brooy, Spatford, & Middlin, 2009).

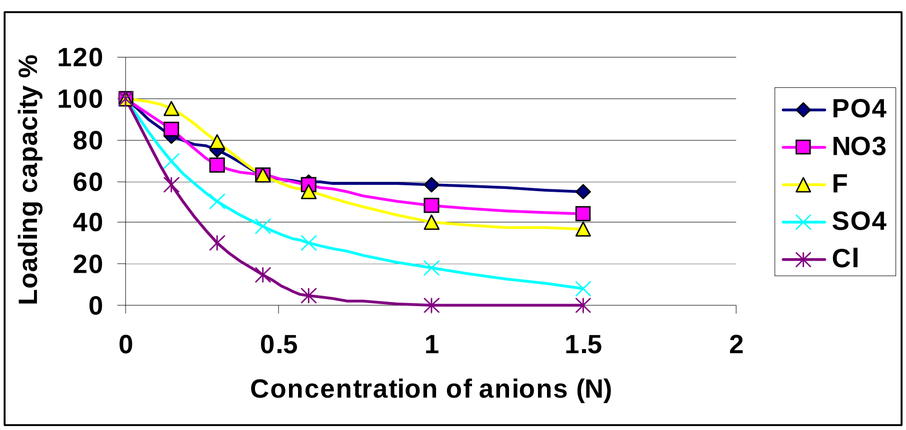


Figure 1: Effect of increasing concentration of anions on SBA resin loading (Zontov, 2006)

Weak base anionic (WBA) resins containing secondary and/or tertiary amine groups are used when high sulphuric acid concentrations are present after leaching. WBA resins are also susceptible to low loadings when high chloride concentrations are present in solution.

Currently, large-scale desalination plants producing potable water are being considered to allow the use of conventional IX and SX processes in saline environments. These desalination plants have exceptionally high capital (>$20M) and high operating costs (>$1/$m^3$).

Clean TeQ has developed the U-HiSAL™ process for extraction of uranium in acidic saline environments. The U-HiSAL™ process extracts 99% uranium in acidic saline solutions and slurries containing in excess of 20 g/L Cl without the requirement for potable water. The U-HiSAL™ process is easily integrated with commercially available product recovery systems. Existing and future uranium plants without access to high quality water have the potential to significantly reduce their capital and operating costs using the U-HiSAL™ process.

U-HiSAL™ PROCESS OVERVIEW

The U-HiSAL™ process flow sheet is analogous to typical IX process routes for uranium extraction. The process is applicable for both slurry and solution applications. The U-HiSAL™ process uses Clean TeQ's R-603 series resin, containing an amphoteric functional group.

Sodium Carbonate/Bicarbonate Process

Figure 2 shows a typical example of the U-HiSAL™ process with sodium carbonate/bicarbonate elution followed by final product precipitation.

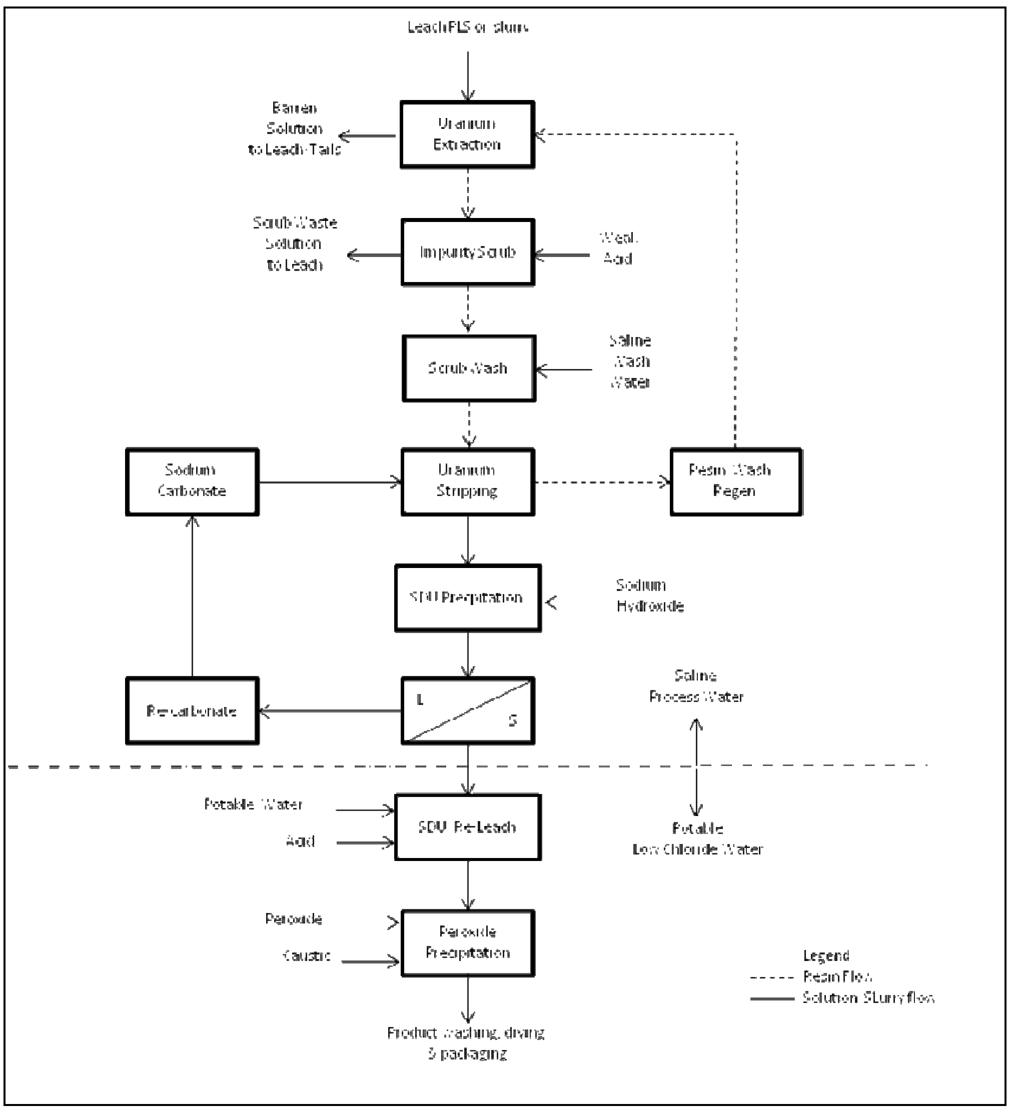


Figure 2: Clean TeQ U-HiSAL™ process using sodium carbonate/bicarbonate as eluant

An acidic saline pregnant leach solution containing soluble uranium is contacted with Clean TeQ's R-603 series amphoteric resin to selectively extract uranium from solution. Conditions are controlled to ensure the saline barren solution or slurry contains less than 5-10ppm U_3O_8 before it is recycled to the comminution or leach circuit as process water.

Prior to stripping and scrubbing, the resin is washed to remove any solid particulates on the resin from the extraction stage. Some minor impurities (such as iron, vanadium, zirconium or thorium) may also co-load onto the resin. These can be scrubbed by contacting the loaded resin with a solution of weak sulphuric acid or sulphurous acid (for iron removal). Dilute sulphuric acid will remove minimal uranium from the resin. The scrub step is optional depending on the amount of impurities present. After scrubbing, the resin is typically washed with saline water to remove any entrained scrub solution. The spent scrub solution is normally sent to leach, as it can contain acid and a small amount of uranium.

Loaded resin is then stripped with sodium carbonate or sodium bicarbonate to generate a uranyl carbonate product solution. After stripping, the barren resin is washed with saline water to recover any entrained sodium carbonate/bicarbonate. The resulting weak sodium carbonate solution is recycled as make-up solution for stripping.

The product solution containing uranyl carbonate is precipitated with sodium hydroxide to form sodium diuranate (SDU). This point in the flow sheet provides the segregation between saline and low chloride water within the circuit. The resulting SDU precipitate is filtered and washed with potable water. The SDU filtrate is carbonated to allow sodium carbonate to be regenerated for uranium stripping.

SDU precipitate is repulped in low chloride water and dissolved in sulphuric acid. The resulting uranyl sulphate is precipitated with hydrogen peroxide to form uranyl peroxide product, with sodium hydroxide used to maintain pH at the optimum peroxide precipitation conditions. Final uranyl peroxide product is thickened, filtered and dried.

SDU and peroxide precipitation methods are widely used within the uranium industry. Because sodium carbonate from SDU precipitation can be recycled within the process, the benefit of the U-HiSAL™ process is the significant reduction of the reagent costs associated with uranium elution and recovery.

Ammonium Carbonate/Bicarbonate Process

A combination of ammonium carbonate/ammonium bicarbonate can also be used as eluants in an Ammonium Uranyl Tricarbonate (AUT) system. The process up to scrubbing is the same as in the sodium carbonate flow sheet. Once the major impurities have been scrubbed from the loaded resin, the resin is washed with low chloride water to ensure no chlorides are entrained. This point in the flow sheet provides the segregation between saline and low chloride within the circuit.

The resin is then stripped with an ammonium bicarbonate and ammonium carbonate mixture. This produces an ammonium uranyl tricarbonate product solution.

Following stripping, the ammonium uranyl tricarbonate solution is heated with steam to precipitate ammonium diuranate (ADU). This process generates ammonia and carbon dioxide gas (Milbourne, 2008), which is recovered (via a packed bed scrubber) and recycled to stripping. The barren ADU solution is also recycled to elution after solid-liquid separation.

The ADU is calcined to produce final yellowcake product. Ammonia generated from the calcined off-gas is scrubbed and returned to IX stripping make-up.

Figure 3 shows a typical example of the U-HiSAL™ process with ammonium carbonate/bicarbonate elution followed by final product precipitation.

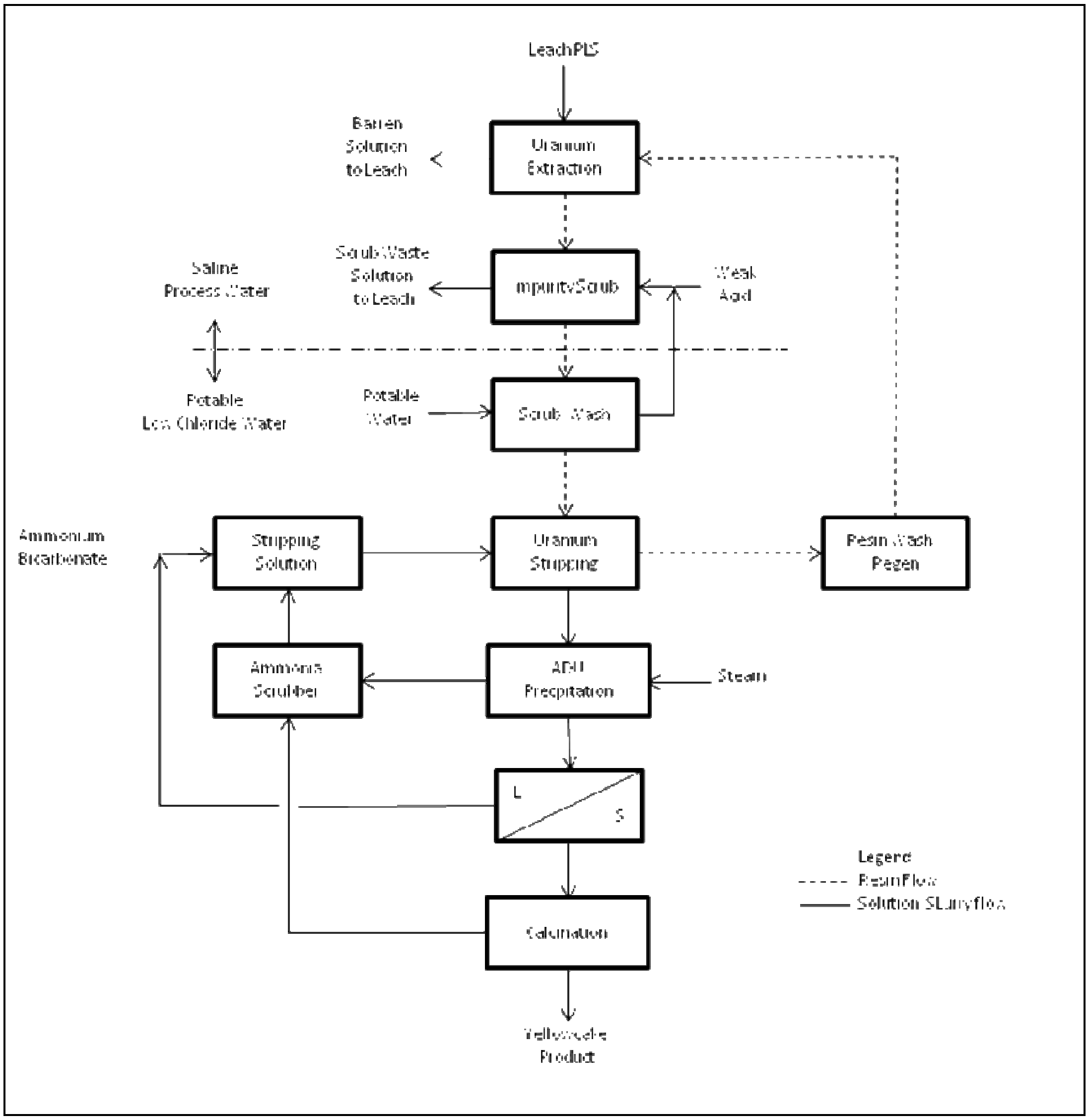


Figure 3: Clean TeQ U-HiSAL™ process using ammonium carbonate/bicarbonate as eluant

The ammonium bicarbonate/carbonate process route is another economically viable product recovery route for the U-HiSAL™ process. ADU precipitation is also used widely in the uranium industry. The majority of the ammonia carbonate is recovered and recycled from ADU precipitation and calcining off-gas, reducing reagent consumption. With proper operation and controls, the AUT product can meet full nuclear grade specifications (International Atomic Energy Agency, 1993).

RESULTS TO DATE

Clean TeQ has performed preliminary uranium loading and elution testwork for the UraniumSA Mullaquana Uranium Project in South Australia. Clean TeQ's R-603B and R-603C underwent isotherm testwork at varying chloride concentrations (up to 20g/L). The results are shown below:

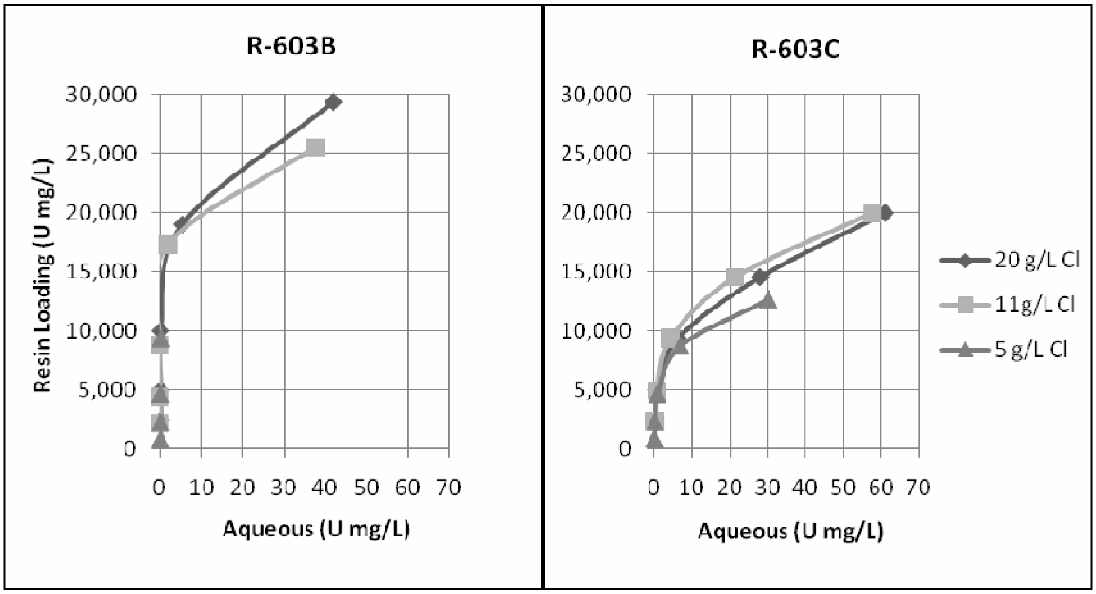


Figure 4: Effect of chloride concentration on R-603B and R-603C uranium loading

The graphs above show uranium loading on the resin was not affected by increasing chloride concentration in solution, suggesting that even higher saline conditions can be used without affecting the loading performance of the resin. Also, as the uranium in solution values are low, resin loadings in excess of 30-35g/L can be expected for typical ISL and heap leach applications, which typically run at 100mg/L uranium in solution.

Below is a graph from Fainerman-Melnikova & Soldenhoff (2010), showing the affect of chloride concentration on uranium loading of WBA resins, and the relative uranium loading of R-603B and R-603C:

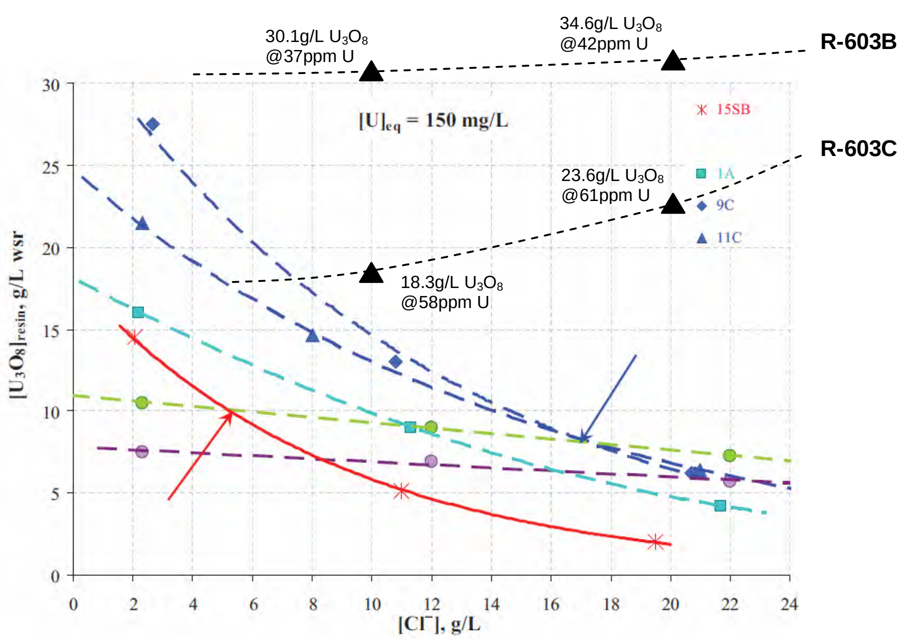


Figure 5: R-603B & R-603C loading capacity compared to weak base (WBA) resins (Fainerman-Melnikova & Soldenhoff, 2010)

It can be seen from this graph, that in saline environments Clean TeQ's R-603 series resin has significantly better loading characteristics compared to WBA resins.

Clean TeQ has also performed elution tests confirming the application of sodium carbonate as a suitable eluant for the U-HiSAL™ process. Loaded resin was contacted with 100g/L sodium carbonate in a single contact at ambient temperature. At these conditions, almost 100% of the uranium was removed, concluding that sodium carbonate elutes R-603B and R-603C extremely well. It is likely that elution conditions can be significantly improved with further work.

IMPLICATIONS FOR THE URANIUM INDUSTRY

As high quality uranium ore bodies become more difficult to find, industry is searching for new processing methods for extraction of uranium in more challenging environments. Recently, uranium provinces in arid regions (most notably Western Australia, South Australian and Namibia) and the growing application of ISL have become the focal points of new uranium exploration. In almost all of these mines, sourcing clean (low salinity) water is becoming a challenge, and in some cases almost impossible.

Initially conventional technologies were applied to allow the development of these mines. In Namibia, large scale sea water desalination (SWRO) plants are being constructed to supply the fresh water for mine operation. The capital and operating costs of these plants is very high, and have the potential to seriously impact the economic viability of projects, depending on their size and grade.

In ISL and heap leach applications, the uranium concentration in solution is relatively low (100 mg/L or less). As conventional IX is not suitable for saline environments, SX is an alternative as it can extract uranium in these conditions (e.g. Honeymoon Uranium Mine). However, SX is not economically attractive at lower uranium feed tenors when compared to IX, due to inefficiencies in the process. Therefore, at the lower uranium concentrations for ISL and heap leach, the SX plant needs to be larger to ensure adequate recovery of uranium. This increases the capital and operating costs of the SX system. In addition to these higher costs, the inherit risks of SX remain. An IX system which can operate in saline environments would offer significant cost savings, when compared to SX.

U-HiSAL™ now allows processes analogous to standard IX and RIP to be used in high saline environments. U-HiSAL™ used in these conditions significantly reduces the amount of fresh water required for the mine (>90% in some cases) and eliminates the requirement for SX. Due to the high resin loadings and simple elution processes, U-HiSAL™ is a low-cost process route for the next generation of uranium mines.

The potential impacts of this process could be enormous. Because of the ability to operate in high saline environments, previously uneconomical ore bodies can now have attractive returns. The elimination of desalination plants can greatly simplify the approval process for uranium mines, and reduce insurance costs by eliminating the requirement of SX.

CLEAN-iX® CONTINUOUS ION EXCHANGE

While the U-HiSAL™ process can be used in any IX technology, the use of continuous countercurrent IX (CCIX) is the most efficient form of IX available. By continually moving the resin countercurrent to the flow of solution or slurry, the driving force of the reaction is maximised, providing the optimum performance of IX.

Clean TeQ's Clean-iX® is a continuous countercurrent IX technology platform for slurries and solutions. Clean-iX® has enormous cost benefits over conventional IX technology due to its high efficiency and performance. This allows plant sizes and reagent consumption to be reduced, as well as producing a highly concentrated and pure product, reducing downstream process requirements.

The benefits of Clean-iX® over other commercially available IX technologies are:

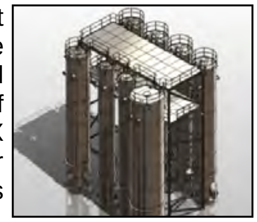
- Continuous countercurrent movement of resin in Clean-iX® systems increase uranium loading capacities and reduce resin inventories and resin impurity loadings.
- As the resin is cleaned in the process, it can handle up to 100 mg/L suspended solids, unlike other technologies, which require suspended solids to be <5 mg/L.

- Clean-iX® systems have no internal mechanical devices and very few internal structures, which greatly improve the reliability and decreases the risk of chemical scaling of the system.
- Clean-iX® systems have 90% turn-down, which allow for greater flexibility in operation.

Continuous Resin-in-Pulp (Clean-iX® cRIP)

Clean-iX® Continuous Resin-In-Pulp (cRIP) is a continuous countercurrent process that directly extracts target metals from leached pulps (up to 50%w/w solids). The cRIP system uses resin mixed directly with the slurry in a series of contactors. The contactors can be agitated mechanically or with air and the resin is transported between contactors using airlifts or recessed impeller pumps. In some applications, Continuous Resin-In-Leach (cRIL) can be used, where resin is contacted with slurry during the leaching process, giving higher leach recovery rates and a reduction in leaching lixiviants.

Continuous Resin-in-Column (Clean-iX® cLX)



Clean-iX® Continuous Resin-In-Column (cLX) is a continuous countercurrent process that directly extracts target metals from clarified leach solutions. The cLX system uses ***moving packed bed*** columns, whereby solution is passed through the adsorption column in an up-flow direction, with discrete packets of resin being transported between columns using airlifts. The Clean-iX® cLX system is the most efficient method of adsorption available and is suitable for large and small flow rates. Continuous ***moving packed bed*** IX technology is widely used in Kazakhstan, the world's largest uranium producer.

Elution

Clean-iX® Elution systems use continuous countercurrent processing of loaded resins from adsorption to produce highly concentrated and pure product eluates. The elution system can either use straight column elution (using a moving packed bed column) or Clean TeQ's patented concentration desorption U-Column. The U-column both concentrates the target metal in the tenor and scrubs impurities from the resin, allowing for the reduction or elimination of downstream purification processes. Clean-iX® Elution systems can be coupled with cRIP or cLX Adsorption plants, as well as Kemix Carousel RIP plants.

CONCLUSIONS AND FURTHER WORK

At time of writing (Feb, 2011) Clean TeQ is about to undertake an extensive metallurgical testwork and engineering study program to provide a commercial solution to the marketplace. The program will focus on the following areas:

- Loading capacity sensitivity to chloride (up to 120 g/L), other ions, and pH;
- Optimum elution conditions;
- The potential to use Clean TeQ's U-Column concentration desorption to increase the uranium concentration of product eluates; and
- Develop a complete process package for the U-HiSAL™ process.

Both R-603 resin and Clean-iX® technology are commercially available for immediate assessment on real applications.

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