

Technical Paper Notes of Practical Ion Exchange in Uranium Extractive Metallurgy

Presented by
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NOTES OF PRACTICAL APPLICATION OF ION EXCHANGE RESINS IN URANIUM EXTRACTIVE METALLURGY

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Uranium has been recovered via ion exchange resins since the 1950's. The worldwide demand for alternative energy sources has resulted in a renewed interest in the uranium industry. Purolite has been supplying ion exchange resins for uranium recovery for many years and has accumulated much experience in the requirements of the industry.

This paper provides a summary of the various considerations when choosing a resin for a specific application, be it uranium recovery from an acidic or alkaline environment, employing either a resin-in-solution or resin-in-pulp process. The resin of choice will have a high capacity for uranium, while at the same time exhibiting good selectivity for uranium over other impurities in the leach liquor. Additionally, a strong, durable resin is required, especially when contacted directly with pulps. At the same time, resin-in-pulp applications desire a large resin bead, for ease of separation of the loaded resin from pulp. These are a few of the items on the wish-list of the metallurgist.

As often happens, the optimum characteristics of an ion exchange resin is a compromise between sometimes contradictory requirements. It is attempted in the following to provide guidance to the metallurgist in this difficult choice.

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1. URANIUM CHEMISTRY BACKGROUND

Development of economically effective processes for leaching of natural uranium resulted in three chemically different routes:

- Sulfuric acid leach;
- Bicarbonate leach;
- Carbonate leach.

These three methods produce pregnant leach solution (PLS) with different alkalinity/acidity and, sometimes, different uranium concentrations. Typical pH range for the acid route is from 0.5 to 2.5 and uranium concentration can vary from 60 ppm to 2 g/l depending on process design and ore grade. Bicarbonate leaching produces PLS with pH from 6 to 8, while carbonate leach liquor has pH about 11. Of course, in reality there are no pure forms and both bicarbonate and carbonate will be present in solution, their specific concentrations are defined by equilibrium constants dependant on pH: the higher pH, the more carbonate and vice versa.

A few applications of uranium extraction from phosphoric acid also exist.

Uranium is leached from ores in the 6^+ oxidation state and exists in PLS in cationic (as hydrated uranyl UO_2^{2+}) and anionic forms (mainly as uranyl trisulphate or uranyl tricarbonate). The relative ratio between the cationic and anionic forms depends on the solution pH and anion background.

1.1 MATRIX OF PRODUCTIVE LEACH SOLUTION

The presence of certain components in the PLS has an influence on the uranium sorption performance of ion exchange resin. These components can be sorted into three different groups:

1. Substances depressing uranium sorption: compounds which strongly compete with uranium for ion exchange sites. Common examples are vanadate, molybdate, chloride, and nitrate.
2. Substances fouling ion exchange resins: compounds which form inert deposits or salts inside and/or on the surface of ion exchange resins. Such deposits are not removed by common treatment and require special care. A typical example is fouling of strong base anion (SBA) resins by silica.
3. A smaller group is presented by substances which don't affect uranium extraction itself but may create some troubles downstream. It was reported that zirconium causes the formation of foam in downstream uranium solvent extraction (SX) refinery circuits.

Silica as silicate anion has low affinity for SBA resins. While present in the PLS in its monomeric form, it does not create problems related to resin fouling. However, at low pH levels (as experienced during acidic leaching of uranium) the silica tends to polymerize forming deposits on different surfaces. For ion exchange resins (IXR) this phenomenon is known as silica fouling. Silica fouling is not a problem in the case of bi- and carbonate leach processes where the high pH is not favorable for polycondensation of silica.

South African researchers reported fouling of anion exchange resins by polymerized cobalt cyanide species in the case of sorption of uranium from acidified gold cyanidation tails.

1.2 METHODS OF LEACHING AND SORPTION

There are two principle methods of ore processing: extraction of ore from the ground (it may be underground mines or open pits) and in situ treatment. Extracted ore is transported, crushed, beneficiated and milled for further processing. When in situ leach (ISL) is used, the ore remains underground and uranium is dissolved by appropriate lixiviants directly from the ore body. The ISL produces “clean” PLS with Total Suspended Solids (TSS) less than 50 ppm.

Leaching of uranium from milled ore can be arranged in the following ways:

- Heap leaching. This method is the most economical for processing of low grade ores.
- Batch leaching. This method can be modified as autoclave leaching, tank leaching, vat leaching.

For our consideration it is important to notice that heap leaching and tank leaching, followed by sedimentation pond and CCD respectively, produce “clean” PLS similar to those obtained from ISL operations.

Leaching in autoclaves or tanks produces mixtures of finely milled ore and PLS. Such mixtures, known as “pulp”, can be treated further in two ways:

1. Mineral solids are filtered off; clarified solution continues to the uranium recovery step.
2. Sorption of uranium is carried out directly from the pulp, defined as ‘resin-in-pulp’ (RIP). Uranium pulp can be supplied as by-product of other metals recovery like gold (in South Africa) or copper. For some types of ores, leaching of uranium from milled ore can be combined with its sorption in the same vessel, called ‘resin-in-leach’ (RIL). From standpoint of sorption technique it is very similar to RIP.

2. DESIRABLE RESIN CHARACTERISTICS

The combination of different process parameters creates a variety of conditions for exploitation of ion exchange resins for uranium recovery. These conditions, in turn, have their reflections in resin properties required for the best economical performance.

The resin properties are to be chosen to suit specific working conditions. Starting from the top of the hierarchical pyramid, the following general requirements apply:

- High operating capacity
- Efficient regeneration
- Service life durability

Each of these requirements splits on to lower levels:

High operating capacity means:

- High chemical affinity of the resin functional groups towards uranyl compounds

- High selectivity of the functional groups towards uranyl compounds; i.e. lower affinity for undesirable species present in the feed source
- High kinetics of ion exchange, both during adsorption and elution

The following properties define the efficiency of regeneration:

- Applicability of available reagents
- Obtaining of lower volume of more concentrated desorbates
- Prevention of fouling impurities build-up
- Low residual content of uranium in the regenerated resin

The service life durability is defined by the following main factors:

- Mechanical strength
- Resistance to chemical fouling or degradation
- Resistance to osmotic shock

As always, the optimum characteristics of an ion exchange resin is a compromise between sometimes contradictory requirements. It means that to enforce one specific property of the resin we have to sacrifice some others. To ensure the best resin for a particular project is chosen, all these aspects have to be considered. This can be a daunting task. Some of the resin requirements are discussed in more detail below.

1.3 OPERATING CAPACITY OF THE RESIN

Over the years, many types of ion exchange resins have been tried for the extraction of uranium. However, so far only strong base anion exchange resins are widely used across the world to extract natural uranium (both type I and type II). Though some authors advocate different performance of these two resin types, Purolite has not observed any meaningful difference. In further narration, no differentiation is made between these types of SBA resins.

Uranium operating capacity of SBA resins changes in correspondence with their total capacity defined for the chloride-anion, as shown in Figure 1.

The data illustrated in Figure 1 was generated for sulfuric acid artificial PLS with a uranium concentration of 100 mg/L. This dependence is more or less accurate for all typical SBA resins used in the industry.

It becomes clear that gel type resins, due to their higher volume capacity, will generally have higher uranium capacities than porous resins.

The uranium loading capacity of a resin with common strong base groups is limited. Purolite has introduced a new products line of SBA resins employing a different quaternary ammonium functional group. These new products exhibit much higher uranium loadings, when compared to resin with conventional functional groups. Data in Table 1 compare the uranium loading capacities of these new resins, both gel-type and macroporous, to that obtained for conventional resin.

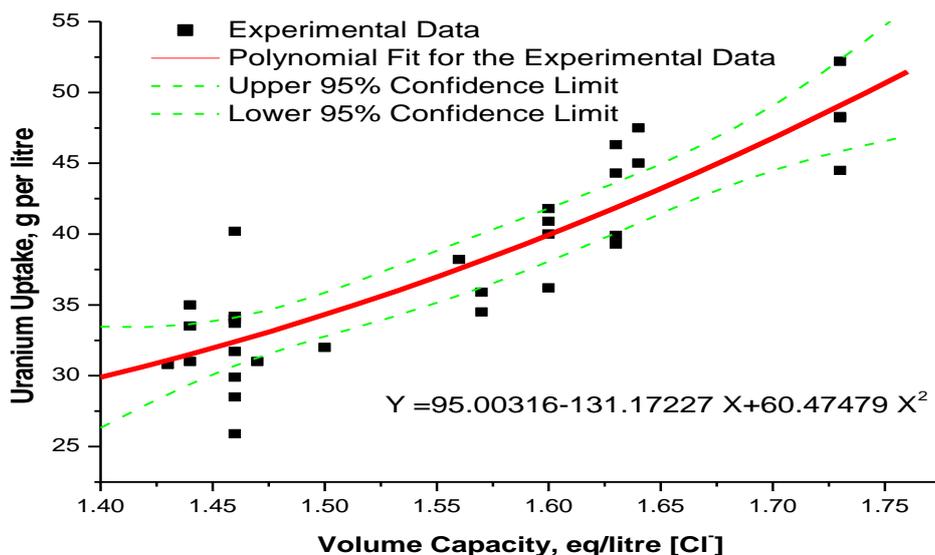


Figure 1: Dependence of uranium uptake on chloride capacity of strong base anion gel Type I resin (Purolite®).

Table 1 represents data on uranium fixation obtained under the same conditions as for Figure 1. It is remarkable that while resin no. 1 with common strong base anion groups matches the approximation curve pretty well, the other SBA resins, numbers 2, 3 and 4 having different quaternary ammonium groups demonstrate much higher uranium loadings.

Table 1 Uranium fixation on resins with different functionality

| | Ion exchange resin | Total volume capacity per chloride, eq/l | Uranium fixation, g/l | Ratio of U fixation to chloride capacity, g/eq |
|---|-----------------------------------|--|-----------------------|--|
| 1 | PFA600/4740 (gel) ^a | 1.63 | 39.8 | 24.4 |
| 2 | A560/4758 (porous) ^b | 1.18 | 46.7 | 39.6 |
| 3 | A660/4759 (gel) ^b | 1.45 | 53.0 | 36.6 |
| 4 | PFA460/4783 (porous) ^b | 1.37 | 55.0 | 40.2 |

a – conventional

b – "new"

Even porous Purolite® A560/4758 resin with the lowest chloride capacity has higher uranium fixation than common gel type PFA600/4740.

Higher operating capacity presents to the user such advantages as:

- Lower resin flow rate
- Less resin inventory and less capital expenditure (CAPEX) of the project
- Less operating expenditures (OPEX) related to auxiliary operations associated with the resin flow rate: resin losses, energy, rinsing waters, wastes, man power etc

For further comparison, as shown in Table 2, three Purolite® resins were investigated in the laboratory on the solution of the following composition (g/l): Uranium – 0.104; Sulfate – 10.5; Nitrate

– 0.50; Chloride – 1.05; Fe³⁺ – 1.02; Al³⁺ – 0.35; Si – 0.06; pH = 2.0. Such solution simulates typical pregnant solution produced by sulfuric acid ISL operations. The resins tested were:

- A500U/2788: macroporous, size distribution 800-1300 µm (92% >800 µm), “conventional” product
- PFA460/4783: gel-type, uniform beads, size distribution 520 – 630 µm, “new” product
- PFA600/4740: gel-type, uniform beads, size distribution 520 – 630 µm, “conventional” product

Table 2 Comparison of general sorption parameters for different strong base anion resins

| | Purolite [®] resins | | |
|--|------------------------------|--------------------------|--------------------------|
| | A 500U/2788 ^a | PFA460/4783 ^b | PFA600/4740 ^a |
| Sorption time till breakthrough point, hours | 5.90 | 17.0 | 14.2 |
| Uranium fixation on the resin at breakthrough point, g/l | 5.46 | 15.7 | 13.1 |

a – conventional
b – “new”

The laboratory results obtained were used to calculate the sorption time till breakthrough point (accepted for uranium as 0.002 g/l) and the resin capacities at the breakthrough point for a full-scale plant; it was accepted that fixed bed filter has diameter 4 m, resin bed volume is 28.6 m³ and feed flow rate is 259 m³/hour.

The results presented in Table 2 showed that the time until uranium breakthrough for “new” PFA460/4783 resin was about 20% more, and uranium fixation was also 20% more than for common PFA600/4740 at the same resin bed volume and PLS flow rate. The uranium loading obtained was almost three times higher for the “new” PFA460/4783 than for “conventional” A500U/2788, with a similar increase in the time till breakthrough.

1.4 RESIN LOSSES

One of the most frequent questions is about resin losses rate.

Resin leaves the process loop generally with flows of barren pulp or solution; we can nominate such losses as ‘technological’ ones. Some losses can also be attributed to mishandling, spillage etc. Under normal process conditions, resin breaks down to produce fine particles which pass through the screening circuits.

Resin breaks down due to different physical forces:

- compression failure
- percussive action
- abrasion
- osmotic shock

Let’s consider them separately.

Compression failure is more typical for resins working in columns in fixed beds. This is the most common design for in-situ and heap leach operation. In the fixed beds the resin is exposed to a linear pressure gradient attributed to solution flow along the column axis.

Percussive action is common in fluidized bed, resin-in-pulp and moving-bed, and resin inter-stage transfer designs/operations. Resin beads collide with walls of equipment, breaking down to debris. Abrasion can be attributed to fluidized bed and resin in pulp processes where resin beads are abraded by contact with ore particles. It is supposed that the diameter of the resin beads decrease due to abrasion.

Resin changes its ionic form as it moves from one stage to the next. It leads to change of specific volume of the beads due to differentiated swelling of different ionic forms. Changes in resin swelling create osmotic pressure within the resin beads and this pressure affects the integrity of the polymer backbone. This phenomenon is known as 'osmotic shock'. The osmotic shock can rupture the resin bead without participation of external forces. Modern resins used in hydrometallurgical practice have high resistance to osmotic shock. However, continuous exposure to osmotic shock weakens the resin beads and makes them more prone to breakage by external mechanical forces.

Under real conditions all these factors contribute to resin destruction and further losses with barren flows. Depending on the particular flowsheet and equipment design the proportional effect of a specific factor can be higher while others can be negligible.

Manufacturers and consumers of ion exchange resins can evaluate possible resin loss rate by means of different experimental data:

- Breaking weight measured by dynamometer for large random population of resin beads. This parameter is expressed as a portion of the beads with breaking weight below, say, 200 g per bead and/or averaged breaking weight. This method is of course mostly relevant to fixed bed designs, as is typical for industrial water treatment. Good resin must have 0% below 200 g and averaged breaking weight from several hundred grams to 2-3 kilogram per bead.
- Disintegration rate by ball mill test. In this test a small cylindrical vessel is filled with a known volume of resin, water and steel or ceramic balls. After rolling of the cylinder for a set time, the fraction of resin retained by a specified mesh is measured. This parameter is expressed as a volumetric percentage of the retained fraction. Because Purolite sells significant volumes of ion exchange resins in the FSU it has implemented the ball mill protocol similar to Russian standard. By Purolite specifications on the resins dedicated to RIP operations the resins must have the ball mill parameter 92-100% retained on the 800 μm screen after six hours of milling.
- Attrition rate by abrasion test. This method is similar to the ball mill test but fractionated quartz sand is used instead of balls.
- Resistance to osmotic shock is measured by cycling of the resin between acid and alkaline treatments. The resin loss is expressed as a percentage of resin fraction of the initial volume retained by specified mesh after such cycling.

These methods provide a quick comparison between different resins, but none of them can sufficiently simulate real operation conditions. So, the process engineer has to decide what method or combination of them to use for evaluation of resin losses in new project.

With reference on RIP plants continuously operating in the FSU for more than 50 years, we can say that ball mill test gives quite fair prognosis of the resin wear rate in the process.

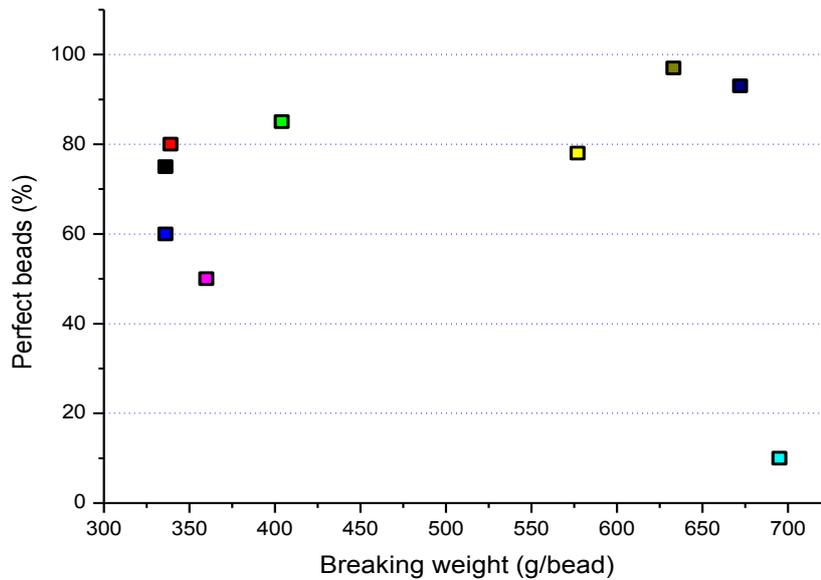


Figure 2: Relation between ball mill and dynamometric tests (Purolite®.)

It is interesting to notice that breaking weight and ball mill parameters don't necessarily collate, as illustrated by Figure 2. The breaking weights of a number of resins were compared to the results of the Ball Mill test.

It is logical to assume that resin wear rate is linked with resin flow rate in the process. Higher resin flow rates will result in higher collisions frequency, collision momentum and frequency of regenerations. The combined effect of these will result in increased breakage of the resin.

Resin flow rate is determined by uranium mass balance of the process. Metal flow (kg/hour) through the plant must be equilibrated by flow of resin exchange capacity. The latter is defined as multiplication of resin operating capacity (kg/m_R^3) by resin flow (m_R^3/hour). Thus we see that resins with higher operating capacity have advantage due to less wear rate, other conditions being equal.

Averaged resin losses reported by operating uranium RIP plants are 175-220 g of dry resin per 1 tonne of treated ore or about 60-80 m^3 resin per 100 thousand tones of treated ore. It represents about 20% make-up of the total resin inventory. Actual make-up can vary from 15 to 45% depending on different operating parameters.

1.5 GRADING OF RESIN

Grading of ion exchange resins will comply with the following demands:

- Effective separation from productive leach media, either, clean solution or dense pulp.
- Low hydrodynamic resistance by resin bed to solution flow in fixed beds (low pressure drop across the bed). This is provided by narrow size distribution of the resin beads.

Purolite produces resins with different grading depending on particular application:

- Purofine grade: mean diameter 520-620 μm with uniformity coefficient 1.2 max.
- Special grade for RIP processes: 1% max below 710 μm and 5% max below 800 μm .

1.6 POLYMER MATRIX AND MOISTURE RETENTION

Most of the commercial resins suggested on the world market are made of styrene as a monomer and divinylbenzene (DVB) as a crosslinker. Structure of the resins can be either gel or porous. Characteristics of porous structure depend on the resin manufacturing method.

Being functionalized with quaternary ammonium the resin becomes very hydrophilic. It retains water due to hydration and coordination via hydrogen bonding. Typically such water retention varies for different resins from 45 to 60% depending on the extent of resin crosslinking and the concentration of functional groups in the polymer matrix.

Porosity, extent of crosslinking and moisture retention capacity play an important role in operating performance under real conditions. Combination of these parameters defines operating capacity of the resin, rate of ion exchange reaction, osmotic and mechanical resistance, and resistance to silica fouling.

Eventually, optimized performance is a trade-off among these parameters.

High kinetics of exchange is an important parameter which has great influence on resin performance especially for PLS of low grade as of restoration wells for example. For processing of low grade solutions, say below 30 ppm of uranium, the macroporous or low-crosslinked gel resins are preferable, due to their higher kinetics and total efficiency.

For high grade solutions, conventionally above 50-60 ppm, higher resin capacity is preferable. Gel resins typically have higher total capacity than macroporous resins. For example, total capacity as per chloride anion is around 1.2 eq/l for Purolite® A500U/2788 (macroporous) and 1.6 eq/l for Purolite® PFA600/4740 (gel-type) resin.

1.7 SILICA FOULING

Silica fouling remains one of the main concerns when a new project is investigated. The chemical behavior of silica is complicated and difficult to control.

Silica fouling issues are typical for acid leach conditions. It is known that silica tends to polycondensation at acidic pH with formation of large polymeric molecules which in turn form colloidal particles. Thus, in acidic solution we face monomeric anionic forms of silica as well as polymerized and colloidal forms. Reported solubility of monomeric silica is around 300 ppm. In real productive leach media silica concentrations can range from about 400 to 2,000 ppm.

Monomeric form of silica has low affinity for strong base functionality of the resin. It can be easily removed from the resin at uranium desorption stage. It is assumed that all forms of silica existing in the solution participate in the fouling process.

It is known that the rate of silica accumulation on the resin is much higher for macroporous resins than for gel resins. An operating RIP plant using acid leach has reported results obtained in 30 sorption-desorption cycles using real solution: silica accumulation for a gel resin was 1.1 w. w. % while for macroporous resin it was 17.4 w.% after 30 cycles. Silica concentration in the feed solution was about 2 g/l.

Silica build-up drastically affects the rate of uranium sorption and, consequently, the operating capacity of the resin. When the fouling reaches some critical value the resin may be treated by

alkali to convert the silica to the soluble form and strip it from the resin. Ideally such treatment should be organized as kidney loop system providing the same rate of silica withdrawal as it's build-up rate is. The silica build-up rate should be defined at the pilot stage of a project.

Real data of dependence of uranium uptake on silica build-up is depicted in Figure 3. Samples of the resin were taken from the process over the course of a few months. It should be mentioned that fresh resin was added to the process during this time, to ensure the desired resin concentration was maintained.

When making a decision regarding the installation of an alkaline treatment circuit, one should keep

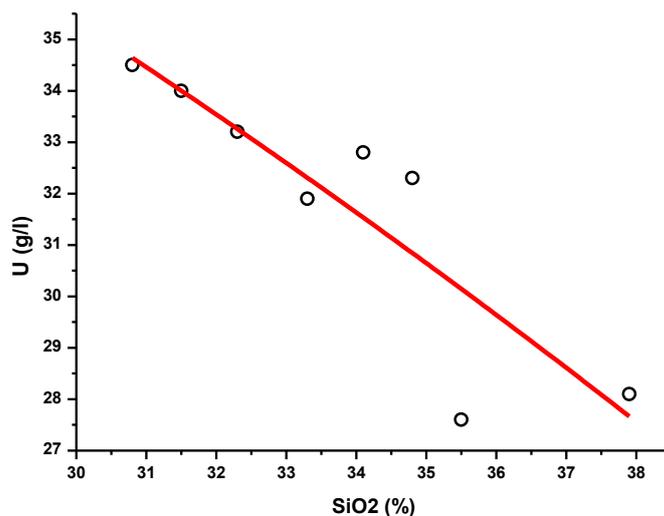


Figure 3: Dependence of uranium sorption on silica build-up on a macroporous resin, year 1999.

in mind that uranium capacity loss attributed to silica fouling can be compensated by fresh resin top-up which is necessary to do because of the resin wear. So, if silica fouling rate isn't too fast, it is possible to avoid alkaline treatment.

In practice, under reasonable conditions, the alkaline process allows to strip about 20-25% of silica from heavily fouled macroporous resin per treatment. Obviously, in case of gel resin silica can be stripped more efficiently for two reasons:

- less fouling;
- silica is layered mainly on external surface of resin beads.

One property is in favor of macroporous resins: they are more resistant to osmotic shock caused by alkaline treatment.

1.8 SORPTION FROM "CLEAN" SOLUTIONS

Clean PLS can be based on different chemical background: acid, bi- or carbonate leach. In practice such solutions contain about 50 ppm and less of suspended solids. This fact must be considered when sorption contactor design is to be chosen.

So, if fixed bed is chosen then it is necessary to provide shorter sorption service with backwashing of the resin to remove entrapped fines.

Designs with moving or fluidized bed are preferable, since these designs negate problems with pressure drop increase and provide excellent productivity.

Gel resins with narrow bead size distribution with mean diameter about 570 μm have a well established reputation for sorption from clean solutions. Their main advantages are good kinetics of ion exchange and low specific pressure drop across the bed.

Choice of resin structure depends on the chemistry of particular PLS. One should remember about possible silica issues and chemical stability of the resin.

3. RESIN IN PULP AND RESIN IN LEACH PROCESSES

Sorption from pulps makes specific demands for resin choice. Ore pulps used for sorption contact can bear up to 50-55 w.% of solids. Comminution grade of the ore (milling fineness) shall be defined as trade-off between costs of milling and leaching efficiency.

In practice the fineness of mineral solids in pulp is 90-95% smaller than 75 μm and the balance is less than 150 μm . These parameters define total openings of mesh screens which must secure designed pulp flow. In reality the opening is 600 μm . For effective separation of resin from pulp the resin must be about 200 μm bigger than the mesh opening.

Purolite's specifications on all resins dedicated to RIP or RIL processes have less than 1% below 710 μm and less than 5% below 800 μm .

4. BY-VALUES RECOVERY

Uranium ores may contain different by-metals or it can be recovered as a by-metal itself. A group of major by-metals can include such elements as gold, vanadium, and molybdenum. A group of minor metals is wider and can include metals from the first group and others, for example rhenium, scandium, yttrium and rare earths.

When the potential value of by-metals in processed flows is significant it is worth of consideration of their recovery. The Witwatersrand gold-bearing ores in South Africa contains, apart from gold, uranium in economical quantities (typical head grades 100-500 g/t). During the previous uranium boom in the 1970's and 1980's, uranium was recovered as a by-product of gold at 27 different sites. Initially, acid leaching followed cyanidation, mainly since this involved no change to the existing gold circuits. Further research showed that improved gold recovery could be achieved by performing the acid leach first, to extract uranium, followed by neutralization and cyanidation to recover gold. This sequence was known as the "reverse leach". A further advantage of the reverse leach was that it prevented poisoning of the resin by cobalt cyanide.

We will consider two cases of by-metals recovery in more detail.

1.9 VANADIUM

In processing of vanadium-uranium ores the vanadium is usually present as a major by-metal. When uranium is leached by sulfuric acid or carbonate lixiviant the vanadium is also oxidized to the 5⁺ state and co-extracted into the PLS as vanadate oxoanion together with uranium. In some cases

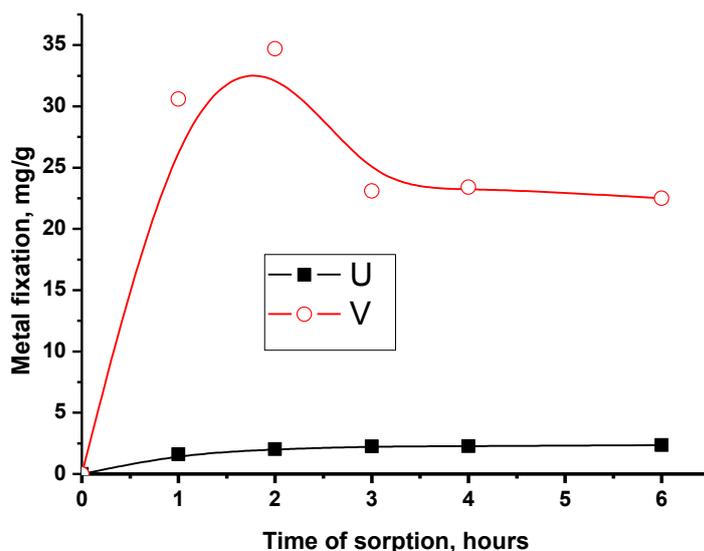


Figure 4: Kinetic curves for sorption of uranium and vanadium by strong base resin Purolite® PFA600/4740 from simulating PLS.

the ratio of uranium and vanadium in the PLS can be as high as 1 to 1. Both metals are efficiently adsorbed by strong base anion resins, hence, their separation can create difficulties for production of pure uranium oxide.

One of the available options for the “vanadium” problem is reduction of the element to the 4^+ state in the PLS. In this oxidation state, vanadium will be present as a cation and will not be fixed by strong base anion exchange resins. This approach requires high accuracy as uranium must be kept in its 6^+ state. It also requires a significant expansion of the flowsheet, making it an unattractive option in practice.

Guaranteed purification of uranium oxide with a lot of vanadium contamination usually results in relatively high losses of uranium.

Purolite has done test work that showed that the separation of bulk vanadium from uranium PLS can be achieved by one step sorption on the same resin which can be used for downstream sorption of uranium. The method is based on the significant difference in sorption kinetics for these two metals on the strong base, gel type resin Purolite® PFA600/4740.

Artificial solution with the following composition was used (g/l): uranium – 0.5; V^{5+} - 0.34; CO_3^{2-} - 13.5; HCO_3^- - 6.5; SO_4^{2-} - 5.8. The alkalinity of the solution was adjusted by NaOH to pH 9.6. Contact of the resin with the solution was carried out in five beakers with ratio of resin to solution of 1 to 1000 (by volume). The obtained kinetic curves are depicted on the Figure 4. One can see that time till maximal loading of vanadium was about 1.5 hours while for uranium loading about 4 hours were required.

Processing of obtained kinetic data allowed to find optimal parameters for separation of vanadium from the uranium stream. The calculation were made for columns of moving bed design, with internal diameter 3 m and the PLS flow rate $250 \text{ m}^3/\text{hour}$. The goal was to decrease the concentration of vanadium in the PLS to $< 10 \text{ mg/l}$.

The calculated parameters of the process were as follows:

- Each 4 hours 20.2 m³ of the resin is off-loaded from the bottom of the column (at the same time, a similar volume of fresh resin is added to the top of the column).
- Metal fixations in the off-loaded resin are about 12.4 kg Vanadium/m³ and 0.24 kg Uranium/m³.
- Metal concentrations in the outlet solution are about 0.01 g Vanadium/l and 0.39 g Uranium/l (for the latter 97.5% of the feed concentration).

This simple flowsheet can separate a vanadium/uranium composite stream into two single metal streams. This is a train of two columns; while the lead column having higher resin flow rate removes vanadium, the lag column with slower resin flow recovers uranium from the vanadium depleted PLS. Both lead and lag columns use the same type of resin, i.e. Purolite® PFA600/4740. The main advantage of such a flowsheet is that it allows downstream processing of vanadium and uranium streams separately and independently. This method of vanadium separation requires minimal capital costs.

1.10 RHENIUM

Rhenium is among a group of scattered metals which don't have their own mineral deposits but often accompany other metals. In many cases rhenium is leached together with uranium from the ores. In contrary to the case of vanadium considered above, rhenium always belongs to the group of minor by-metals: its concentration in uranium PLS rarely exceeds 5 ppm, typically it is below 1 ppm.

It is worth to consider the rhenium by-recovery in many cases, when taking in consideration such factors as

- high demand for rhenium from turbine building and oil processing industries,
- high price of this metal,
- significant volumes of the uranium PLS processed.

Rhenium is easily leached by sulfuric acid as the perrhenate anion (ReO₄⁻). In contrast to vanadium the strong base resins commonly used for uranium sorption, adsorb rhenium much slower than uranium. For one uranium sorption cycle about 90% of feed rhenium passes through the resin bed and reports to the uranium barren solution. The fixed 10% or less of rhenium is not stripped from the resin at uranium desorption stage. Thus, rhenium is accumulated in the strong base anion exchanger with time. Some operators periodically strip the adsorbed rhenium by concentrated nitric acid, generating large volumes of diluted rhenium desorbate.

Purolite has commercialized the weak base anion exchange resin Purolite® A170/4675, which is very selective for the perrhenate anion. This resin has been installed by several operators who recover rhenium from different raw sources. Particularly, one commercial installation has been made by a uranium ISL operator using acid leach. The general flowsheet for this installation is depicted in Figure 5.

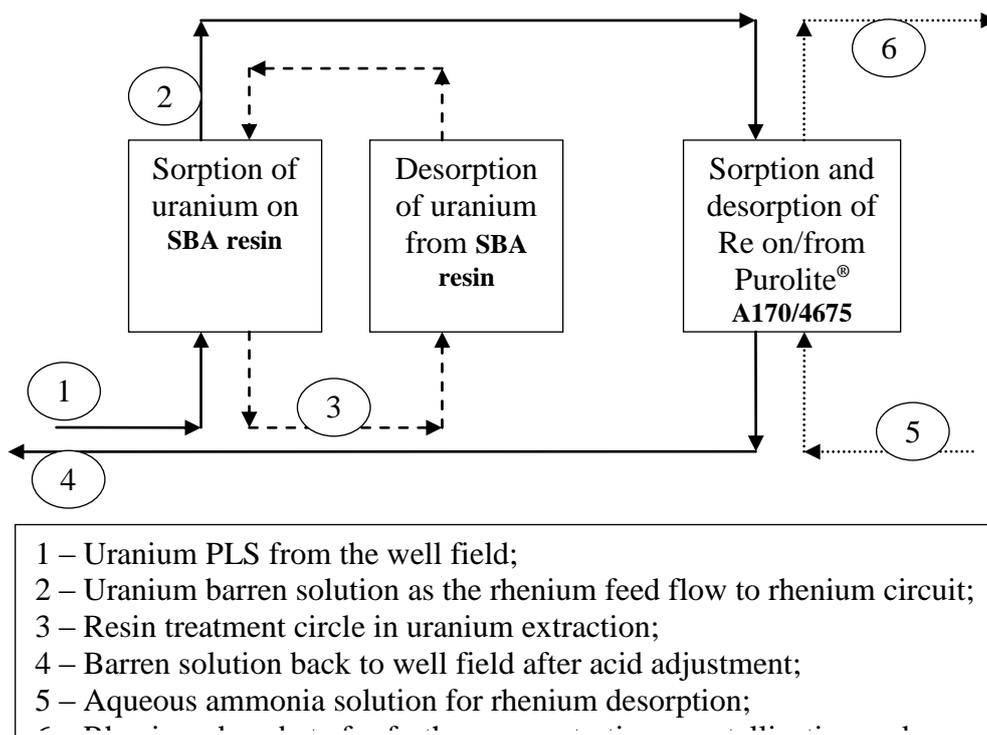


Figure 5: General flowsheet for recovery of rhenium from uranium barren solution.

The advantage of this scheme is in its minimal affect on the main process of uranium extraction. Uranium barren solution passes through the column with Purolite® A170/4675 resin in the sulfate form. Since the resin is in the sulfate form, no external contaminants are brought in the uranium process loop. Acid losses attributed to neutralization are negligible, as these are approximately equivalent to the exchange capacity of the A170/4675 resin. The required volume of resin for rhenium recovery is very small relatively to the volume of the treated acidic stream.

Supposed technical parameters for the process are as the followings:

- Rhenium concentration in the feed after uranium sorption 0.6-1.0 ppm;
- Rate of rhenium recovery from the feed onto the resin - 80-90%;
- Minimal contact time in sorption 350-400 hours.
- Rhenium loading onto the resin – 3-6 kg/m³;
- Rhenium concentration in desorbate – 0.35-1 g/l (feed to desorbate concentrating factor around 750);
- Volume of rhenium desorbate less than 10-12 BV.

Concentration of sum of rare earths, scandium and yttrium in uranium acidic PLS can reach several hundred ppm. They also can be recovered in bulk without significant impact on the main process of uranium extraction.

As off-topic it can be noticed that co-recovery of minor metals as commodities despite their own commercial value is often ignored by uranium mining companies. Mainly because the total value of the recovered minor metal is much less than that of uranium produced. However such business can

be interesting for smaller companies who could “lease” the uranium barren solution to recover all by-values and return adjusted solution to the main uranium circle.

5. CONCLUSIONS

Ion exchange technologies play a leading role in industrial extraction of natural uranium. There are a number of different flowsheets that can be considered, depending on the specific nature of the ore. Uranium is extracted from ore via three chemically different routes, resulting in either an acidic or alkaline feed to the ion exchange circuit. At the same time, the ion exchange design can consist of either a fixed-bed, fluidized-bed or resin-in-pulp contactor.

Strong base anion exchange resins are used, regardless of the matrix of the solution/pulp. Desirable characteristics of the optimum resin are dependent on the nature of both the leach liquor and the design of the ion exchange circuit. Factors that should be considered when choosing a resin are the operating capacity of the resin, elution efficiency, durability and resistance to fouling of the resin.

Purolite has been providing ion exchange resins to the uranium industry, as well as for extraction of gold, molybdenum and other metals, for many years and has a deep understanding of the requirements of the industry. The company is continuously busy with the improvement of existing products as well as development of new products, both customer-driven and in-house.



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