

**ALTA 2019**  
18 - 25 May  
Perth, Australia

**24<sup>th</sup> Annual Conference Proceedings**

**Uranium-REE  
Conference**

*Including*

**Developments in IX Forum**

**Organised in cooperation with**



**IAEA**

International Atomic Energy Agency

**15<sup>th</sup> Annual Uranium Event**

**7<sup>th</sup> Annual Rare Earth Elements Event**

**ALTA Metallurgical Services, Melbourne, Australia**

**[www.altamet.com.au](http://www.altamet.com.au)**

# PROCEEDINGS OF ALTA 2019 URANIUM-REE SESSIONS

*Including*  
**Developments in IX Forum**

23 May 2019  
Perth, Australia

978-0-9946425-6-1

## ALTA Metallurgical Services Publications

### All Rights Reserved

Publications may be printed for single use only. Additional electronic or hardcopy distribution without the express permission of ALTA Metallurgical Services is strictly prohibited.

Publications may not be reproduced in whole or in part without the express written permission of ALTA Metallurgical Services.

The content of conference papers is the sole responsibility of the authors.

To purchase a copy of this or other publications visit [www.altamet.com.au](http://www.altamet.com.au)



***Celebrating 33 years of service to the global mining and metallurgical industry.***

**ALTA Metallurgical Services** was established by metallurgical consultant **Alan Taylor** in 1985, to serve the worldwide mining, minerals and metallurgical industries.

**Consulting:** High level metallurgical and project development consulting.

**Conferences:** ALTA conferences are established major events on the international metallurgical industry calendar. The event is held annually in Perth, Australia. The event comprises three conferences: Nickel-Cobalt-Copper, Uranium-REE-Lithium and Gold-PM.

**Short Courses:** Technical Short Courses are presented by Alan Taylor, Managing Director.

**Publications:** Sales of proceedings from ALTA Conferences, Seminars and Short Courses.

**MetBytes:** Free technical articles offering metallurgical commentary and insights.

**Free Library:** Conference proceedings and technical papers. The library is expanded regularly, providing a major ongoing resource to the industry.

## Uranium-REE Keynote

### URANIUM IX – PAST, PRESENT AND FUTURE

By

**Dr Karin Soldenhoff**

Technology Manager - Minerals  
ANSTO, Australia

khs@ansto.gov.au

#### ABSTRACT

Ion exchange has played an important role in nuclear power generation. The development of resins in particular was spurred by the challenges posed by the recovery of uranium from leach liquors on the one hand and the purification of water used for reactor cooling on the other.

The application of ion exchange resins for the separation, concentration and purification of uranium leach liquors is the subject of this paper. Major developments of this technology, which has come in waves in response to the fluctuating prices and demand for uranium, are highlighted.

The first wave of uranium mining activity occurred in the nineteen fifties, underpinned by military applications and interest in nuclear power. These plants used strong base polystyrene-divinylbenzene gel resins in fixed bed systems with nitrate based elution.

The uptake and construction of new nuclear power plants in the sixties was slower than projected and a decline in uranium demand ensued. This was reversed by the oil crisis in the seventies which brought about increased uranium production and a series of innovations to the uranium hydrometallurgical flowsheet, including the coupled ion exchange/solvent extraction or Bufflex/Eluex processes, using sulfate elution, and the adoption of fluidized continuous ion exchange to treat unclarified liquors.

Two decades of sustained low uranium prices, reduced demand and draw down of military inventories, resulted in virtually no new uranium developments. Second generation plants, which commenced operation in the eighties treating higher grade ores, tended to use solvent extraction as the preferred separation technology. Ion exchange has maintained its relevance with technologies such as resin-in-pulp and in-situ recovery processes that are applied to lower grade deposits. Ion exchange has been adopted by three of the most recently built tank leaching operations, Langer Heinrich, Kayelekera and Husab, and continues to be used in all operating ISR projects in the USA, Kazakhstan and Australia.

Looking to future innovations, this paper discusses the potential of ion exchange to address particular challenges and niche areas in uranium processing such as:

- The use of resins with functionalities other than conventional strong base for recovery of uranium from saline and phosphoric acid liquors;
- The use of ion exchange to facilitate reagent re-cycle;
- Improvements in elution to target more concentrated eluates; and
- Coupling ion exchange with other technologies.

*Keywords: ion exchange, uranium, strong base resins*

## INTRODUCTION

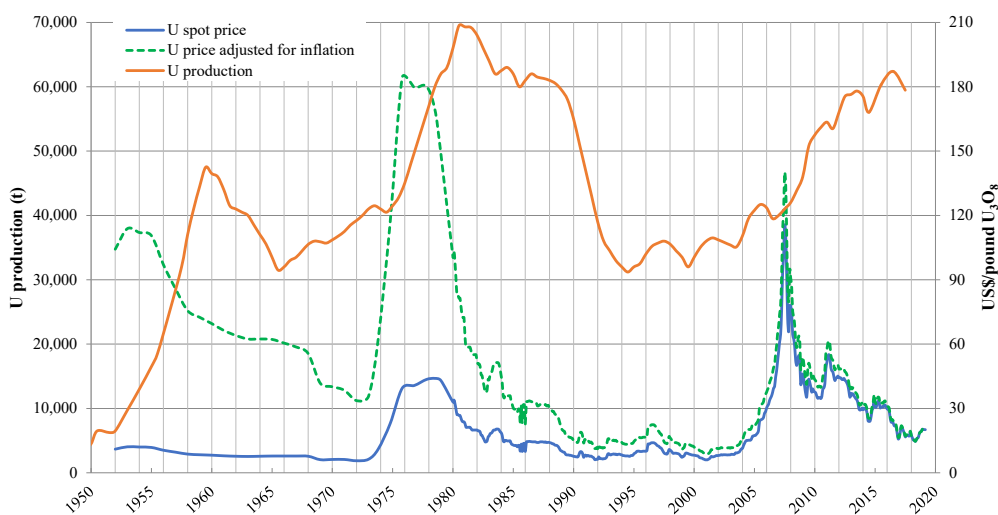
Ion exchange (IX) has played an important role in nuclear power generation. Developments of this technology relating to the hydrometallurgy of uranium recovery have come in cycles that can broadly be matched to fluctuating prices and demand for uranium<sup>(1-4)</sup>. Uranium production and uranium price data, adjusted to take inflation into account, is presented in **Figure 1**. Over seven decades there have broadly been three peak periods of relatively high prices as responses to drivers such as number of planned and operating reactors, the total uranium production, the availability of uranium from military inventories and major reactor related incidents.

The first wave of uranium mining activity occurred in the nineteen fifties, underpinned by military applications and interest in nuclear power. These plants used strong base polystyrene-divinylbenzene gel resins in fixed bed systems with nitrate based elution.

The uptake and construction of new nuclear power plants in the sixties was slower than projected and a decline in uranium demand ensued. This was reversed by the oil crisis in the seventies which brought about increased uranium production and a series of innovations to the uranium hydrometallurgical flowsheet. Second generation uranium processing plants tended to use solvent extraction as the preferred separation technology. However, many innovations in IX technology applicable to low tenor liquors were introduced, including the development of coupled IX/SX Bufflex/Eluex processes using sulfate elution, the adoption of fluidized continuous ion exchange (CIX) to treat unclarified liquors and the introduction of resin-in-pulp (RIP).

Innovations are fueled by new mining activity and a constant drive for lower operating costs. However, sustained and prolonged low prices reduce the incentives for research and the opportunities to nurture human capital. This is essentially what happened in the nineties and early 2000's, when limited emphasis was placed on research into new IX technologies. The new mining projects that were built in Africa, when high prices briefly returned, were largely based on technologies developed in the seventies and eighties. Improvements relating to equipment design were adopted from other applications such as carbon-in-pulp and carbon in leach used in the gold industry<sup>(5)</sup>.

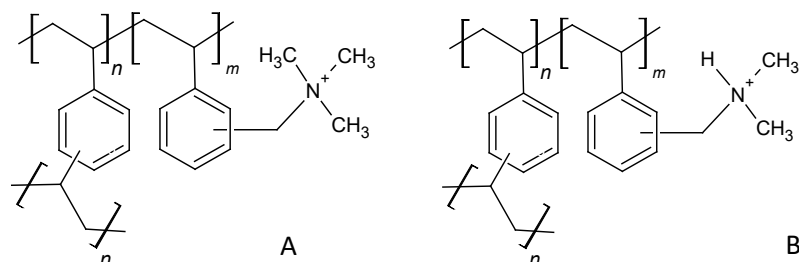
This paper highlights some of the advances in the field of IX technology as applied to the separation, concentration and purification of uranium leach liquors. Many excellent reviews on the developments of IX have been written so past and present applications are only briefly discussed<sup>(5-12)</sup>. This paper focuses on potential opportunities for future developments, where IX maintains its relevance in the uranium processing flowsheet in slightly different or novel ways.



**Figure 1 – Uranium Production and Uranium Price (1947 – 2017)<sup>(1,2,4)</sup>**

## RESIN CHEMISTRY

The development of resins was spurred by the challenges posed by the recovery of uranium from leach liquors and the purification of water used for reactor cooling and steam generation. Sulfonated polystyrene-divinylbenzene strong acid (SA) cation exchangers have been most widely used in the nuclear industry, while strong base (SBA) anion exchangers are standard in the mining industry.

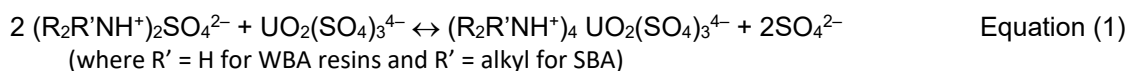


**Figure 2 – Polystyrene-divinylbenzene Anion Exchangers**  
(A) SBA quaternary amine (B) WBA tertiary amine

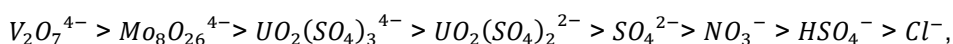
Polystyrene resins, cross linked with divinylbenzene, both gel and macroporous, have been widely used for uranium recovery from both acid and alkali leach liquors. The physical properties of the resin beads, such as size, bead uniformity, surface area, density, porosity, water retention and mechanical strength have a significant impact on the resin performance. For example macroporous resins, which have much larger surface areas than gel resins, exhibit faster elution kinetics for equivalent resins. Macroporous resins also have greater resistance to attrition and are therefore more useful for CIX and RIP applications.

The chemical properties of the resin, namely the type of functional groups and the number of active sites on the resin have an impact on metal loading and selectivity.

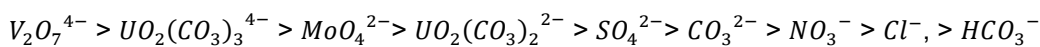
Strong base resins extract uranium from sulfate based acid liquors by an anion exchange type mechanism as outlined in equation (1). These resins are also effective for extracting uranyl carbonate complexes from alkali leach liquors.



Other anions in solution compete for the active sites with the following affinities in acidic liquors:



In alkali liquors at pH 9-10:



The resins can be eluted by elevated concentrations of anions such as nitrate, bisulfate, chloride and bicarbonate.

Weak base anion (WBA) exchange resins extract by the same mechanism as SBA resins but are only effective in acidic liquors. Macroporous weak base resins were investigated in the past but slower kinetics were reported for both loading and elution<sup>(41)</sup>. They have not found wide application. In addition, it was thought that macroporous resins were more significantly impacted by silica uptake when compared with gel type resins. More recent studies have confirmed higher silica uptake in macroporous resins when compared to gel resins, however, deterioration in performance was more significant with gel resins.

Chelating resins extract uranium via a cation exchange mechanism and are therefore subjected to cation rather than anion competition. A wide range of chelating functional groups are available and their use is application specific.

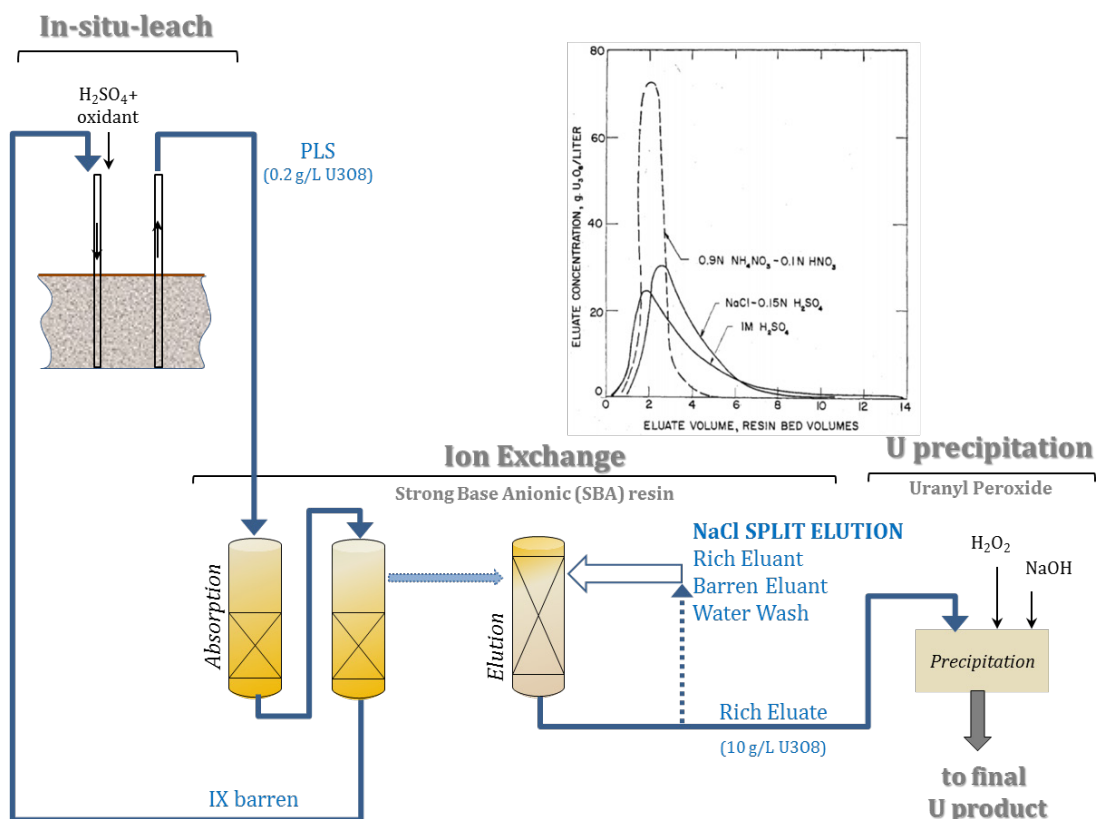
## EARLY IX PROCESSES FOR URANIUM RECOVERY

Fixed bed ion exchange (FBIX) technology found widespread use in South Africa, Australia, USA and Canada. In the late 1950's, 65 mills were operational in these four countries and some 50 plants used FBIX technology<sup>(7,9)</sup>.

These plants were operated with sets of three ion exchange cylindrical pressure vessels, of which two were used in series for adsorption operated in downflow mode. The third column would be off-line to allow for washing, elution and regeneration. The resin bed would typically occupy half the column to allow for bed expansion during upflow washing. In this type of arrangement, adsorption and elution is carried out in the same column and therefore there is no resin transfer. Resin loss was low and reported to be less 5% of total resin inventory per annum<sup>(5)</sup>. These systems were designed to treat clarified liquors containing < 20 ppm solids<sup>(13)</sup>. Nitrate based elution was used as a first choice because it is more effective than either sulfate or chloride as highlighted by the column data presented in **Figure 3A**.

Some of the drawbacks of the early FBIX processes were:

- Leakage can occur before the resin in the lead position is fully loaded. This leads to more frequent elution cycles which adds to cost of recovery;
- Operation of elution in downflow mode results in the resin at the bottom of the column being eluted the least and yet this value determines the lower limit of uranium concentration in the barren;
- The degree to which the columns can be scaled up is limited;
- No dissolved solids can be tolerated so highly clarified liquors are required in order to prevent blinding of the resin bed.



**Figure 3 – Fixed Bed IX Process – Beverly Uranium Mine, South Australia**<sup>(14,15)</sup>  
**Figure 3A (insert) – Elution of SBA resin with nitrate, chloride and sulfate**<sup>(16)</sup>

FBIX processes are still in use today, in particular for in-situ uranium recovery where filtration is not required. An example of an operating mine using FBIX is presented in **Figure 3**. The Beverley Mine, operated by Heathgate Resources, is situated in the Flinders Ranges in South Australia. It was



## In-Situ-Recovery (ISR) and Continuous Ion Exchange (CIX)

In-situ-leaching (ISL), also known as in-situ-recovery (ISR), is a very cost effective way of production, provided the deposits are amenable to ISR mining. Productivity is very high and capital costs are relatively low since there is no requirement for excavation, crushing, grinding and major solid liquid separation. The ease of site remediation, once the resource is exhausted, is an added attraction. Parallel development of this technology occurred in the USA and the Soviet Union in the 60's. The proportion of uranium recovered by ISR since the 2000's has become significant. In 2010 the IAEA reported an annual production by ISR of 22 905 t U, representing some 42% of total uranium production for that year. This proportion has steadily increased to 50% for 2017. Major current operating mines using ISR are listed in **Table 1**<sup>(22)</sup>.

Both alkaline and acid leaching can be used with ISR. The tenor of uranium in the PLS tends to be relatively low (< 200 mg/L U) and therefore IX has been adopted as the preferred separation and purification method. The development of continuous ion exchange using fluidized beds allows for treatment of unclarified liquors containing up to 2% solids<sup>(13)</sup>. Many designs have been proposed over the years<sup>(23,24)</sup>. The NIMCIX technology, developed in South Africa in the 70's, has been particularly successful and has been adopted for recent new builds (e.g. Husab Uranium and Langer Heinrich expansion in Namibia<sup>(12)</sup>).

In Kazakhstan, a modular approach using standardized designs (**Figure 5**), has contributed to rapid growth in uranium production in that country. Adsorption takes place in moving bed columns, operated upflow. Regenerated resin enters the top of the column at periodic intervals, and a similar volume of loaded resin leaves the column at the bottom. Resin elution takes place in a U-shaped contactor. The loaded resin leaving the sorption column, referred to as pre-loaded resin, enters the U-tube in the first leg, where it comes into contact with product liquor moving in a counter-current direction. In this section of the U-tube, further loading of uranium onto the resin occurs resulting in scrubbing of impurities such as ferric ion. Elution takes place in the second leg of the U-tube. Ammonium nitrate is commonly used as the eluent. The product liquor leaves at the bottom of the U-tube. Denitration of the resin is carried out with sulfuric acid followed by a water rinse. This can be done in separate columns, but denitration can also be carried out in the U-tube.

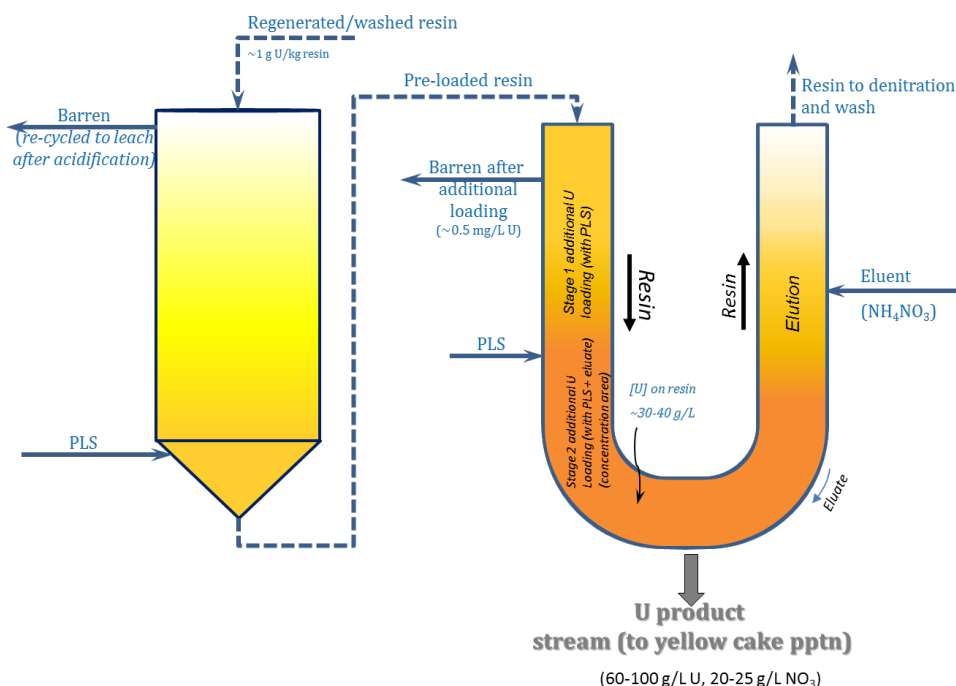


Figure 5 – ISL and CIX in Kazakhstan [24, 25]



Table 1 Production of Uranium by ISR in 2016<sup>(22)</sup>

Country	Production Centre	Principal Owner as of Dec. 2011	Start Up Year	Capacity (t U/a)	Leach Type	Resin	Eluant	U PLS* mg/L U	
Australia	Beverley	Heathgate Resources	2001	850	sulfuric acid	Dow 21K XLT	sodium chloride	-	
China	Yining II	CNNC	1994	300	sulfuric acid	-	ammonium nitrate (60 g/L)	82	
Kazakhstan	Akdala	Uranium One/KAP	2001	1,000	sulfuric acid	Amberlite IRA 910	ammonium nitrate	76	
	Budenovskoye 1, 3 and 4	Uranium One/KAP	2009	2,000	-	-	-	-	
	Budenovskoye (Karatau)	Uranium One/KAP	2007	2,000	sulfuric acid	Amberlite IRA 910 CI or MP-60021	ammonium nitrate	163	
	Central Mynkuduk	KAP	2007	2,000	sulfuric acid	Amberlite IRA 910	ammonium nitrate	-	
	Chieli (North and South Karamuran)	Mining Group-6 (KAP)	1985	1,250	sulfuric acid	-	ammonium nitrate	84	
	Inkai	Cameco/KAP	2002	2,000	sulfuric acid	-	ammonium nitrate	163	
	Irkol	KAP/China	2007	750	sulfuric acid	-	-	-	
	Kharasan 1	Uranium One/KAP/Energy Asia	2008	3,000	-	-	-	-	
	Kharasan 2	KAP/Japan	2009	2,000	sulfuric acid	Amberlite IRA 910 CI or MP-60021	ammonium nitrate	71	
	Muyunkum / Totkuduk	AREVA/KAP	2001	4,000	sulfuric acid	-	ammonium nitrate	-	
	Semizbai	KAP/China	1982/2009	500	sulfuric acid	-	-	-	
	South Inkai	Uranium One/KAP	2007	2,000	sulfuric acid	Amberlite IRA 910	ammonium nitrate	176	
	Pakistan	Stepnoye (Uvana, East Mynkuduk)	Stepnoye (KAP)	1978	1,300	sulfuric acid	-	ammonium nitrate	79
Taukent (Kanzugen, Moinkum)		Taukentskiy MCC (KAP0)	1983	1,200	sulfuric acid	-	ammonium nitrate	68	
West Mynkuduk		KAP/Japan	2008	1,000	sulfuric acid	-	ammonium nitrate	143	
Zarechnoye		KAP/ARMZ (Uranium One)	2007	1,000	sulfuric acid	-	ammonium nitrate	152	
Qabul Khel		PAEC	1995	40-60	ammonium bicarbonate	strong base anion	sodium chloride (2 M) and sodium bicarbonate (0.4 g/L)	-	
Russian Federation		Dalur	TVEL	2002	1,000	sulfuric acid	-	-	-
USA		Alta Mesa	Mestena	2006	680	alkaline groundwater	Dowex 21K XLT	sodium chloride	68
	Crow Butte (including Big Red)	Cameco Resources	1991	450	sodium bicarbonate	Dowex 21K XLT	sodium chloride	71	
	Hobson (Central Plant)	South Texas Mining Venture	-	450	-	-	-	55 (64)	
	Hobson-Palagana	South Texas Mining Venture	2011	450	alkaline - carbon dioxide	Dowex 21K XLT	9% sodium chloride 2% sodium carbonate	76	
	Smith Ranch Highland	Cameco Resources	1997	2,500	alkaline - carbon dioxide	Dowex 21K XLT	9% sodium chloride 2% sodium carbonate	204	
	Willow Creek (Irigary-Christensens Ranch)	Uranium One	1989/2011	590	sodium bicarbonate and carbon dioxide	Dowex 21K XLT	sodium chloride and sodium bicarbonate	62	
Uzbekistan	Mining Division No. 5 (Zafarabad)	Navoi Mining and Metal	1971	900	sulfuric acid	Resins State Enterprise Ukraine - AMP	ammonium nitrate	-	
	Southern Mining Division (Nuradad)	Navoi Mining and Metal	1966	650	-	-	-	-	
	Northern Division (Uchkuduk)	Navoi Mining and Metal	1964	750	-	-	-	-	

\*Italics - estimates of solution U concentration

The use of U-tube technology has been widely adopted in Kazakhstan with the following advantages being reported<sup>(24,25)</sup>:

- Reduced operating and capital costs;
- Replacement of 8-10 separate columns;
- More efficient elution with lower U in eluted resin leading to lower IX barrenness;
- Increased uranium concentration in the product stream (to 60–100 g/L U);
- Significant reduction of U elution time; and
- Simplified process with reduced resin inventory.

### **Resin-in-Pulp (RIP)**

A significant advantage of using resin rather than solvent extraction for uranium recovery is that resin processes can be very tolerant of solids including slurries. An additional potential benefit is the minimization of soluble uranium losses due to preg-robbing. Resin-in-pulp processes were developed in the late 1950's in both the USA and the USSR. Contactors comprised a series of agitated tanks through which the slurry and resin passed in a counter-current direction. Air lifts or pumps were used to screen resin and pass it on to the next tank. These Screen-Mix RIP Systems could tolerate pulp densities of 12-20% solids<sup>(5,6)</sup>. Extensive application of carbon-in-pulp technology, originally developed for the gold industry in South Africa, has provided improved designs applicable to RIP, sparking renewed recent interest in the application of RIP technology. The Kaylekera Uranium Mine in Malawi, operated between 2009 and 2014, used an acid leach/RIP/H<sub>2</sub>SO<sub>4</sub> elution and uranyl peroxide precipitation process. The development team examined a CCD/SX option but reported that the RIP based process offered lower capital and operating costs, better plant operability and reduced project risk<sup>(26)</sup>. RIP based flowsheets have also been tested at pilot plant scale for the Mantra Project in Tanzania<sup>(27)</sup>, the Mulga Rock Project in Western Australia<sup>(28)</sup> and at demonstration scale for the Harmony TPM Uranium Project in South Africa<sup>(29)</sup>.

## **FUTURE TRENDS AND INNOVATIONS**

In the pursuit of lower operating costs improvements will need to target greater process efficiencies through innovations relating to equipment design, process chemistry and process design. In the context of improved IX process performance this may be realized through the use of different resin functionality, improved elution methods and increased reagent recycle. Following are examples of such approaches, some of which have already been implemented in plant operations, whilst others have been piloted or are still in the research phase.

### **IX – Facilitating Reagent Recycle**

Reagent recycle within a process makes sense at many levels. The primary driver is operating costs reduction through decreased direct reagent addition, but this is often accompanied by other benefits such as reduced water requirements, reduced burden on waste water treatment and reduced salt formation. These additional benefits have positive environmental outcomes and help sustain a social license to operate.

#### ***Coupling IX Elution with Nanofiltration***

The conventional IX process using a strong base resin is very versatile in that elution is possible with a variety of reagents including sulfuric acid, sodium chloride and sodium bicarbonate. The cost of elution is a very significant component of operating costs for the IX process, so any reduction in eluent make-up is very attractive. A number of approaches and technologies have been coupled with IX for reagent recycle. The use of nanofiltration coupled with IX elution in particular, has been successfully implemented by Paladin Energy for both bicarbonate and sulfuric acid recycle to elution. At the Kaylekera Uranium Mine in Malawi using a sulfuric acid elution, 85% acid recovery has been reported, with savings amounting to US\$ 3/lb U<sub>3</sub>O<sub>8</sub>, including the savings associated with reagent addition for neutralization. At the Langer Heinrich Plant in Namibia, the application of nanofiltration to the concentrated IX eluate allowed for the recycle of 77% of sodium bicarbonate with a saving of US\$ 6/lb U<sub>3</sub>O<sub>8</sub>, including those of NaOH used for uranium precipitation<sup>(30)</sup>. In addition to allowing for reagent recycling, the coupling of IX with nanofiltration also provides a way of concentrating the

uranium which is similar to coupling the IX and SX as per the Eluex/Bufflex process.

Nanofiltration for eluent recycle can also be applied to sodium chloride based eluents. This was first applied in the context of rehabilitation of uranium mines in Germany<sup>(31)</sup> and was later tested by ANSTO in the context of an IX process to recover uranium from saline liquors containing 10 g/L chloride (**Figure 6**). The presence of chloride has a negative impact on the loading of uranium on SBA resins (**Figure 9A**). The ANSTO work demonstrated that weak base anion exchange (WBA) resins were a more appropriate choice of resin for this application and that nanofiltration could effectively be coupled with NaCl elution. Sodium chloride recoveries of 72% to the permeate were reported, with the uranium being upgraded in concentration from 0.23 g/L  $U_3O_8$  in the PLS to 6.7 g/L  $U_3O_8$  in the retentate from nanofiltration<sup>(32)</sup>. An additional benefit is that WBA resins tend to be slightly more selective than SBA resins and direct recovery from the nanofiltration retentate is possible. Sodium chloride elution coupled with nanofiltration was adopted by VIMY Resources for the Mulga Rock project in Western Australia. Pilot plant testing of the acid leach, RIP, NaCl elution and Nanofiltration process demonstrated an upgrade from ~ 0.5 g/L  $U_3O_8$  in the RIP feed to 20 g/L  $U_3O_8$  in the nanofiltration retentate<sup>(28)</sup>.

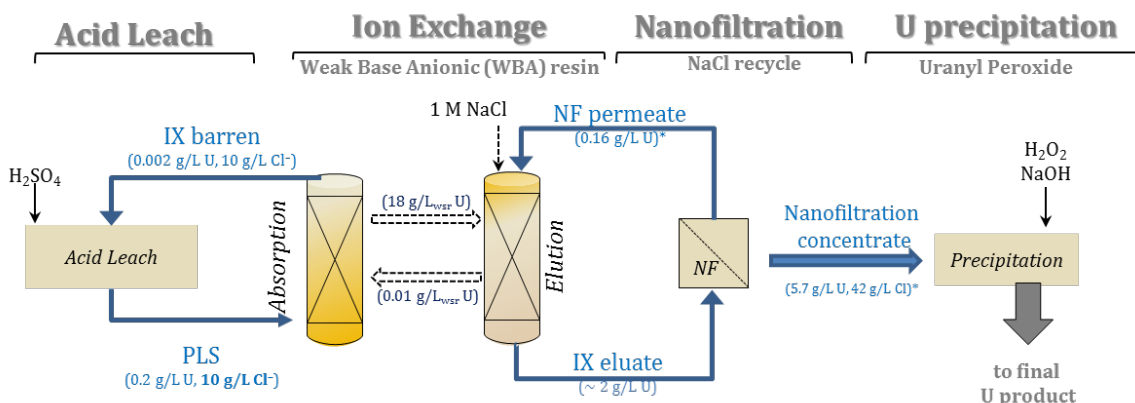


Figure 6 – ANSTO Process for Saline Liquor (10 g/L Cl) Using a Weak Base Resin<sup>(32)</sup>

### Recycling Acid with Chelating Resin

A novel approach to reagent recycle has been proposed by A-CAP for treatment of the Lethakane deposit in Botswana, where an SX/IX combination is proposed, which is the reverse of the established Eluex/Bufflex Process. The challenge here was the requirement for a high acid leach in a heap leaching operation, where acid recycle was highly desirable. Solvent extraction coupled with a strong acid strip was used for recovery of uranium from the PLS. Ion exchange was used to extract uranium from the strong acid strip solution to allow for acid recycle back to the solvent extraction strip circuit. For this duty, a conventional SBA resin is not effective as the strong acid strip is carried out at ~ 400 g/L  $H_2SO_4$ . Chelating cation exchangers, however, can function at various acidic environments, depending on the particular resin functionality<sup>(38)</sup>. In this case an aminophosphonic acid functionality was chosen which can achieve relatively high uranium loadings, as outlined in the data presented in **Figure 9C**. In this application a primary purpose of the IX circuit is to facilitate acid recycle.

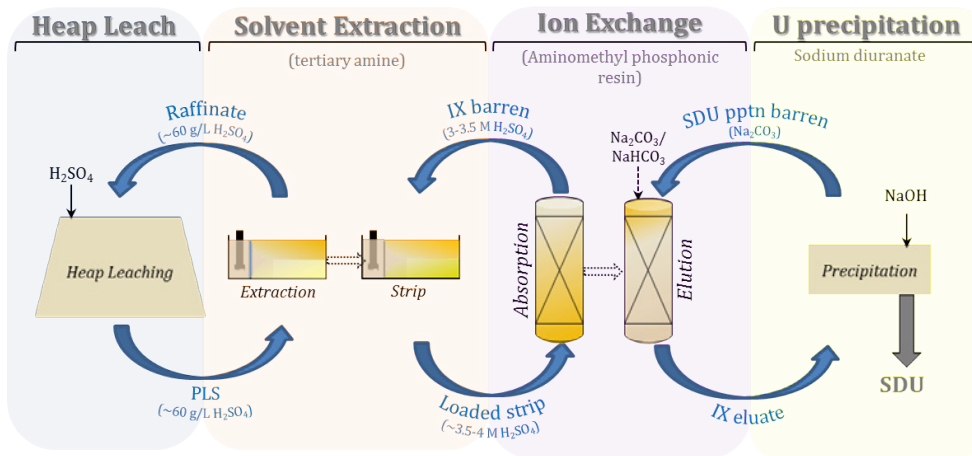


Figure 7 – Acid Recycle Proposed for the Letlhakane Project in Botswana<sup>(33)</sup>

**IX for Impurity Removal to Facilitate Nanofiltration**

This application refers to the coupling of IX with nanofiltration, but it differs from the previous examples in that the IX function is not to concentrate and purify uranium but to support nanofiltration, which in turn facilitates reagent recycle. The application is in the context of an alkali uranium leach process, where the PLS contains sodium carbonate and sodium bicarbonate. There are two principle routes to recover uranium from the alkaline PLS, namely; direct precipitation of SDU from the PLS, and extraction of uranium using a SBA resin. In both cases, the uranium barren after precipitation or ion exchange, is recycled back to the leaching step to allow for reagent recycle. This application provides a third option, namely concentration of the PLS using nanofiltration. This is particularly useful for low-grade uranium ores, particularly when chloride is present and conventional IX is not applicable. The function of the IX process is to prevent supersaturation of divalent Ca and Mg in the retentate, which causes fouling and scaling. For this purpose, a chelating resin with an aminophosphonic or iminodiacetic acid can be used. The approach is presented in **Figure 8**.

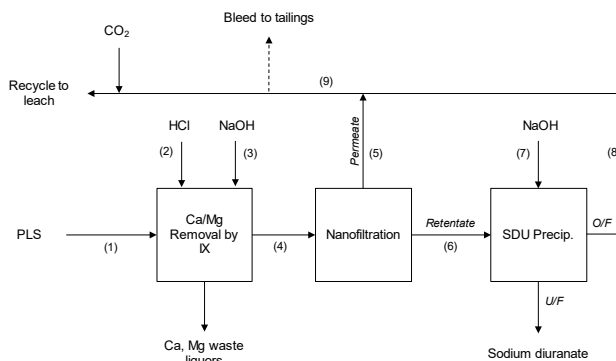


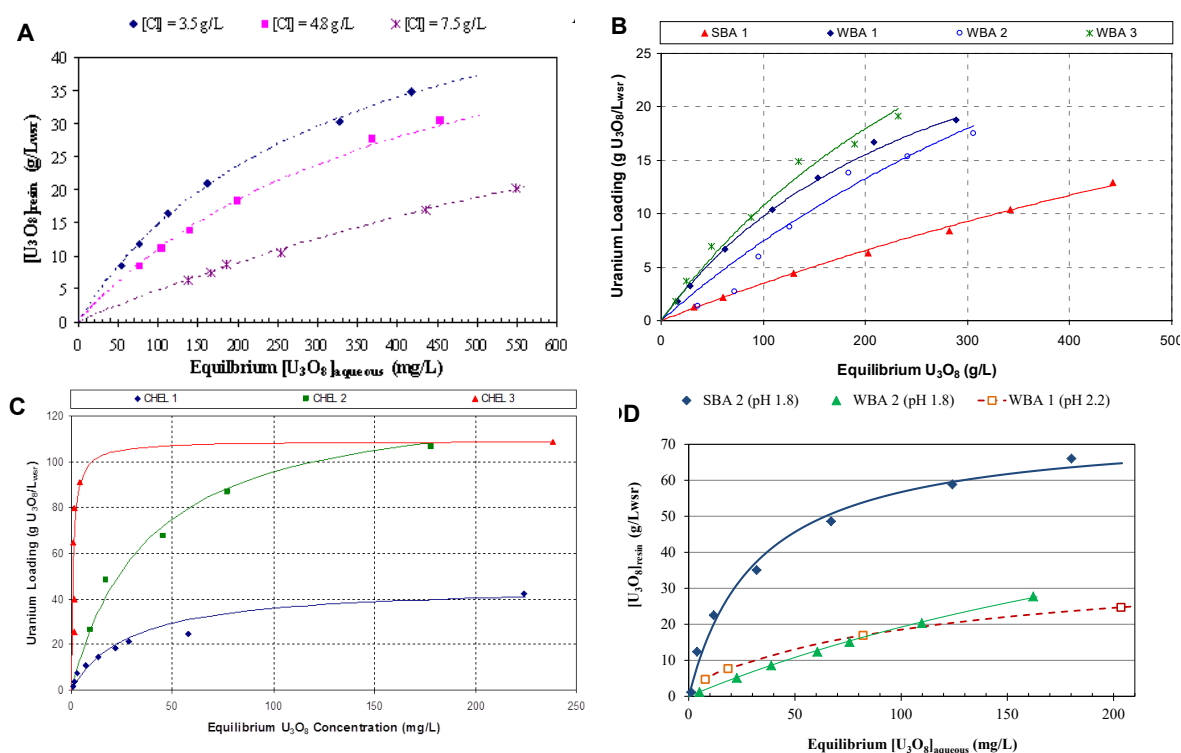
Figure 8 – IX in the Uranium Alkaline Flowsheet for Ca and Mg Removal<sup>(34)</sup>

**IX Processes Addressing Challenges Related to Saline Liquors**

The application of IX to the recovery of uranium from saline liquors can be problematic due to reduced loadings with conventional SBA exchange resins. To address this challenge particular attention needs to be paid to resin chemistry. The data presented in **Figure 9A** demonstrates why 5 g/L chloride in the PLS is generally considered an upper limit for operation of an IX process based on conventional SBA resins. As discussed in a previous section, WBA exchange resins are more tolerant of chloride. Data presented in **Figure 9B**, shows that at chloride concentrations in the PLS of 12 g/L, a range of WBA resins with tertiary amine functionality significantly outperform the reference SBA resin.

Chelating resins with various functionalities are not impacted by chloride at all and very high loadings can be achieved (**Figure 9C**). However, chelating resins are not selective and extract a range of cations including ferric ion. In some cases co-extraction of ferric with uranium can be tolerated. This approach was considered in laboratory studies for the Sapphire Uranium Project in South Australia, where an iminodiacetic chelating resin was used to extract uranium from a PLS containing 23 g/L Cl at pH 1.5. The loaded resin was eluted with 1 M H<sub>2</sub>SO<sub>4</sub> and iron removed by lime addition prior to uranium recovery<sup>(35)</sup>.

More recently, significant progress was made in identifying a resin with superior loading performance in the presence of chloride. The resin is a macroporous SBA resin with complex quaternary amine functionality and an acrylic matrix. Loading isotherm data obtained at ~ 9 g/L Cl, highlighting the enhanced performance of this SBA resin compared with two WBA resins with tertiary amine functionality, is presented in **Figure 9D**. This resin was successfully tested by Boss Resources at the Honeymoon site in South Australia, in an ISR Field Leach Trial integrated with uranium recovery by IX. Sodium chloride was used to elute the resin. The trial achieved a concentration upgrade factor of ~ 50 from a PLS containing 50 mg/L U<sub>3</sub>O<sub>8</sub>. The IX eluate uranium concentration achieved was ~2.5 g/L U<sub>3</sub>O<sub>8</sub><sup>(36)</sup>.



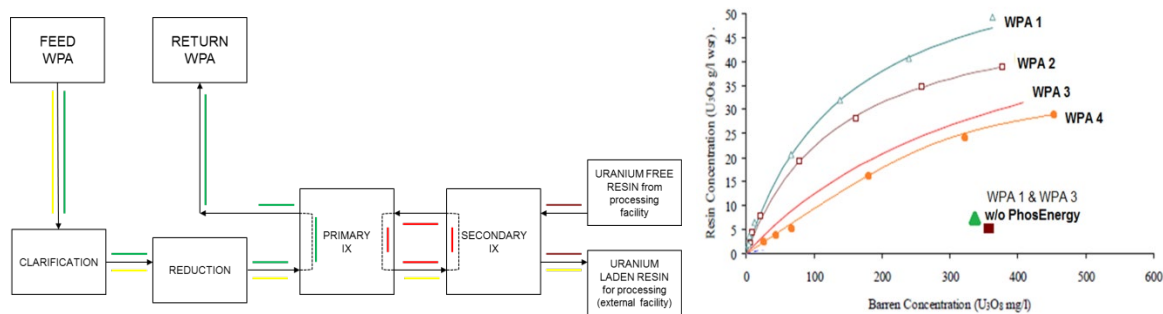
**Figure 9 – Impact of Resin Functionality of Efficacy of Uranium Loading**

- A. Impact of Chloride: SBA Dowex 21KXLT, pH 1.8, 9 g/L sulfate<sup>(17)</sup>  
 B. Impact of Chloride: SBA 1:Amberjet 4400, pH 1.2, 12 g/L Cl, WBA 1-3 Tertiary amine<sup>(32,37)</sup>  
 C. CHEL1: iminodiacetic; CHEL2: phosphonic/sulphonic; CHEL3: aminophosphonic  
 pH 1.6, 22 g/L Cl<sup>(32,38)</sup>  
 D. SBA complex quaternary amine; WBA: tertiary amine, pH 1.8, 8.8 g/L Cl<sup>(36)</sup>

## IX for Uranium Recovery from Phosphoric Acid

The PhosEnergy® process, outlined in **Figure 10A**, removes uranium from wet phosphoric acid (WPA), with no impact on the downstream production of phosphoric acid, which in turn is a precursor for fertilizer production. Thus this process offers a dual benefit of uranium by-product recovery and impurity removal from WPA. This patented technology is being commercialized by Urtek LLC<sup>(39)</sup>. The process, jointly developed with ANSTO, is based on ion exchange technology. The primary ion exchange process uses a chelating aminophosphonic acid resin to extract uranium from the WPA. Elution is carried out with sodium carbonate and a secondary IX process, using a conventional SBA resin is used, to allow for eluent recycle. Specialized, pre-treatment of the feed to primary IX, targeted at each individual WPA feed, is important to ensure appropriate resin loadings are achieved (**Figure**

**10B).** This process highlights the potential for IX to become more relevant in the recovery of uranium as a by-product, by exploiting different resin chemistries.



**Figure 10A – The PhosEnergy® Process<sup>(39)</sup>**

**Figure 10B – Impact of Pre-treatment on Uranium Adsorption in the Primary IX<sup>(39)</sup>**

### Innovation with Respect to IX Elution

Elution is a significant component of operating costs in an IX process and therefore, targeting reagent recycle, increased resin loading to reduce number of elutions per unit of uranium produced, and increased concentration of uranium in the eluate are likely targets for innovation. Partial eluate recycle to boost the concentration in the eluate is conventional practice in FBIX processes. In Kazakhstan, eluate recycle is practiced in a manner akin to product scrubbing in solvent extraction. Namely, the recycle of product stream at elevated uranium concentrations boosts the uranium loading on the resin which in turn increases the equilibrium concentration of eluate feeding the product recovery. This practice, which is different from the split eluate recycle, has not yet been adopted elsewhere. However, there are suggestions that this approach could be used with good effect in merry-go-round CIX systems, where post adsorption scrubbing, potentially with product liquor, could be implemented<sup>(5)</sup>.

Less common has been the suggestion of a novel approach to elution differing from what has been historically performed, based on variations of chloride, sulfuric acid, ammonium nitrate and ammonium bicarbonate elution. These elution schemes are appropriate for elution of conventional SBA and WBA resins. As more complex resin functionalities are explored, the elution also becomes more complicated. For example, the resin used in the Boss Resources pilot plant, with a complex strong base functionality, cannot be eluted with sulfuric acid. Sodium chloride elution, although feasible, is not very favourable. In order to address this challenge, ANSTO has devised a new patented elution method, which first converts the loaded uranyl sulfate into the carbonate form, prior to elution with chloride. This approach allows for a higher concentration of uranium to be achieved in the eluate stream.<sup>(40)</sup>

### CONCLUSIONS

The application of IX technology is still very relevant to the modern hydrometallurgical flowsheet for uranium recovery. Ion exchange has found particular relevance in in-situ recovery applications, where lower grade tenors in the PLS and the need to avoid solvent contamination in liquors returning to the wellfields are drivers for IX technology. The high tolerance of resins for solids, including slurries, provides additional flexibility for process design.

Looking to the future, innovations are likely to occur where ion exchange has the potential to address particular challenges either on its own or coupled with other technologies such as nanofiltration and solvent extraction. Drivers relating to reduction in reagent consumption, increased product purities and recovery of uranium from challenging liquors will drive the exploration of different resin chemistries.

**REFERENCES**

1. Uranium 2016: Resources, Production and Demand. A Joint Report by the Nuclear Energy Agency and the International Atomic Energy Agency; 2016.
2. World Uranium Mining Production. <http://www.world-nuclear.org/information-library/nuclear-fuel-cycle/mining-of-uranium/world-uranium-mining-production.aspx>.
3. American Uranium. Ready to Go Further (by Energy Fuels). <http://www.energyfuels.com/wp-content/uploads/2017/03/Last.pdf>.
4. International Monetary Fund (Commodity Data Portal). <https://www.imf.org/en/Research/commodity-prices>.
5. A. Taylor Emerging Trends in the Development and Application of Uranium IX Systems, ALTA 2015 Uranium-REE Conferences, Perth, Australia, 2015; pp 310-322.
6. R. C. Merritt, The extractive metallurgy of uranium. Johnson Publishing Company: Boulder, Colorado, 1971.
7. Ion Exchange Technology in the Nuclear Fuel Cycle; IAEA-TECDOC-365; International Atomic Energy Agency: Vienna, 1986.
8. M. Streat; D. Naden, Ion Exchange in Uranium Extraction. In Ion Exchange and Sorption Processes in Hydrometallurgy, John Wiley & Sons: 1987; Vol. 19 pp 1-55.
9. M. A. Ford, Uranium in South Africa. J South Afr Inst Min Metall. 1993, 93 (2), 37-58.
10. The Development of Processes for Uranium Recovery; Application report no. 16.; Council for Mineral Technology (South Africa): Randburg, South Africa, 1996; p 53.
11. K. C. Sole; P. M. Cole; A. M. Feather; M. H. Kotze, Solvent Extraction and Ion Exchange Applications in Africa's Resurging Uranium Industry: A Review. Solvent Extr Ion Exc 2011, 29 (5-6), 868-899.
12. K. C. Sole; M. B. Mooiman; E. Hardwick Present and Future Applications of Ion Exchange in Hydrometallurgy: An Overview, Ion Exchange 2016, Cambridge, UK, 6-8 July; 2016.
13. D. van Tonder; D. Lunt; S. Donegan Selecting the Optimum IX System for Uranium Recovery, ALTA 2010 Nickel-Cobalt-Copper, Uranium & Gold Conferences, Perth, Australia, 2010.
14. H. Märten, Environmental Management and Optimization of In-situ-Leaching at Beverley. In Uranium in the Environment: Mining Impact and Consequences, Merkel, B. J.; Hasche-Berger, A., Eds. Springer-Verlag: Berlin Heidelberg, 2005; pp 537-546.
15. B. Jeunken; H. Marten; R. Phillips Uranium ISL Operation and Water Management under the Arid Climate Conditions at Beverley, Australia, Mine Water and the Environment. Proceedings 10th IMWA Congress, Carlovy Vary, Czeck Republic, June 2-5, 2008; 2008; pp 487-490.
16. A. H. Greer; A. B. Mindler; J. P. Termini, New Ion Exchange Resin for Uranium Recovery. Ind Eng Chem. 1958, 50 (2), 166-170.
17. K. Soldenhoff; J. Davidson Uranium Recovery from Highly Saline In-Situ Leach Solutions by Ion Exchange, First Extractive Metallurgy Operators Conference, Brisbane, Australia, 2005; pp 47-51.
18. B. Jones; H. Marten ISL Uranium Mining at Beverley Mine, Australia - Development Issues and Wellfield Design Optimisation, Global Uranium Symposium, Casper, Wyoming, US, Casper, Wyoming, US, 11-13 July, 2005; 2005.
19. G. M. Joost; M. H. Kotze; D. Auerswald The Advantages of True Continuous Counter Current Elution in Uranium Processing, ALTA 2010 Nickel-Cobalt-Copper, Uranium & Gold Conferences, Perth, Australia, 2010.

20. D. Lunt; P. Boshoff; M. Boylett; Z. El-Ansary, Uranium Extraction: the Key Process Drivers. *J South Afr Inst Min Metall.* 2007, 107 (7), 419-426.
21. K. C. Sole; A. M. Feather; P. M. Cole, Solvent Extraction in Southern Africa: an Update of Some Recent Hydrometallurgical Developments. *Hydrometallurgy* 2005, 78 (1-2), 52-78.
22. In Situ Leach Uranium Mining: An Overview of Operations; NF-T-1.4; IAEA: 2016.
23. Uranium Extraction Technology; Technical reports series No. 359; International Atomic Energy Agency: Vienna, 1993.
24. Y. V. Nesterov, Иониты и ионный обмен. Сорбционная технология при добыче урана и других металлов методом подземного выщелачивания (Ion exchangers and ion exchange. Sorption technology in the extraction of uranium and other metals by in-situ leaching. Unicorn-Izdat: Moscow, 2007.
25. Инструкция (Методические рекомендации) по подземному скважинному выщелачиванию урана (Guidelines for In-Situ Leaching of Uranium). Kazatomprom: Almaty, 2006.
26. D. Marsh; D. Hladun An Overview of the Kayelekera Uranium Mine in Malawi, ALTA 2010 Nickel-Cobalt-Copper, Uranium & Gold Conferences, Perth, Australia, 2010.
27. S. J. Archer; J. A. Coetzee; E. L. Forner; N. Morgan; M. H. Kotze Solvent Extraction versus Nano-Filtration for Upgrading Uranium and Recovery of Acid from an Ion Exchange Eluate, ISEC 2014: International Solvent Extraction Conference, Würzburg (CCW), Germany, 07–11 September 2014; 2014.
28. C. Czerny; A. Wylder; T. Chamberlain Pilot Testwork for the Process Development of the Mulga Rock Project, ALTA 2017 Uranium-REE Conference, Perth, Australia, 2017; pp 56-71.
29. D. Auerswald; T. Udayar; M. Kotze; J. Scheepers Operation of a Resin- In-Pulp (RIP) Demonstration Plant for Recovering Uranium from a South African Gold Pulp, ALTA 2011 Uranium Conference, Perth, Australia, 2011; pp 103-115.
30. M. Peacock; S. McDougall; P. Boshoff; D. Butcher; M. Ford; S. Donegan; D. Bukunkwe Paladin Energy LTD - Nano-Filtration Technology for Reagent Recovery, ALTA 2016 Uranium-REE Conference, Perth, Australia, 2016; pp 264-275.
31. G. Kiessig; R. Gatzweiler; A. T. Jakubick Remediation Options and the Importance of Water Treatment at Former Uranium Production Sites in Eastern Germany; IAEA-TECDOC--1419; International Atomic Energy Agency (IAEA), 2004; pp 127-143.
32. A. Wilson; M. Fainerman-Melnikova; K. Soldenhoff What are the Options for an Integrated IX Process to Recover Uranium from Saline and Hypersaline Liquors, ALTA 2011 Uranium Conference, Perth, Australia, 2011; pp 116-126.
33. G. Dunn; Y. Y. Teo Recovery of Uranium from a Strong Sulfuric Acid Loaded Strip or Eluate, ALTA 2015 Uranium-REE Conferences, Perth, Australia, 2015.
34. A. Manis; J. Quinn; K. Soldenhoff; B. Ring Process for Uranium Recovery from Alkaline Liquors. AU2018100122, 2018.
35. S. Hall Metallurgical Development of the Samphire Uranium Project, ALTA 2012 Uranium Conferences, Perth, Australia, 2012; pp 151-166.
36. K. Soldenhoff; J. E. Quinn; T. Safinski; K. Bowes; M. Ford In Breakthrough in Uranium Recovery from Saline Liquors by Ion Exchange, Extraction 2018, Davis, B. R.; Moats, M.; Wang, S., Eds. Springer International Publishing: 2018; pp 2137-2147.
37. M. Fainerman-Melnikova; K. Soldenhoff, Uranium extraction from saline solutions using weak base anionic resins. *CIM Journal* 2012, 3 (2), 117-124.



38. M. D. Ogden; K. Soldenhoff The Role of Chelating Resins in Uranium Processing, ALTA 2013 Nickel-Cobalt-Copper Uranium-REE & Gold-Precious Metals, Perth, Australia, 2013.
39. M. Penington The PhosEnergy Process: Uranium from Phosphates, The AusIMM International Uranium Conference, Perth, Australia, 2014.
40. J. Quinn; K. Soldenhoff; A. Brennan Method of Eluting an Anion Exchange Resin Loaded with Uranium. AU2018101344, 2018.
41. F. X. McGarvey, J. Ungar The Influence of Resin Functional Group on the Ion Exchange Recovery of Uranium. J South Afr Inst Min Metall. 1981, 93-100