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ALTA 2010
URANIUM

PROJECT DEVELOPMENT

MINERALOGICAL VARIATION IN THE LETLHAKANE URANIUM PROJECT, BOTSWANA AND IMPLICATIONS ON PROCESS OPTIONS

By

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and

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Talk Outline

- Geological setting of the Letlhakane Uranium deposit.
- Variation in the mineralogy of the three main ore types – primary, oxide and secondary.
- Summary of the metallurgical test work conducted to date on these 3 ore types.
- Discussion of the potential process options for the project.

Project Location

Letlhakane Uranium Project

Project Location

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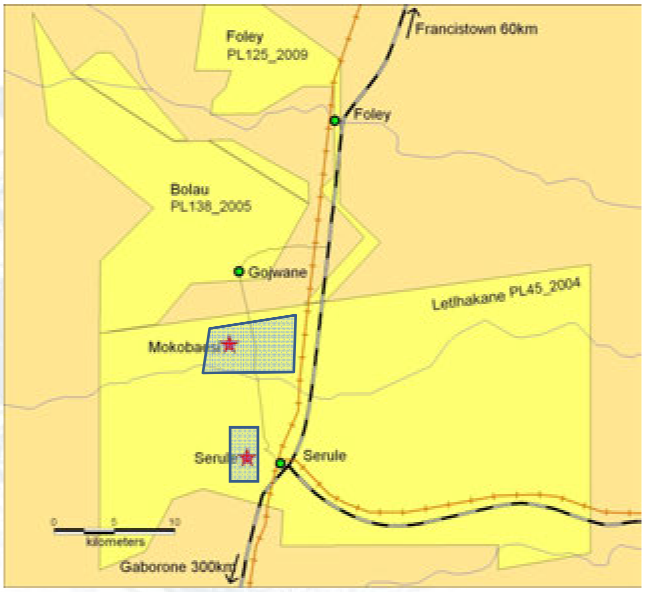

Regional Geology

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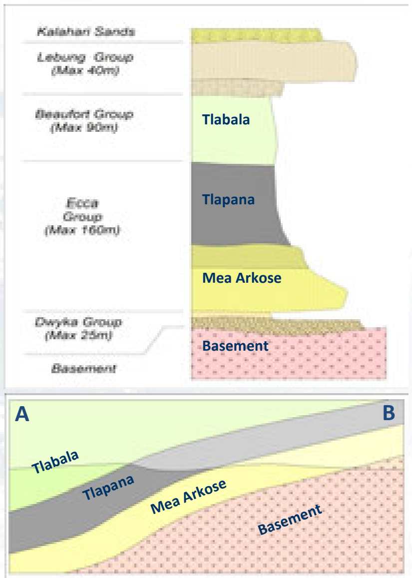
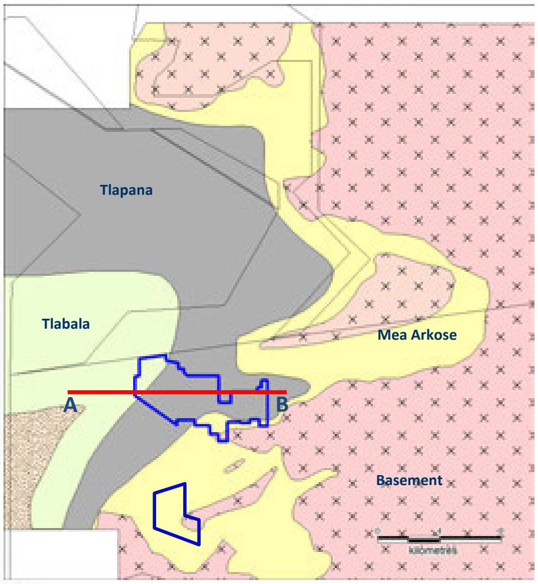
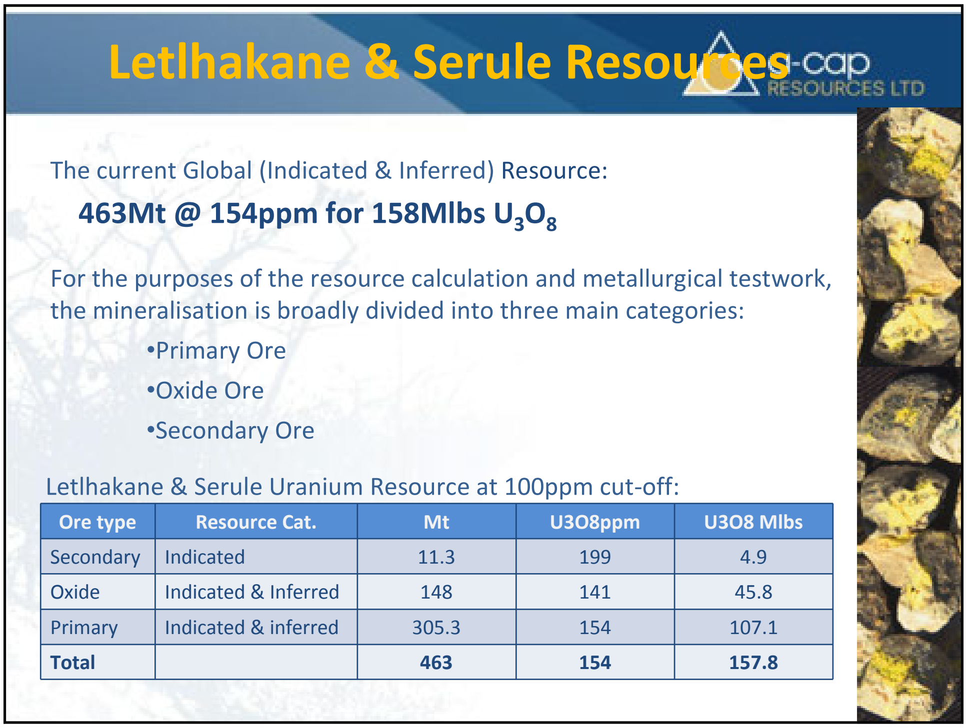






Letlhakane & Serule Resources

The current Global (Indicated & Inferred) Resource:

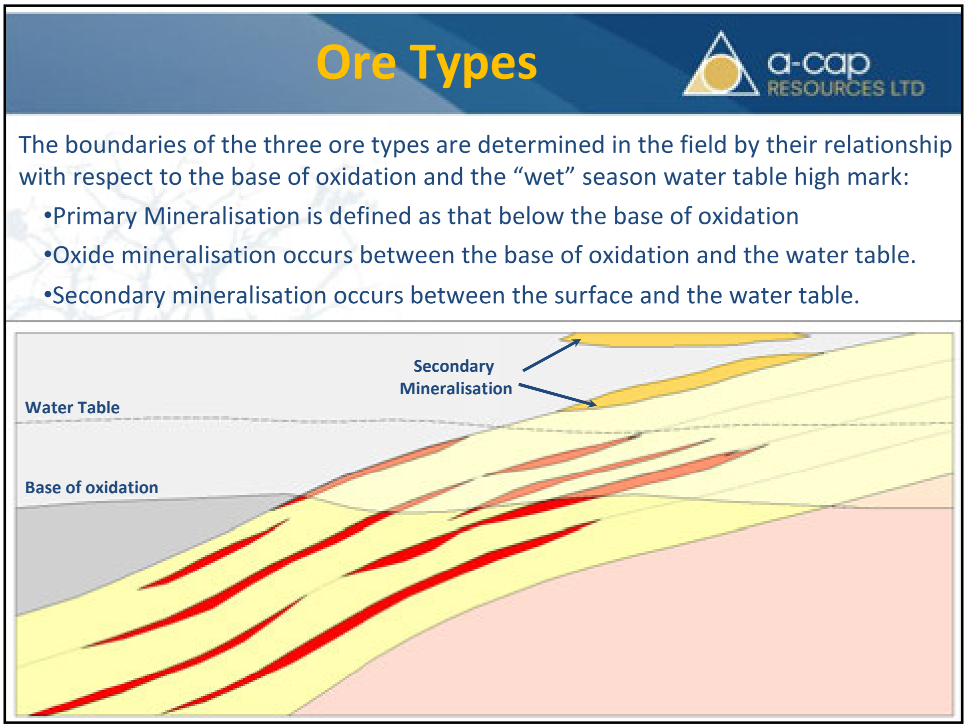
463Mt @ 154ppm for 158Mlbs U_3O_8

For the purposes of the resource calculation and metallurgical testwork, the mineralisation is broadly divided into three main categories:

- Primary Ore
- Oxide Ore
- Secondary Ore

Letlhakane & Serule Uranium Resource at 100ppm cut-off:

Ore type	Resource Cat.	Mt	U3O8ppm	U3O8 Mlbs
Secondary	Indicated	11.3	199	4.9
Oxide	Indicated & Inferred	148	141	45.8
Primary	Indicated & inferred	305.3	154	107.1
Total		**463**	**154**	**157.8**



Ore Types

The boundaries of the three ore types are determined in the field by their relationship with respect to the base of oxidation and the "wet" season water table high mark:

- Primary Mineralisation is defined as that below the base of oxidation
- Oxide mineralisation occurs between the base of oxidation and the water table.
- Secondary mineralisation occurs between the surface and the water table.

Primary Ore

Three different types of primary ore are recognised below the base of oxidation:

- Syn- sedimentary – Placer Style Ore
- Syn-sedimentary – Humate Ore
- Re-distributed Channel Ore

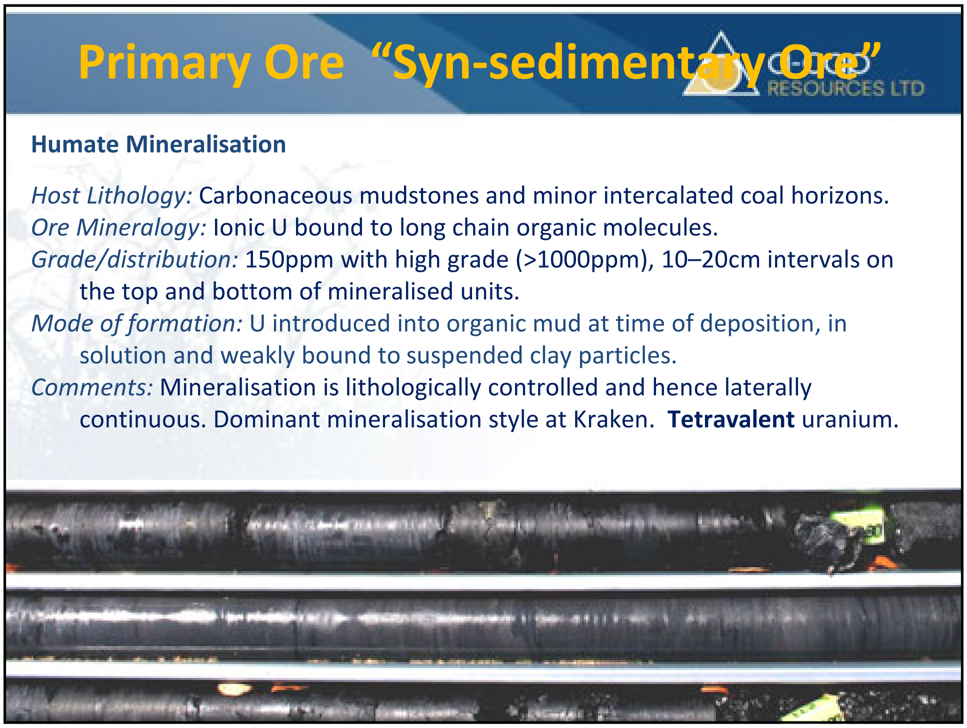
These ores are mineralogically distinct and have different metallurgical characteristics.

Primary Ore “Syn-sedimentary Ore”

Placer Mineralisation

Host Lithology: Arkosic Sandstones
Ore Mineralogy: Orthobrannerite & uraninite
Grade/distribution: Grades of up to 1000ppm U over < 1m. Concentrated in 1-2cm bands.
Mode of formation: Heavy mineral accumulates and as disseminated grains.
Comments: Strong correlation with Ti, Fe & Zr, Limited contribution of overall resource. All **tetravalent** uranium species.

Depth	U	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Zr
28.01 - Spot 1	212	671	15	12	539	9	0	17	7	39	257	27311
28.01- Spot 2	**1155**	**15476**	299	175	**10428**	126	83	578	87	377	312	**233193**
28.01 - Spot 3	**761**	**6393**	160	94	**4641**	51	50	250	40	180	292	**111795**
28.01 - Spot 4	142	483	11	5	422	4	-2	10	2	18	383	11809



Primary Ore "Syn-sedimentary Ore"

Humate Mineralisation

Host Lithology: Carbonaceous mudstones and minor intercalated coal horizons.

Ore Mineralogy: Ionic U bound to long chain organic molecules.

Grade/distribution: 150ppm with high grade (>1000ppm), 10–20cm intervals on the top and bottom of mineralised units.

Mode of formation: U introduced into organic mud at time of deposition, in solution and weakly bound to suspended clay particles.

Comments: Mineralisation is lithologically controlled and hence laterally continuous. Dominant mineralisation style at Kraken. **Tetravalent** uranium.

Primary Ore – Re-distributed Channel Ore

Host Lithology: Upward fining, intercalated sandstone, siltstone & mudstone.

Ore Mineralogy: Uraninite & coffinite (secondary uranophane), humate bound uranium and pitchblende.

Grade/distribution: Aver. grade of 150ppm with high grade (>1000ppm), <1m intervals associated with reductants.

Mode of formation: U leached from other primary ore types by circulating groundwater, re-precipitates uranium in highly reductive portions of the channel facies.

Bitumen bands within fine sandstone(X4 Field of View – 2.8mm PPL)

Fine grained, sandstone with uraninite grain; X10 Field of View – 1.16mm PPL

Oxide Ore

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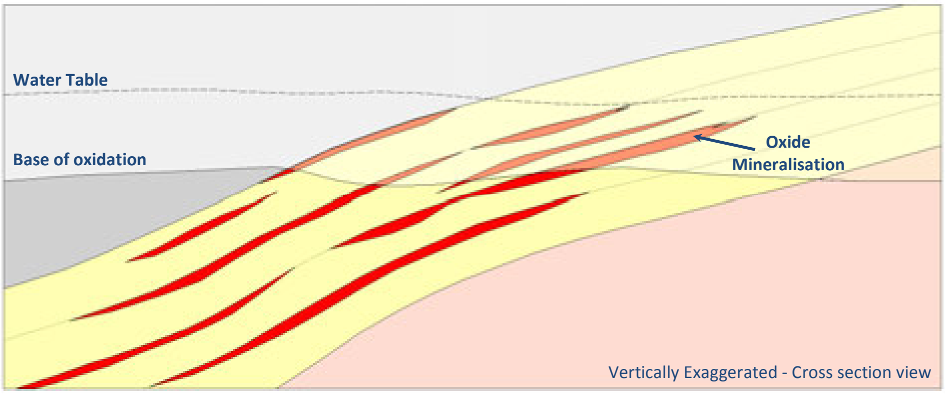
The oxide mineralisation is developed due to the vertical migration of groundwater (water table fluctuations) through the pre-existing primary mineralisation over time.



Oxide Ore

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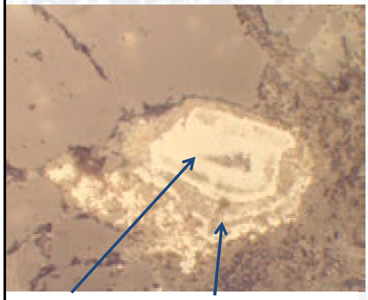
Host Lithology: Primary host lithologies.

Ore Mineralogy: Coffinite, uranophane, becquerlite, ferganite, francvillite, protasite,, strelkinite, tyuyamunite, umohoite & remnant uraninite & orthobrannerite

Grade/distribution: Similar distribution and grade to the primary ore styles.

Mode of formation: Insitu weathering and oxidation of host rocks and mineralogy. Uranium has NOT been transported out of original host lithologies

Comments: Transitional to primary ore. U minerals are **tetra and hexavalent.**

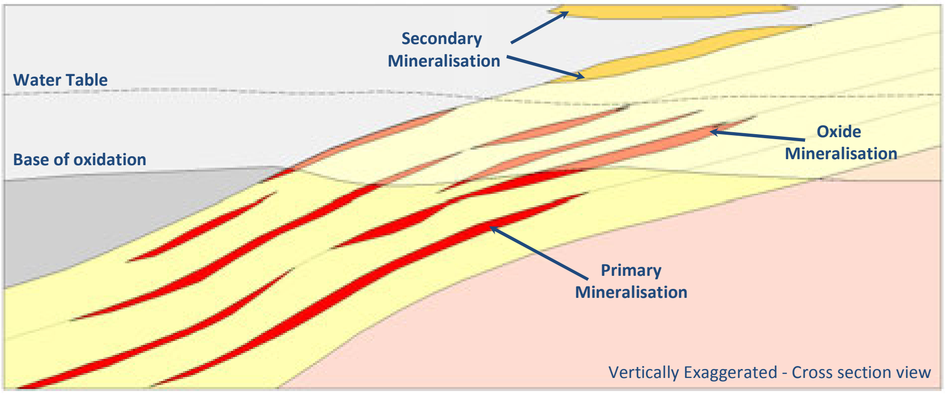


Uraninite replaced by coffinite . **X40 Field of View – 0.28mm ;RL**

Secondary Ore

Two styles of "Supergene" secondary ore have been identified:

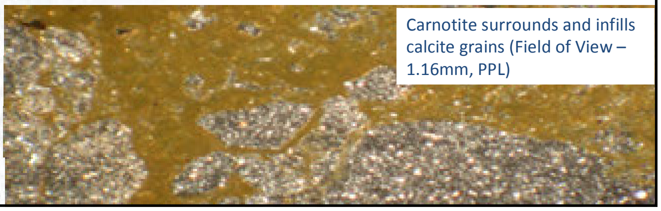
- Calcrete hosted ore (1 – 5m depth)
- Mudstone hosted ore (8 – 18m depth)



Secondary Ore

Calcrete Hosted Ore

Host Lithology: Pedogenic calcrete
Ore Mineralogy: Francvillite, schoepite, tyuyamunite, carnotite, fourmarierite, margarsitasite,S-U-V-OH & Fe-U-oxide
Grade/distribution: Aver. grade of 200ppm.
Mode of formation: U leached from primary & oxide ore, and is transported into near surface lithologies where it is precipitated.
Comments: Uranium minerals are hexavalent and coarse grained ensuring excellent leach characteristics.



Carnotite surrounds and infills calcite grains (Field of View – 1.16mm, PPL)

Secondary Ore

Mudstone Hosted Ore

Host Lithology: Highly weathered mudstone

Ore Mineralogy: Francvillite, schoepite, tyuyamunite, carnotite, fourmarierite, margarsitasite,S-U-V-OH & Fe-U-oxide

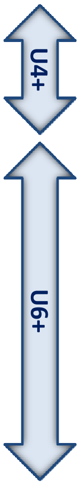
Grade/distribution: Aver. grade of 200ppm.

Mode of formation: U leached from primary & oxide ore, migrates into near surface lithologies and is precipitated via several different mechanisms

Comments: Uranium minerals are hexavalent and coarse grained ensuring excellent leach characteristics.

MOKD0031 – 15m

Summary of ore types - Mineralogy

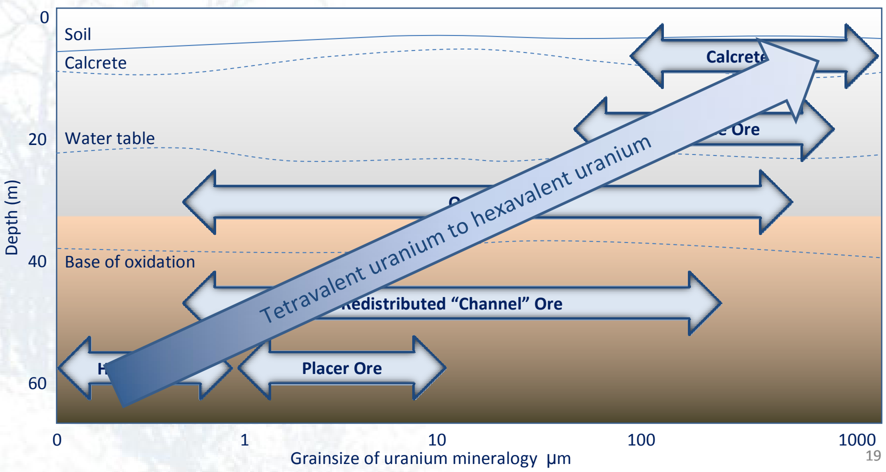


	Primary			Oxide	Secondary
	Humate	*Placer*	*Re-distributed*	*All types*	*All types*
Humate U	■		■		
Pitchblende	■		■		
Orthobrannerite		■	■		
Uraninite		■	■		
Coffinite			■	■	
Uranophane			■	■	
Becquerlite				■	
Ferganite				■	
Francvillite				■	■
Protasite				■	
Schoepite				■	■
Strelkinite				■	
Tyuyamunite				■	■
Umohoite				■	
Carnotite					■
Fourmarierite					■
Margarisitasite					■
Sr-U-V-OH					■
Fe - U Oxide					■

R. Bowell, 2009

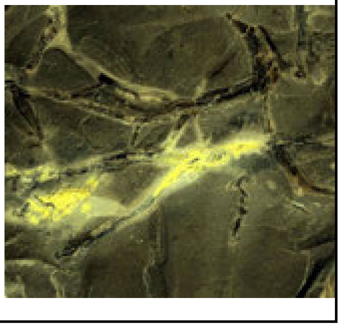
Summary of Ore Types - Grainsize

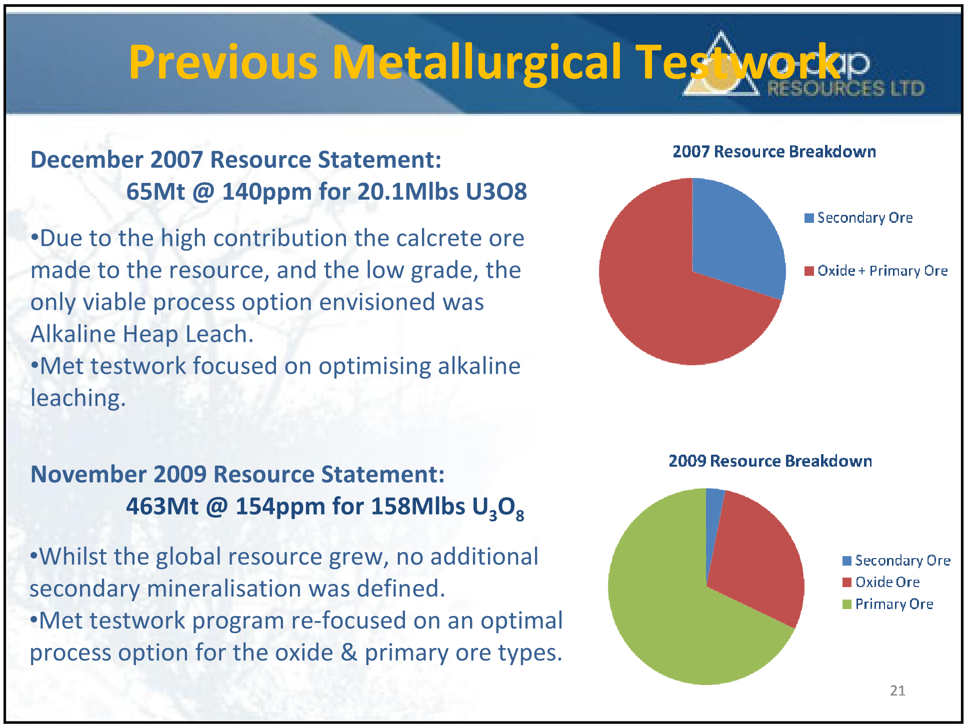
- Increasing oxidation and remobilisation results in an overall increase in the grain size of the ore forming minerals.



Metallurgy



Previous Metallurgical Testwork

December 2007 Resource Statement:

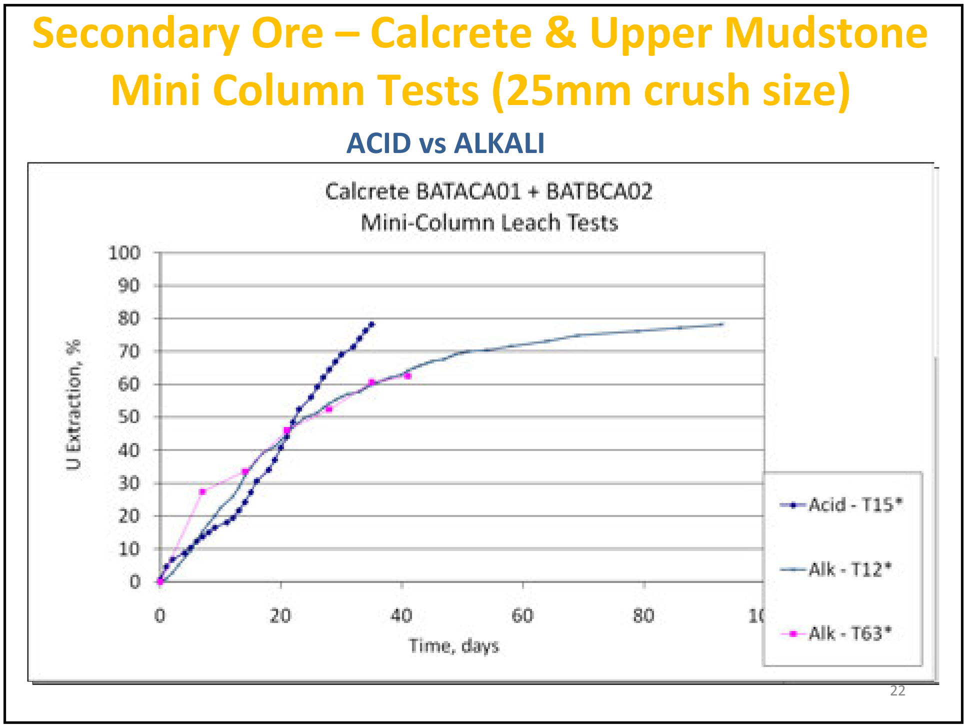
65Mt @ 140ppm for 20.1Mlbs U3O8

- Due to the high contribution the calcrete ore made to the resource, and the low grade, the only viable process option envisioned was Alkaline Heap Leach.
- Met testwork focused on optimising alkaline leaching.

November 2009 Resource Statement:

463Mt @ 154ppm for 158Mlbs U_3O_8

- Whilst the global resource grew, no additional secondary mineralisation was defined.
- Met testwork program re-focused on an optimal process option for the oxide & primary ore types.

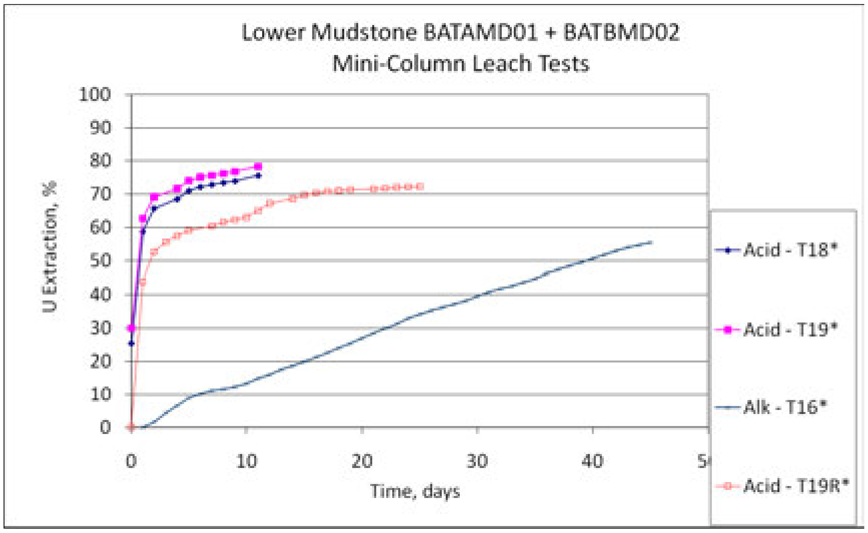


Secondary Ore – Calcrete & Upper Mudstone Mini Column Tests (25mm crush size)

ACID vs ALKALI

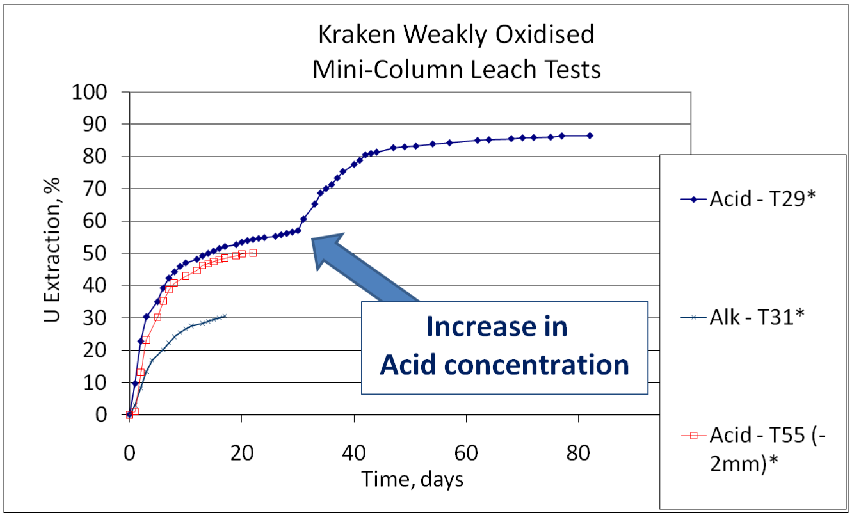
Secondary Ore – Lower Mudstone Mini Column Tests (25mm crush size)

ACID vs ALKALI



Oxide Ore Mini Column Tests (8mm crush size)

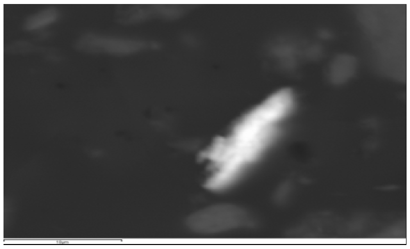
ACID vs ALKALI

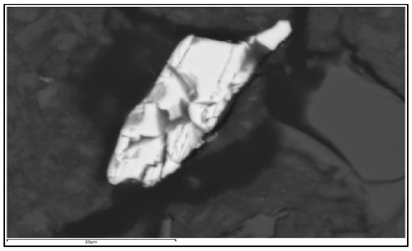


Increase in Acid concentration

Oxide Ore
Mini Column Tests (8mm crush size)

A) Column residue from a weak acid attack:- Strelkinite grain (Na-U vanadate 5-56microns) partially encapsulated in the illite matrix. The strong acid addition liberates these encapsulated grains by modifying the enclosing clay.


A


B

B)Column residue from a strong acid attack:- Fine grained zircon encapsulated in kaolinite and iron oxide, with a high reflectance rim composed of a thin band of coffinite. Some of these U rich rims are leached during strong acid attack.

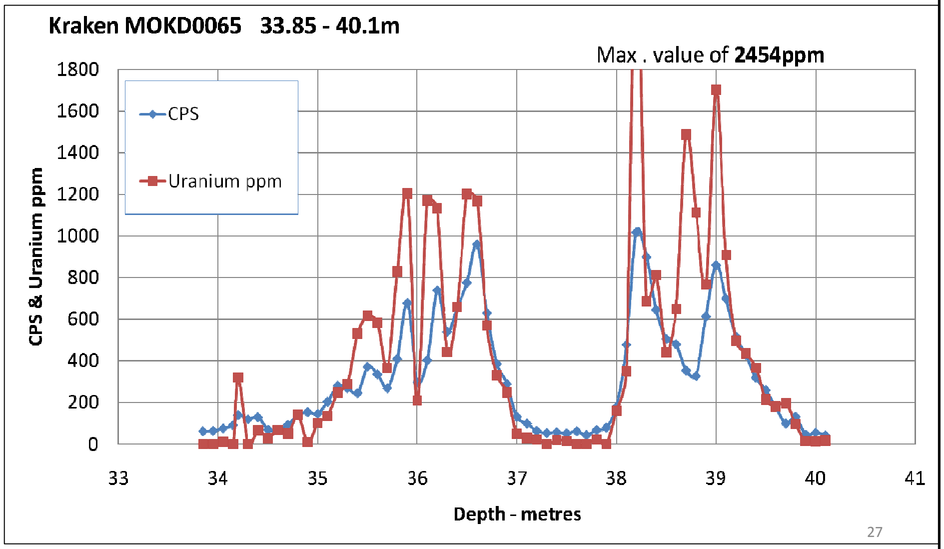
Primary Ore
Metallurgy

Metallurgical testwork on finding an optimal process option for the primary ore is now underway:-

- Column Leach Testwork - acid

- Beneficiation
  - Radiometric sorting
  - Gravity
  - Flotation

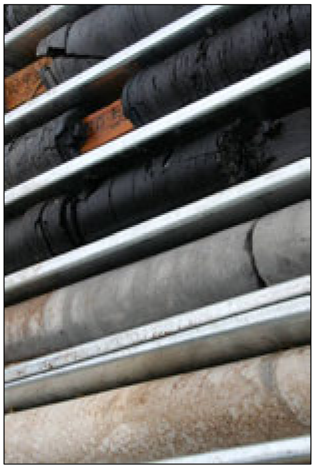
Primary Ore
Scintillometer & U Profiles



Primary Ore
Beneficiation – Radiometric Sorting

The samples tested so far include:-

A. ROM Primary Channel Ore
B. Low grade Primary Channel Ore
C. Low grade Primary Humate Ore
D. Low grade Primary Humate Ore
E. ROM Weakly Oxidised Channel Ore
F. ROM Oxide Channel Ore

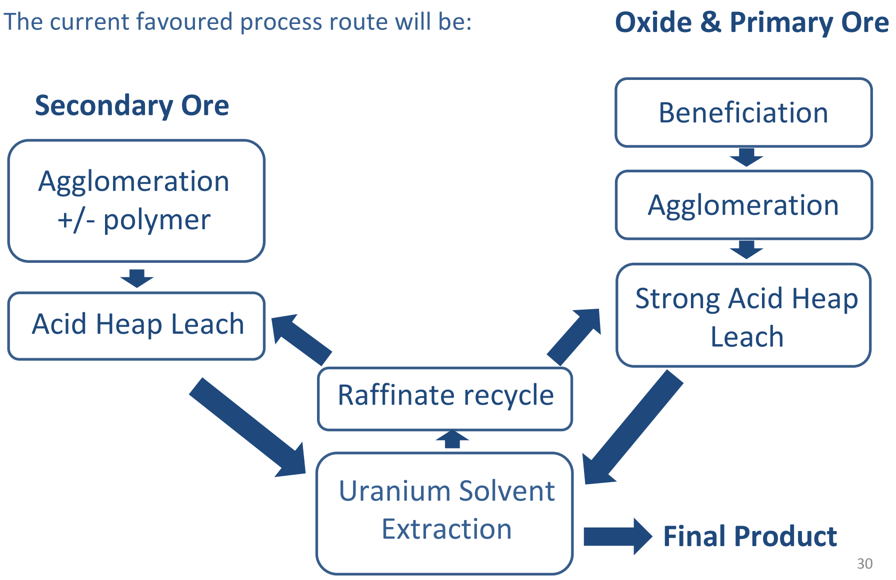


Radiometric Sorting - Results

Sample	Initial grade U ppm	Beneficiated Grade U ppm	U Accepted %	Mass accepted %
ROM Primary	265	**590**	68	30
B	106	**181**	36	21
C	128	**226**	41	23
D	138	**222**	33	20
ROM Oxide	249	**511**	76	37
ROM Oxide	403	**589**	75	52

Process Options

The current favoured process route will be:



Oxide & Primary Ore

Secondary Ore

Agglomeration +/- polymer

Acid Heap Leach

Beneficiation

Agglomeration

Strong Acid Heap Leach

Raffinate recycle

Uranium Solvent Extraction

Final Product

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AN OVERVIEW OF THE KAYELEKERA URANIUM MINE IN MALAWI

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CONTENTS

ABSTRACT:

In April 2009, production began at the Kayelekera uranium in Malawi, Africa. The mine is owned by Paladin Energy Limited, (Paladin) through its subsidiary Paladin Africa Limited (PAL). The mill employs standard unit operations to crush, grind and acid leach uranium ore grading 0.11% U_3O_8. Soluble uranium is recovered and purified using resin-in-pulp technology with strong acid elution. Hydrogen peroxide is used to precipitate uranyl peroxide. Sulfuric acid is generated on site.

1. INTRODUCTION

Paladin currently has two operating uranium mines in Africa. The Langer Heinrich mine (LHM) located in Namibia, approximately 80km east of Swakopmund, started operation in 2007 at a design production rate of 2.7 Mlb/annum U_3O_8 and has undergone an expansion to 3.7 Mlb/a. This operation is currently in the midst of a second expansion to 5.2 M lbs scheduled for mechanical completion by end of 2010. Paladin's second African mine, Kayelekera, is located in Malawi and started production in 2009. It is designed to produce 3.3 Mlb/annum U_3O_8 by treating 1.5 Mt of ore at a grade of +/- 1,100 ppm U_3O_8.

2. MINE LOCATION

The Kayelekera uranium deposit is located in northern Malawi, 52km west (by road) of Karonga:

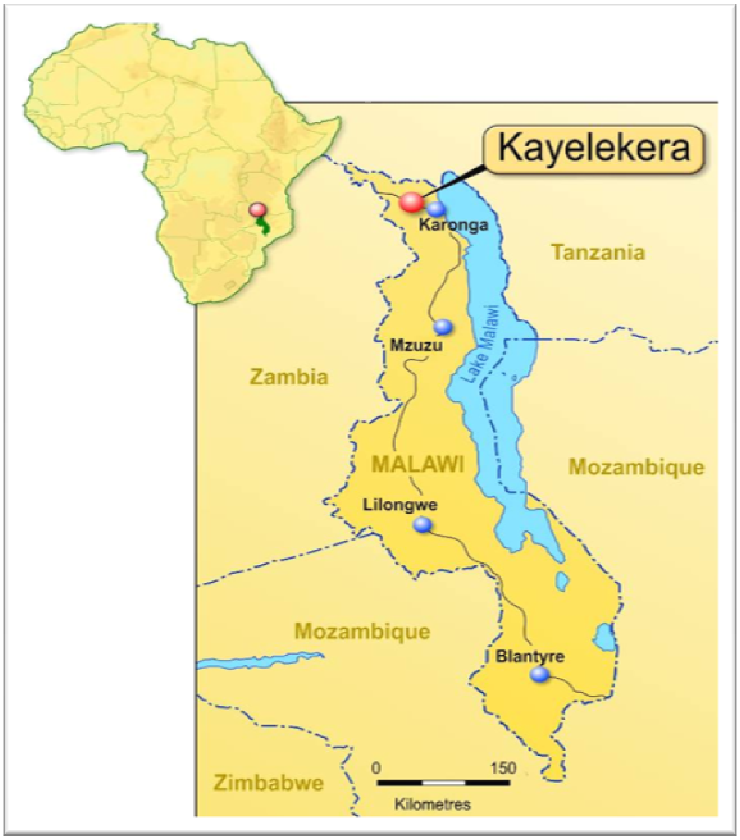

Figure 1: Location map of Kayelekera Mine Site

3. HISTORY OF KAYELEKERA DEPOSIT

A chronological history of the Kayelekera project is listed below:

1960s-77	Airborne geophysical Surveys identified anomalous areas
1977-82	Agip followed up the anomaly
1982-88:	Central Electricity Generating Board of Great Britain (CEGB) licence application over anomalous areas Extensive drilling-defined inferred resources of 11.6 tonnes at 0.15% U_3O_8 Pre-feasibility studies completed-results positive
1989-92:	Final feasibility study completed by Wright Engineers of Canada (1991)
1998:	Paladin joint venture with Balmain Resources PVT LTD
1999:	Paladin acquired 90% interest in the Project, Balmain 10% to completion of BFS.
2000-04:	Prefeasibility study updated
2005-06:	Bankable Feasibility Study commenced; Resource drilling and bulk sample analyses, metallurgy, Environmental Impact Assessment
2007:	Development agreement with Government of Malawi who obtained 15% of project; BFS finalised; EIA approved: licence granted
2007-09	Construction, Resource/Reserve Drilling
2009	Commissioning and Ramp Up

4. GEOLOGY OF OREBODY

The orebody at Kayelekera is underlain by basement complex-metamorphic and igneous rocks of the Pre-Karoo Basin. The basement is overlain by small basins of Karroo sediments. These sediments comprise gritty, arkosic sandstones and shale's with thin coal seams near their bases.

The Kayelekera site is located close to the northern tip of the north Rukuru basin which is 50Km along strike (N-S) with maximum width of 6.5Km. The North Rukuru basin contains a thick basin of Karroo sediments which are 1.5Km thick preserved in a semi-graben.

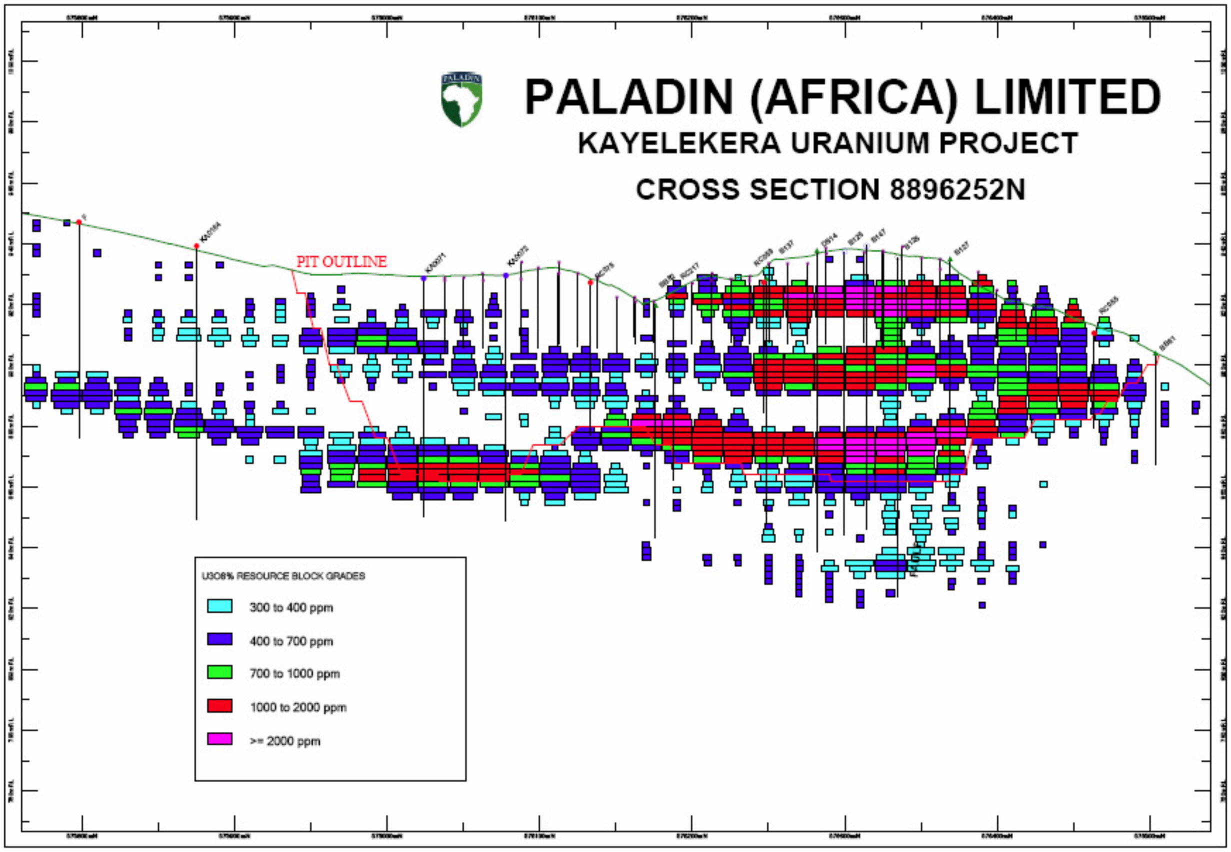

Figure 2: Cross Section of Kayelekera Orebody

Primary mineralization present within reduced facies, pyritic Arkose is intimately associated with matrix disseminations, and larger pieces, of carbonaceous debris. Coffinite has been positively identified as the principal uranium bearing species and occurs together with minor uraninite.

5. ORE CLASSIFICATION

The ore has been classified into four types based on visual identification of the oxidation-reduction state of the hosting lithology. These include:

Reduced Ore: within the Arkose units is characterized by fresh feldspars and carbonaceous debris with pyrite and chlorite in the matrix. The principal uranium mineral is coffinite with minor uraninite. A U-Ti mineral, possibly betafite or tanteuxenite, has also been noted. Reduced ore is most prevalent in the lower arkose units of the deposit.

Oxidized Ore: is characterized by feldspar deterioration and the prevalence of iron oxide in the matrix. Near surface weathering of primary (reduced) ore has produced a zone of oxide ore characterized by yellow and green secondary uranium minerals. In general, the oxidized arkoses appear more red or orange-brown than their reduced counterparts and are easily distinguished visually. The uranium mineralization is predominately secondary, with the principal minerals being meta-autunite (bright green) and boltwoodite. Most of the oxidized ore is found at or near the surface and in zones closer to the periphery of the deposit.

Transition Ore: is a mixed ore that exhibits varying degrees of oxidation.

Mudstone Ore: is a reduced ore and contains mainly coffinite with some uraninite in a matrix of clay minerals. It is concentrated along the Arkose/mudstone boundary and close to or within faults.

Approximately 50% of the total ore is reduced Arkose, 30% oxidized Arkose, 10% mixed Arkose and 10% of the ore is of the Mudstone type.

The gangue minerals are principally feldspar, quartz and iron minerals (hematite, pyrite) with minor amounts of carbonaceous debris and calcite. In common with most sandstone type uranium mineralization, the mineralogy and textural features noted at Kayelekera could derive from either a syngenetic or epigenetic ultimate source.

6. ORE RESOURCE & RESERVES

Current ore resources will allow the Kayelekera operation to continue until 2018.

	U_3O_8 Tonnes	U_3O_8 Mlbs	% U_3O_8	Cut Off ppm
Resources	21,032	46.4	0.08	300
Reserves	13,285	29.3	0.11	400

7. MINING

Mining is done from a single open pit on a contract basis by Mota-Engil using Komatsu Articulated Dump Trucks matched with Komatsu excavators and front end loaders.

8. SUMMARY OF FLOWSHEET DEVELOPMENT

Standard metallurgical test work performed at Mintek in Johannesburg using blends of core samples revealed that the ore was amenable to conventional acid leach, counter-current-decantation (CCD), solvent extraction (SX) and ammonium diuranate precipitation. A bankable feasibility study and cost estimate was conducted on this flow sheet. An optimization review and subsequent test work at ANSTO in Australia found that a process utilizing Resin-in-Pulp (RIP) technology and hydrogen peroxide precipitation offered lower capital cost, lower operating cost, and better plant operability with reduced project risk. The following factors contributed to selection of the RIP process over the CCD/SX process:

- A significant reduction for transportation of hazardous chemicals over a poor access road;
- Reduced foot-print requirements with RIP;
- Higher potential for fires with SX circuit;
- Potential impact of ammonia and nitrates on water systems;
- Susceptibility of CCD plant to high clay ores affecting solution clarity and crud build up in SX;
- Reduced labour force requirements;
- Higher uranium recovery;
- Less Safety Health and Environmental concerns with RIP process.

9. PROCESSING PLANT DESCRIPTION

The Kayelekera mill facility includes ten unit operations for yellowcake production from crushing to tailings disposal plus a number of ancillary facilities. Each unit operation was conservatively designed with enough spare capacity to continue operations when equipment is taken off line for maintenance. The unit operations at Kayelekera are described below.

Crushing: Ore from the open pit is delivered into dedicated stockpiles classified by ore type including dirty arkose (a mixture of clean arkose and mudstone) and mudstone (free of arkose). Both ore types are reclaimed from the respective stockpiles in a ratio to control plant feed grade.

A front end loader is used to transport run of mine ore from each stockpile to a dump hopper fitted with a 500mm static grizzly. Ore is drawn from the hopper using a variable speed apron feeder that discharges into a rotary-toothed mineral sizer. Crushed ore discharged from the mineral sizer is transported by a mill feed conveyor equipped with weightometer to the SAG mil. Grinding media is also added to the mill feed conveyor as required.

Recently, a primary jaw crusher was also added to the circuit to supplement the mineral sizer and provide greater crushing flexibility.

Grinding: Crushed ore from the mill feed conveyor, cyclone underflow and water are fed into a semi-autogenous grinding mill. The SAG mill discharge is fed to a cluster of hydro-cyclones operating in closed circuit with the SAG mill. Water is added to the SAG mill discharge to control the cyclone feed density. Mill discharge is screened through a trommel, oversize passes underneath a magnet to remove worn grinding media and oversize is returned back to the mill via two recycle conveyors. The target grind size is P_{80} of 180μm (P_{100} of 300μm). Cyclone overflow is directed to a rotary trash screen and then gravitates to the pre-leach thickener.

Cyclone overflow is thickened in a pre-leach thickener to increase solids density. Diluted flocculent is added to the feed launder and/or feed well to thicken the solids. Thickener underflow is pumped to the leaching circuit at a specific density of approximately 1.44. Thickener overflow gravitates to a process water tank and is reused in the SAG mill.

Leaching: Atmospheric leaching at ambient temperature is conducted in six mechanically agitated tanks. Bypass launders allow a leach tank to be taken off line for maintenance while the remaining leach tanks continue to operate. Concentrated sulfuric acid (98% minimum) is added to the leach tanks to control the leach pH and hydrogen peroxide is used as an oxidant to oxidize uranium to the hexavalent state. Provision is also made to add hydrogen peroxide directly into leach tank #2, #3 and #4 if required.

Leached slurry discharged from the last leach tank gravitates to a screen which removes any tramp oversize material which is then washed on a vibrating screen and removed to tailings. Screened slurry is pumped to the Resin-in-Pulp plant.

Resin-in-Pulp (RIP): The RIP plant comprises a series of agitated slurry tanks (contactors) containing resin beads which extract the dissolved uranium from the leached slurry. The contactors are operating in series but also in a carousel mode. Each contactor is equipped with a Kemix Pumpcell mechanism (see Figure 3 below) that performs the following four functions:

- A down pumping hydrofoil agitator designed to keep the pulp and resin in suspension.
- A wedge wire screen (through which the agitator shaft passes) which retains resin beads within the contactor but allows leach slurry to pass through to the subsequent contactor.
- A rotating cage attached to the agitator shaft which creates pulses around the perimeter of the wedge wire screen in order to reduce pegging of the basket by near size solids and resin.

- An up-pumping impeller inside the screen basket and attached to the agitator shaft. The up-pumping impeller develops a head in the open volute sufficient to overcome launder losses and allows for the velocity flow of pulp to the next contactor.

To facilitate the carousel mode of operation, the circuit is designed in such a way that each contactor can be the head or tail cell. A centralized feed launder equipped with plug and gate valves can direct feed (slurry from the leach circuit) to any of the contactors. Similarly, discharge launders and valves are such that slurry can be discharged from any one contactor to the final tailings.

The Kayelekera RIP plant comprises 10 such contactors with 8 on-line at any one time extracting uranium from the leach slurry. The two additional units would be off line and isolated, one of these would be in the process of transferring loaded resin to the elution circuit, while the second tank would be on standby for the receipt of barren resin. Once full of barren resin, this contactor is on standby to become the tail column.

Leach discharge is screened and is pumped to the RIP feed launder and from there into the first RIP contactor. This slurry then progresses through the RIP contactor train where uranium is progressively extracted onto resin through each of the 8 stages. The resin is retained within the individual contactors by the wedge wire screens. In the final (tail) stage the leach slurry is directed to tailings. Slurry from the tail contactor is gravitated over a safety screen before it is pumped to the tailings thickener. The safety screen captures any resin that may leak out of the tail RIP contactor.

A unique uranium loading profile occurs, with the first contactor containing the highest uranium concentration, and the tail contactor containing the lowest uranium concentration. Similarly, the uranium levels in solution are reduced across each successive contactor.

When the resin in the head contactor is sufficiently loaded, that contactor is isolated and taken off line. The entire content of this contactor is pumped over a screen to clean and recover the resin which is then directed to the elution circuit for uranium recovery. The second contactor in the carousel sequence becomes the new head contactor and the contactor on standby containing barren resin is brought on line as the tail contactor.

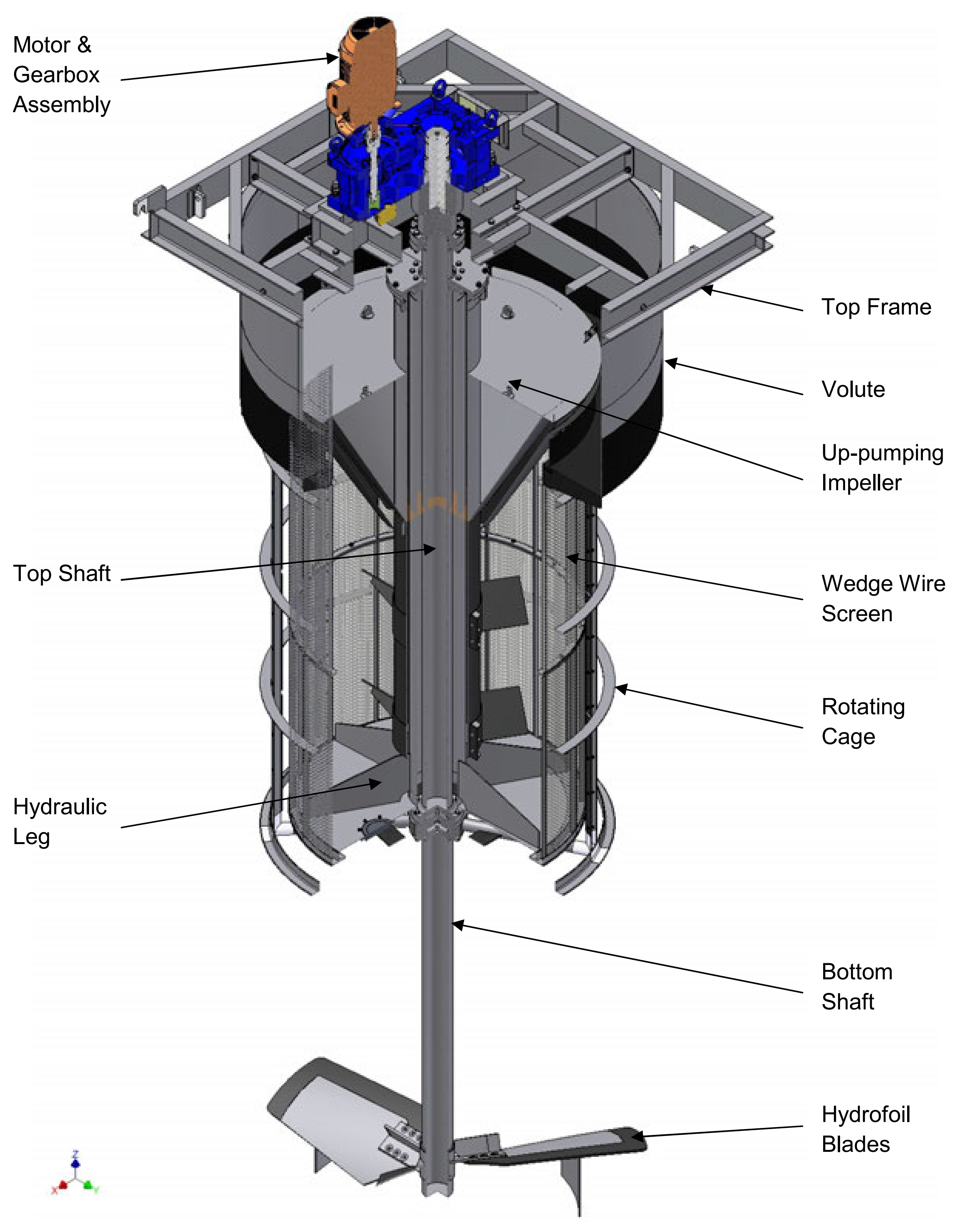

Figure 3: Overview of Kemix Pumpcell Mechanism

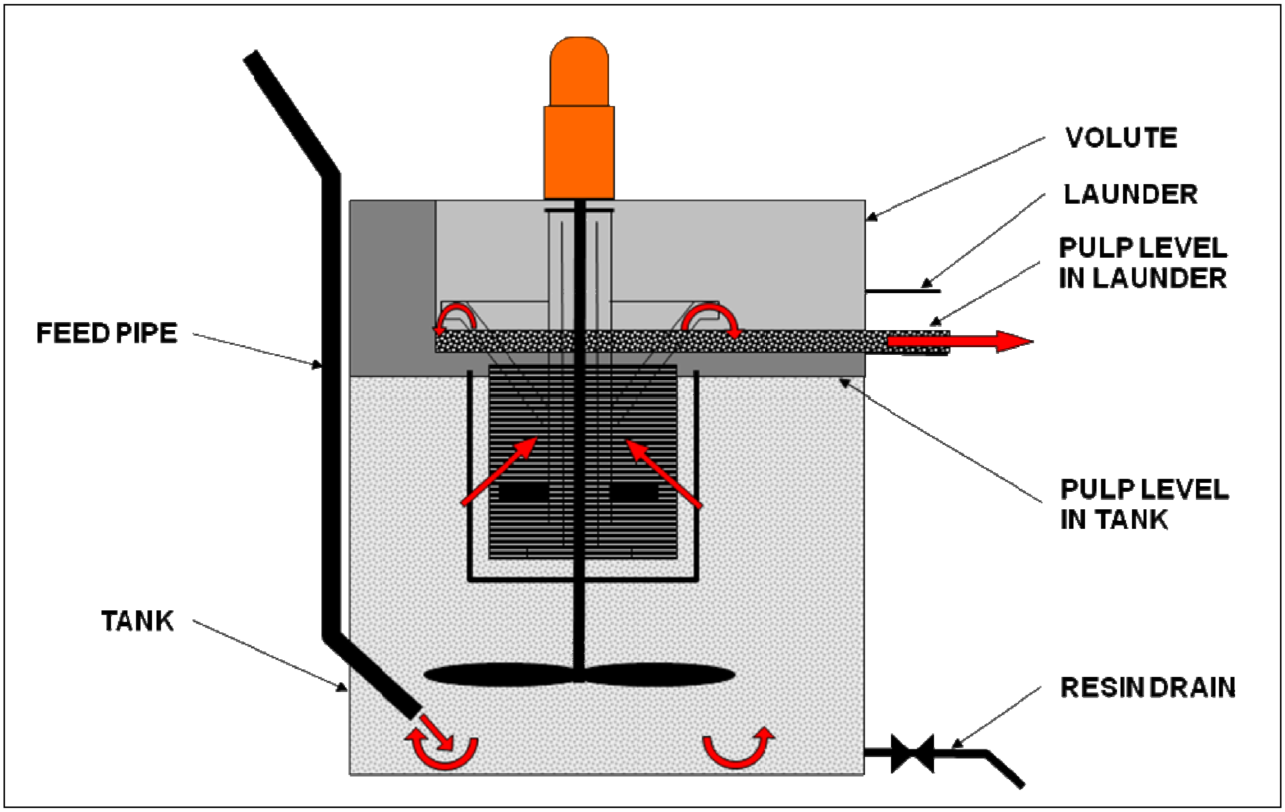

Figure 4: Schematic of flow through Kemix Pumpcell

Elution: The loaded resin from each RIP contactor is collected in one of a series of elution vessels set-up in a multi staged, counter current flow and carousel arrangement. The freshly loaded resin from RIP is added to the last of this train of vessels. Strip eluant (sulphuric acid) is added to the first vessel and passes by gravity flow through each before the conc. eluate is discharged from the last elution vessel. As the eluant passes through the series of vessels it strips the uranium from the resin and hence gradually increases in uranium concentration. Similarly, the uranium concentration on the resin is gradually reduced. When the uranium concentration on the resin in the head (first) vessel reaches a targeted low loading, the resin is transferred back to the RIP circuit for reloading and the second vessel in the series becomes the head vessel. The uranium-rich strip eluate moves forward to the precipitation area.

Uranium Precipitation and Product Washing: Some impurities in the eluate are precipitated from solution and removed by filtration after which hydrated uranyl peroxide is precipitated using hydrogen peroxide; sodium hydroxide is also added to control the pH. Uranium precipitation is done in a batch process using three contactors. At any one time, one contactor is being filled, the second is being used for precipitation and the third is being emptied.

Yellowcake slurry is washed in two counter-current-decantation wash thickeners. Diluted flocculent is added to the feed box to thicken the yellowcake. Thickened yellowcake from the second thickener is pumped to the Drying and Packing plant.

Product Drying and Packing: Thickened yellowcake slurry from the second washing thickener is pumped to a yellowcake storage tank where wash water is added, before the slurry is de-watered to 70 wt% solids in a solid bowl centrifuge. Solids from the centrifuge are blended with a re-cycle stream of dried yellowcake discharged from the dryer and fed to the dryer using a screw feeder. The solids are dried indirectly with hot oil which flows through the screws; heat is transferred from the oil through the screws to the wet yellowcake. The dryer is maintained under negative pressure with the off gases routed to a condenser and dust collector system for product recovery.

Dried product gravitates into a product hopper situated underneath the dryer discharge screw. From there it is fed into 210 litre drums using a rotary feeder. The drums are sealed, weighed, cleaned, numbered and combined in batches of six and a composite sample is made for each batch.

Tailings Thickening, Neutralisation and Tailings Disposal: Acidic tailings from tail RIP contactor are screened on the tailings safety screen and pumped to a tailings thickener where diluted flocculent is added to the feed launder and/or feed well to thicken the solids.

Tailings thickener underflow is pumped to two neutralisation tanks where milk-of-lime is added to elevate the pH. This neutralized slurry is then pumped to the tailings storage facility for permanent disposal of the solids.

Tailings Storage: For the first 5-7 years, tailings will be pumped from the process plant to the TSF A and deposited using a ring main and a network of open-ended deposition spigots. As the tailings settles and compacts, water is released from the deposited slurry and pumped to a decant water pond for storage. Water from the decant pond is pumped back to the process plant for re-use in various areas of the plant.

A schematic flowsheet of the Kayelekera process is shown below (Figure 5):

10. WATER USAGE

Four sources of water are used at Kayelekera:

Potable Water: Potable water is used for drinking, washing, and domestic use. This water is supplied from a 600,000m^3 fresh water pond, designed to collect rain water during a 4 month rainy season and store it. The fresh water is treated in a bank of clarifiers and then through a bank of sand filters. Some of the filtered water is further processed to potable water. The potable water plant includes sand filtration, ultra-filtration (membrane), chloride addition and ultra-violet treatment. Filtered water is also used for reagent makeup.

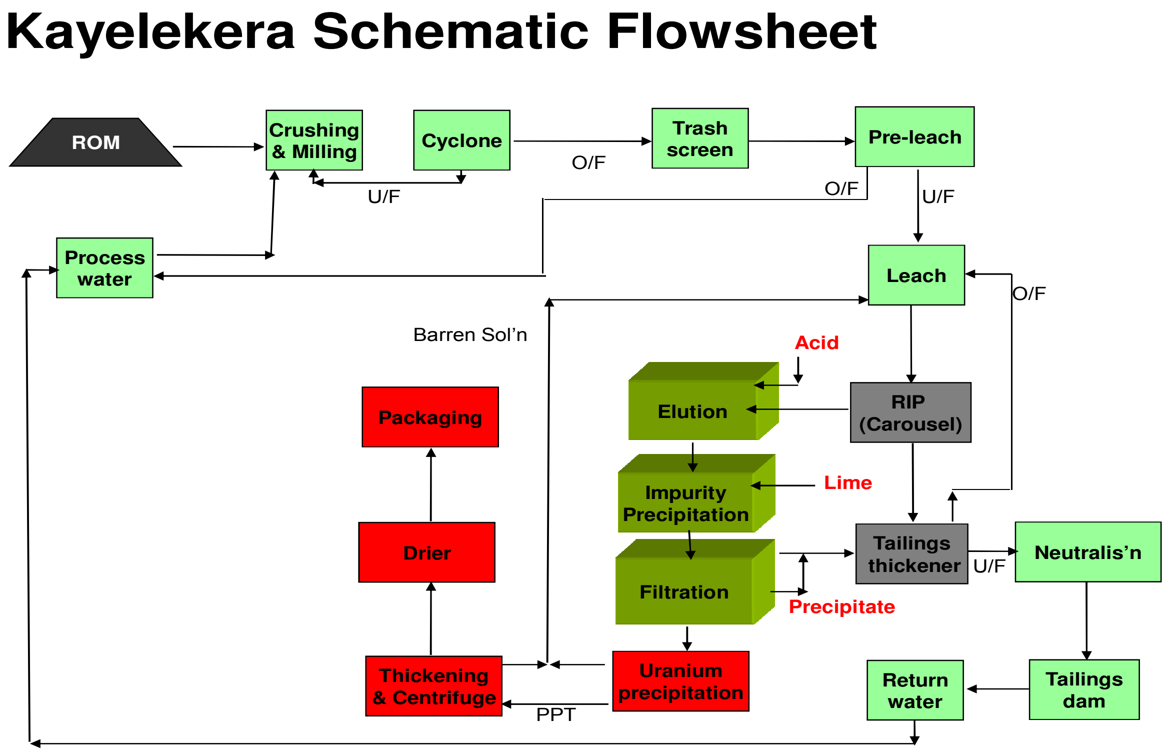

Figure 5: Kayelekera Schematic Process Flowsheet

Fresh Water: Fresh water is used for reagent make-up where water quality is an issue. Fresh water is supplied from the fresh water pond, clarified and processed in sand filters.

Process Water: Process water is supernatant collected from the tailings storage facilities when tailings settle and compact. The supernatant is pumped to a 600,000m^3 decant water pond, from where it is pumped to the process water tank within the plant. The process water tank supplies water to the grinding circuit, reagent makeup and various hose stations.

Site Run-off Water: Mine site runoff water from the ROM pad, waste dump, mine pit and haul roads feeds Run-off Water Pond 2 (RWP 2) via a network of drains. This pond has a capacity of ± 700,000m^3. From here the water is treated for solids and dissolved uranium removal. A portion of this treated water is pumped to the processing plant whilst the balance is collected in Run-off Water Pond 1 (RWP 1). This pond has a capacity of ± 135,000m^3. Water will be stored in RWP 1 for possible use in the process plant during periods of low or no rainfall.

Plant Run-off Water: All run-off from the process plant footprint is collected in a 5,000m^3 Plant Run-off Water Tank and is transferred to the process water tank.

11. PROCESS CHEMICALS

The following reagents are used on site:

Sulfur: Sulfur is the feedstock for the sulfuric acid plant. It is shipped to site as a solid in 1.5t bulk bags and stored in a 40m x 42m storage shed. A front-end loader transfers the bags to the sulfur plant.

Lime (CaO) and Milk-of-Lime ($CaOH_2$): Milk-of-lime is used to neutralize acid. Fine (< 100 micron) calcium oxide (CaO) is received in 1.1 tonne bulk bags and stored in a 30m x 48m storage shed. A fork-lift transfers the bags to a vertical lime slaker where 15 wt% milk-of-lime is made up.

Hydrogen Peroxide (70% H_2O_2): Hydrogen peroxide is used in the uranium leaching section to oxidize uranium from the +4 valence state to the +6 state, in order for it to dissolve in sulfuric acid. It is also used in the precipitation circuit to precipitate uranium as dihydrate uranyl peroxide. The hydrogen peroxide is received on site in 21 m^3 containers (25 tonnes) at 70 v/v% concentration and stored in a 300m^3 stainless steel holding tank.

Flocculent Polyacrylamide: Flocculent assist and enhance solids thickening and is received in 25kg bags as free flowing granular powder. The flocculent is made up to 0.2% stock solution, and further diluted to 0.05% before addition.

Sodium Hydroxide (NaOH): Sodium hydroxide is used for pH control in the uranium precipitation process. The sodium hydroxide is received in 25kg bags and made up to 20 wt% concentration in a batch tank.

Ion Exchange Resin: Ion exchange resin is purchased in 1m^3 bulk bags.

12. ANCILLARY PROCESS FACILITIES

Sulfuric Acid (H_2SO_4) Plant: Sulfuric acid is used as the main lixiviant for uranium leaching and it is used to strip uranium from loaded resin. 98% sulfuric acid is produced on site using a sulfur burning, double absorption and double contact acid plant. The plant comprises sulfur storage, melting, filtration and combustion, sulfur dioxide conversion using vanadium pentoxide catalyst, sulfuric acid production and steam generation. The acid is stored in two tanks adequate to supply the process plants requirements for approximately three weeks. Facilities to enable off-loading of acid from bulk transport tankers have also been provided.

Power Generation: Power for Kayelekera is provided by six 1.7MW diesels driven generating units, providing 10MW total capacity. Each is housed in its own dedicated container with a 'black start' air compressor and generator housed in a separate container. The Control Room and the Switch Room are also housed in separate containers. Each generator is automatically synchronized onto the common bus from which power is distributed around the Plant and Camp at 6.6kV.

Plant Compressed Air: Oil free service air at 690 kPa is provided by two (one standby) rotary air compressors. The air is dried and filtered before reaching the air receiver. Air is distributed from the receiver to the plant and various instrument air mains.

Chemistry Laboratory:__Kayelekera has a chemical laboratory that facilitates chemical assays and testing on various uranium ore samples from the processing plant and water sources within and around the mine site. Assays are performed by X-Ray fluorescence Spectroscopy and Inductively Coupled Photometry. The XRF instrument is use to analyse all Processing plant Uranium samples both solids and liquids and the impurities within the final concentrate. The ICP instrument is used to analyse all environmental monitoring samples including pond discharge waters.

LICENSING STATUS OF NEW URANIUM ISR MINES IN THE UNITED STATES

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Cautionary Statements

This presentation may contain or refer to "forward-looking information" and “forward-looking statements” within the meaning of applicable United States and Canadian securities laws, which may include, but are not limited to, statements with respect to resource estimates, projections, our planned exploration and drilling programs, the availability of future financing for the acquisition or related exploration, and other plans, transactions, projections, estimates and expectations. Such forward-looking statements reflect our current views with respect to future events and are subject to certain risks, uncertainties and assumptions, including, the risks and uncertainties outlined in our most recent financial statements and reports and registration statement filed with the United States Securities and Exchange Commission (the “SEC”) (available at www.sec.gov) and with Canadian securities administrators (available at www.sedar.com). Should one or more of these risks or uncertainties materialize, or should underlying assumptions prove incorrect, actual results may vary materially from those anticipated, believed, estimated or expected. We do not undertake to update forward-looking statements.

Investors are cautioned that the potential quantity and grade described in this presentation is conceptual in nature and does not meet the NI 43-101 classification of "measured", "indicated" or "inferred" mineral resources as defined by NI 43-101 and the CIM Definitions Standards incorporated by reference therein. There has been insufficient exploration to define a NI 43-101 categorized "inferred", "indicated" or "measured" mineral resource on the Arkose Property, and it is uncertain if further exploration will result in the target being delineated as such a categorized mineral resource.

Cautionary Statement for U.S. Investors concerning estimates of potential target mineral resources:
The NI 43-101 Technical Report referenced in this presentation is a requirement of NI 43-101 and includes estimations of potential mineral resources for further targeted exploration by the issuer disclosed pursuant to the applicable provisions of NI 43-101, as described herein. As a company listed on the TSX, we are required by Canadian law to provide disclosure in accordance with NI 43-101. U.S. reporting requirements for disclosure of mineral properties are governed by the United States Securities and Exchange Commission ("SEC") and included in the SEC's Securities Act Industry Guide 7 entitled "Description of Property by Issuers Engaged or to be Engaged in Significant Mining Operations" ("Guide 7"). NI 43-101 and Guide 7 standards are substantially different. For example, the terms "mineral reserve", "proven mineral reserve" and "probable mineral reserve" are Canadian mining terms as defined in accordance with NI 43-101. These definitions differ from the definitions in Guide 7. The NI 43-101 Technical Report and this presentation use or may use the terms "mineral resource," "potential uranium exploration target", "potential mineral resource", "potential mineral deposit" and "potential target mineral resource". U.S. Investors are advised that these terms and concepts are set out in and required to be disclosed by NI 43-101 as information material to the issuer; however, these terms and concepts are not recognized by the SEC or included in Guide 7, and these terms and concepts are normally not permitted to be used in reports and registration statements filed with the SEC. U.S. Investors should be aware that the issuer has no "reserves" as defined by Guide 7 and are cautioned not to assume that any part or all of potential target mineral resources will ever be confirmed or converted into Guide 7 compliant "reserves". U.S. Investors are cautioned not to assume that all or any part of a potential target mineral resource exists, or is economically or legally mineable.

Uranium Solution Mining

Also Called

ISR (In-Situ Recovery) Mining

ISL (In-Situ Leach) Mining

Background ……..

- In-Situ Recovery (ISR) Mining First Tested in the United States (US) in the Late 1960s – Wyoming Shirley Basin
- Commercial ISR Mining Started in the US in Mid 1970s
- Today ~36% of World Primary Uranium Production Comes from ISR Mining in Australia, Central Asia and the US
- Historically, Only Three States in the US have had Commercial Level ISR Uranium Mining; Nebraska, Texas and Wyoming
- Today, all Commercial ISR Production Comes from These Same Three States – Nebraska, Texas & Wyoming

World and US ISR Percentage of Primary Uranium Production (2009)

- World – ~36% (Source: WNA)
- USA – ~84% (of All US Production)
- Total US 2009 Production (ISR & Conventional)

  3,749,500 Pounds as U_3O_8

  (1,442 tU) (source: US EIA)

US ISR Uranium Production in 2009

(approximate)

	lbs. U_3O_8	tU
Nebraska	~800,000	~308
Texas	~535,500	~206
Wyoming	~1,800,000	~692
TOTAL (ISR)	**~3,135,500**	**~1,206**

History of ISR Production in the USA

- Some Testing and Commercial Production in Wyoming in late 1960s (Shirley Basin)
- Commencement of Commercial ISR Operations in Mid 1970s in Texas and Wyoming followed by Nebraska in late 1980s.
- Some Test ISR Mining in Colorado and New Mexico in Late 1970s and Early 1980s

Nuclear (Uranium) Renaissance (USA)

- 2003 Uranium Sales Prices Start to Rise
- Renewed Interest in US to Locate & Develop Uranium Properties (primarily in the West)
- Many New Public & Private Companies Formed to Participate in the Boom (400 plus Worldwide)
- Re-staking and Re-leasing Previously Known Properties
- Emphasis on Potential ISR Minable Properties but Conventional Also
- Some Serious Companies & Some Just Promotional Companies

Then the Air Went Out of the Balloon

- Spot Price Peaked in 2007 at ~$138/lb. and Then Started Down…… Fast
- Coupled with the Recession in the World Economy, Financing Uranium Projects Became Difficult and the Majority of the “New” Companies Went Out of Business or Went into Standby (Survival) Mode
- Those Companies with Good Properties, Strong Management and Sound Financial Base Proceeded to Develop Properties Towards Production
- Some Companies Were Successful In Selling Out at A Good Time – Fortunes were Made… and Lost

Those That Remained in the US…..

- Companies Already in ISR Production or with Properties on Standby Made Plans to Either Expand Production or Resume Production
- New Companies with Attractive Uranium Properties Moved Forward with Development Plans
- These Plans Included Preparing and Submitting Environmental License Applications on Their Better Projects
- In the US it Typically Takes 15 to 18 Months to Gather the Data and Prepare the ISR License Applications

Licensing Process for ISR Projects in the US

- Agreement State – Only State License Needed
  - Texas, Colorado
- Non-Agreement State – Both Federal & State Licenses Required
  - Nebraska, New Mexico, Wyoming
  - Federal Agency – US Nuclear Regulatory Commission (NRC)
  - Duel Jurisdiction / GEIS

Status of Existing ISR Projects

Crow Butte (Cameco) – Nebraska	Producing
Alta Mesa (Mestena) – Texas	Producing
Hobson/Palan.) (Uranium Energy Corp.) – Texas	Standby
Kingsville Dome (URI) – Texas	Standby
Rosita (URI) – Texas	Standby
Vasquez (URI) – Texas	Standby
Smith Ranch-Highland (Cameco) - Wyoming	Producing
Christensen Ranch (Uranium One) – Wyoming	Re-Start (2011)

Other ISR Projects Licensed But Not Constructed

North Butte (Cameco)	Wyoming
Ruth (Cameco)	Wyoming
Gas Hills – Peach (Cameco)	Wyoming
Crown Point (Hydro Resources)	New Mexico

New Projects or Expansions with License Applications Under Review

- Crow Butte North Trend (Cameco) – Nebraska (exp.)
- Crow Butte Plant (Cameco) – Nebraska (exp.)
- Dewey-Burdock (Powertech) – South Dakota (new)
- Goliad (Uranium Energy) – Texas (new)
- Nichols Ranch-Hank (Uranerz) – Wyoming (new)
- Moore Ranch (Uranium One) – Wyoming (new)
- Jab-Antelope (Uranium One) – Wyoming (new)
- Lost Creek (Ur Energy) – Wyoming (new)
- Ludeman (Uranium One) – Wyoming (new)

Licensing Status of New ISR Applications
(does not include expansions)

- Advanced
  - Nichols Ranch - WY (Uranerz)
  - Lost Creek - WY (Ur-Energy)
  - Moore Ranch - WY (Uranium One)
  - Goliad - TX (Uranium Energy)
- Mid-Stream
  - Jab Antelope - WY (Uranium One)
  - Dewey Burdock WY SD (Powertech Uranium)

NRC Letters of Intent for Planned New ISR Projects or Expansion of Existing Projects

Three Crow (Cameco) Crow Butte Exp.	Nebraska
Marsland (Cameco) Crow Butte Exp.	Nebraska
Lost Creek (Ur Energy) Lost Creek Exp.	Wyoming
Lost Soldier (Ur Energy) Lost Creek Exp.	Wyoming
Allemand-Ross (Uranium One) Moore R. Exp.	Wyoming
Smith Ranch (Cameco) Plant Expansion	Wyoming
Reno Creek (NCA Nuclear, Inc) New	Wyoming
Ross (Strata Energy) New	Wyoming
Sweetwater (Wildhorse) New	Wyoming
Ruby Ranch (Cameco) Smith Ranch Exp.	Wyoming

(Source: US Nuclear Regulatory Commission)

LICENSING SUMMARY of ISR PROJECTS

Applications Filed for New ISR Projects or Expansion of Existing Projects	10
NRC Letters of Intent for New ISR Projects or Expansion of Existing Projects (Texas & Colorado Not Included)	10

- If All present and Planned ISR Projects in Production at One Time Total US Production ~ 20 to 25 million lbs./yr (7,700 to 10,000 tU/yr)

US ISR Licensing Issues

- Staffing – Size and Experience (catch-up)
- Duel Jurisdiction – Non-agreement States (MOUs)
- NRC – Distance Between Office and Projects (DC – Wyoming)
- GEIS (generic environmental impact statement)
- License Review/Approval Time Now Two Plus Years (not including time to gather data and prepare the application)

COMPARISON

- **North Butte Project (Wyoming) Licensed in 1990 by Uranerz USA, Inc. took the NRC About One Year to Review & Approve the License Application, and It Took Six Months for the State of Wyoming to Do the Same. [EA, NRC Field Office]**

There is Hope

- With these first three new ISR applications both the federal and state regulatory agencies have been very cautious.
- Federal agency (NRC) inexperienced at first; has now cut its teeth on the first three new ISR applications and will have a much higher technical experience level when the next wave of ISR applications are submitted.
- Negative pressure from outside the regulatory agencies should subside after first three new ISR licenses issued.
- Now with final GEIS issued and when first three new ISR applications approved; I think review times will be cut substantially, perhaps in half.

OPTIMISATION OF THE CALCRETE-URANIUM PROCESS FLOWSHEET : THE IMPLICATIONS OF METALLURGICAL TESTWORK FOR THE MARENICA PROJECT

By

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CONTENTS

ABSTRACT

Marenica Energy is carrying out a study of the recovery of uranium from the Marenica deposit in Namibia. The Marenica deposit is located in the Damara Province in the Erongo region of the Karibib district, some 70 km east of Henties Bay and 60 km west of Usakos. The regional geology of the area is dominated by the northeast trending Damara Mobile Belt, which typically comprises high-grade metamorphics with granitic intrusions. Tertiary aged calcrete deposits, as well as Karoo sediments, also host uranium mineralisation. Deep weathering and erosion of the uranium-rich granites and felsic volcanics, under semi arid to arid conditions, has created valley fill sedimentary deposits within incised Tertiary drainage channels. Uranium was leached from source rocks and transported by slightly alkaline oxidising groundwaters, with subsequent precipitation leading to the formation of surficial calcrete deposits. Calcrete-hosted uranium deposits form within fluvial sediments under arid conditions, where near-surface groundwater and high evaporation promotes the deposition of calcite (± barite, dolomite and celestite) as an intergranular cement. Carnotite is the main uranium mineral and occurs as coatings on grains, along fractures, and as disseminations throughout the calcrete and gypcrete.

Carnotite is readily leached in alkaline solution. Alternative processing techniques were examined in laboratory tests and included ore sorting, heap leach amenability tests and scrubbing/size separation. Although the options are still open, the ore has been demonstrated to be amenable to upgrading by scrubbing and to alkaline leaching. Agitated slurry leach optimisation and uranium recovery testwork is underway and up-to-date results on the progress of this work at ANSTO, and the flowsheet implications, are presented and discussed.

1. PROJECT BACKGROUND

The Marenica deposit is a calcrete-hosted uranium deposit located in the Damara Province, some 90 km northeast of Swakopmund, Namibia. Calcrete deposits, both pedogenic and palaeochannel, are important potential hosts for economic uranium mineralization in many parts of southern Africa.

The basement stratigraphy of the Marenica project forms part of the Damara Sequence and more specifically the Swakop Group of Late Precambrian age (Miller, 2008). Polyphase deformation has resulted in a regional northeast trending dome-basin structural setting across the project area. Lower Cretaceous (135 Ma) dolerite dykes up to 150 m wide, predominantly strike northeast through the project area. Igneous rocks include the Early Palaeozoic Salem Granite, and adjacent to the licence area are the Cretaceous granitoid intrusions of Gross and Klein Spitzkoppe.

The Damara basement at Marenica has been incised by southwest trending palaeochannels, that flowed west from the escarpment during the upper Cretaceous – Lower Tertiary (88-125 Ma), and are now largely filled with calcretised gravels and recent alluvial cover. Groundwater flow is typically directed towards the south-west except where re-directed by topographic barriers.

Uranium occurs as uranium VI phases within palaeochannel calcrete and gypcrete sediments and as mineralisation associated with joints, planes and fractures within weathered basement rocks. Carnotite, a bright yellow, hydrated potassium uranyl vanadate $[K_2(UO_2)2(V_2O_8)_2 3H_2O]$ is the main uranium mineral, occurring as coatings on grains and as disseminations throughout the calcrete and gypcrete (Bowell et al., 2009).

Uranium may occur as uranium VI throughout the weathering profile in the weathered basement bedrock and throughout the palaeochannel (Figure 1).

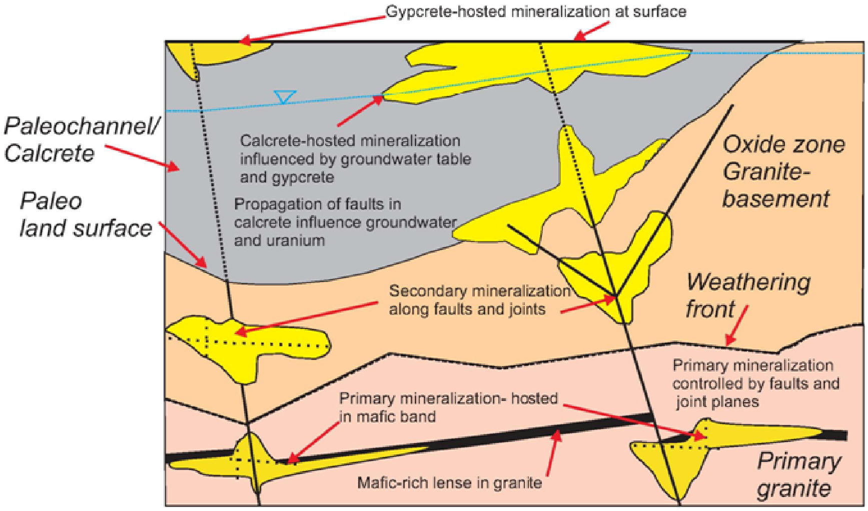

Figure 1: Diagrammatic showing the formation of secondary and calcrete deposits

Grade in the channels is typically higher at shallow depth indicating that evaporation may play a role in precipitating uranium. Basement topographic highs may have acted as barriers where upward groundwater flow and increased evaporation rates allowed CO_2 to be exsolved and the groundwater to mix with more oxygenated, solute-rich waters. Diminished groundwater circulation allows calcrete formation and concentration of uranium and vanadium, which precipitate out as carnotite during evaportation in semi-arid and arid environments. Multiple phases of carnotite formation are indicated in mineral paragenesis suggesting frequent re-working of the deposit, possibly in response to fresh alkaline groundwater. The deposit may have been affected by disequilibrium, where by the daughter isotopes of uranium remain after the parent uranium has been dissolved and removed by groundwaters.

Mineral equilibrium calculations have been used to construct geochemical models to understand ore genesis and assist in exploration. Species activities and mineral saturation indices show that for the deposit, carnotite is close to saturation or is only weakly undersaturated demonstrating that recent or even seasonal dissolution and re-mobilization of uranium may occur, leading to wide hydrogeochemical halos for trace levels of uranium in groundwater around these deposits.

Two ore types were provided as core composites for metallurgical assessment. They were analysed as shown in Table 1. The samples contained uranium in secular equilibrium with its decay chain progeny, as shown in Table 2.

Table 1: Ore Assays

		Calcrete	Weathered Bedrock
DNA (ppm)	U_3O_8	119	273
XRF (%)	Al	4.19	5.45
	Ca	8.57	8.30
	Fe	0.86	2.94
	K	2.87	2.09
	Mg	0.61	1.22
	Mo	0.010	0.010
	Na	0.86	1.19
	P	0.025	0.043
	Si	26.5	24.0
	Sr	0.185	0.408
	V	0.015	0.027
	Zr	0.102	0.112
LECO (%)	S	1.24	1.28
	$C_{org.}$	0.02	0.02
	$C_{inorg.}$	2.10	1.92
	Total C	2.12	1.94

Table 2: Gamma Spectrometry and DNA Results

Sample	DNA		Gamma			U/Ra
	^{238}U		^{230}Th	^{226}Ra	^{210}Pb	
	ppm	Bq/g	Bq/g	Bq/g	Bq/g	
Calcrete	101	1.25	1.35	1.18	1.25	1.06
Weathered bedrock	231	2.86	3.19	2.62	2.79	1.09

In diagnostic "dilute" leach tests, it was shown that the ores were readily amenable to leaching – see Table 3.

Table 3: Dilute Leach Tests

(90°C, 24 h, 0.4 M Na_2CO_3 / 0.1 M $NaHCO_3$, pulverised)

Sample	Head Grade (ppm U_3O_8)	Residue Grade (ppm U_3O_8)	Uranium Extraction (%)
Calcrete	119	4	96.7
Weathered bedrock	273	8	96.9

2. MINERALOGY

The mineralogy of the two ore types was examined using XRD and SEM. The emphasis of this was on the minerals that would likely impact on the process performance of the ore (uranium and vanadium extraction and reagent consumption), such as the source minerals containing iron, silica, calcium, sulphur and carbonate.

The uranium mineralogy in both the calcrete and weathered bedrock ore types is primarily due to carnotite ($K_2(UO_2)_2(V_2O_8)\cdot 1-3H_2O$), although other minerals have been observed in the weathered basement ore, including saléeite, metatymunite, strelkinite, umohoite and fourmarierite in grab samples and core material (all as minor phases) and, in the calcrete, urancalcarite as replacement rims on carnotite.

The main gangue minerals identified were quartz , K-feldspar (microcline-$KAlSi_3O_8$), and calcite. Na-feldspar (albite-$NaAlSi_3O_8$), clays such as palygorskite ($(Mg,Al)_2Si_4O_{10}(OH)\cdot 4H_2O$), which is the dominant component of the clay minerals, illite ($(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$), and smectite ($(0.5Ca,Na)_{0.7}(Al,Mg,Fe)_4[(Si,Al)_8O_{20}](OH)_4\cdot nH_2O$),, hydroxyapatite ($Ca_5(PO_4)_3(OH)$), zircon ($ZrSiO_4$), fluorite, rutile/anatase (TiO_2), illmenite ($FeTiO_3$), monazite ($(Ce,La,Nd,Th)PO_4$), celestine ($SrSO_4$) and barite ($BaSO_4$), magnetite (Fe_3O_4), halite (NaCl), bassanite ($CaSO_4\cdot 0.5H_2O$) and gypsum ($CaSO_4\cdot 2H_2O$) are less abundant.

The carnotite is usually intimately associated with the clay matrix. The clay matrix coats the surface of quartz/feldspar/calcite/biotite particles – see Figure 2. In addition to hosting the uranium mineralisation, the clay matrix also contains other fine grained minerals such as fluorite, halite, iron oxide, quartz, feldspar and calcite. Carnotite also occurrs in association with fluorite and celestine.

Carnotite occurrs mainly as platy crystals and aggregates within the clay matrix, with grainsizes ranging from a few microns up to 50 µm. Occasionally, carnotite is observed as sub-micron to micron size grains scattered through the clay matrix or partly rimming the surface of the clay matrix.

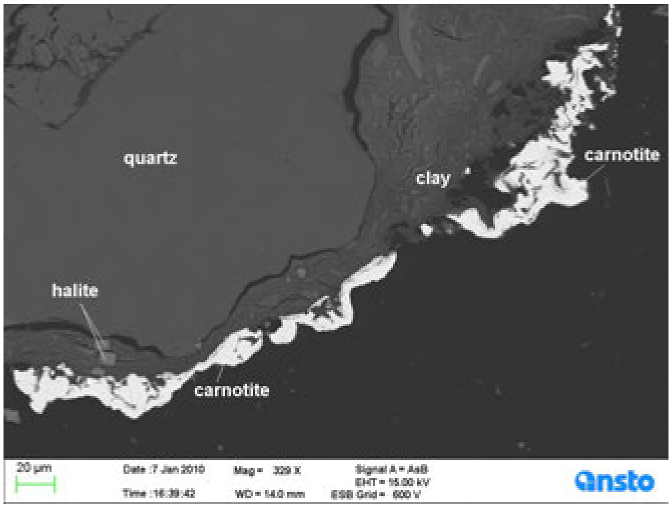

Figure 2: Carnotite coating a clay matrix on quartz

In Figure 3, platy crystals of carnotite are seen partially filling cracks in a biotite particle.

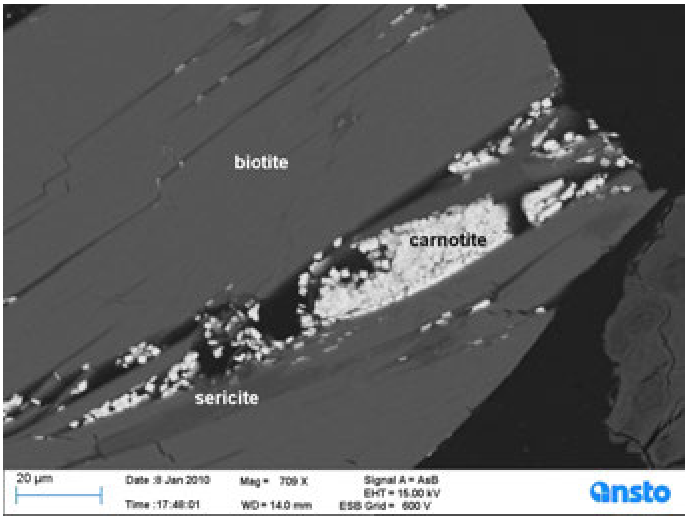

Figure 3: Platy/tabular carnotite partially filling cracks in biotite

The mineralogy of selected size fractions of leach residues (with elevated uranium content) were examined to help understand the reasons for the observed limits to uranium extraction.

The XRD analyses of the residues showed that the gangue mineralogy changed significantly after leaching. The content of microcline was dramatically reduced and no calcium sulfates were detected. Montmorillonite was identified in both residues, most likely forming at the expense of the feldspars.

SEM-EDS examination of the calcrete leach residue showed that most carnotite was dissolved during leaching. Only rare grains of partly dissolved carnotite were found disseminated throughout the clay-rich matrix – see Figures 4 and 5.

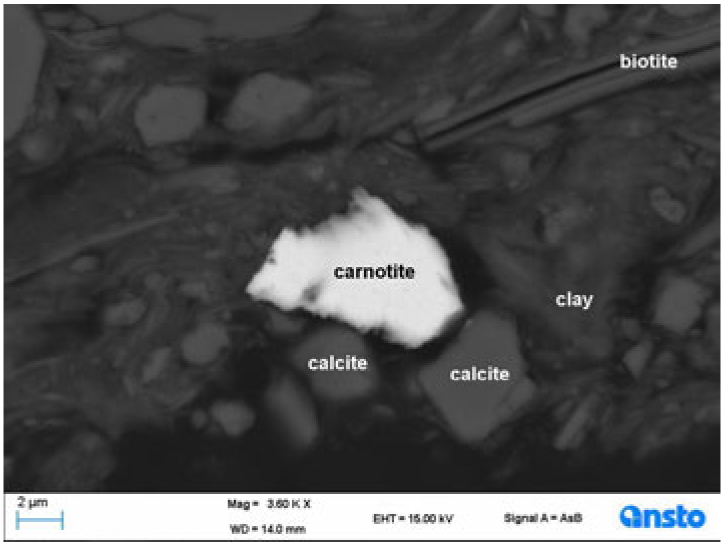

Figure 4: Partly dissolved carnotite grain within the clay rich matrix.

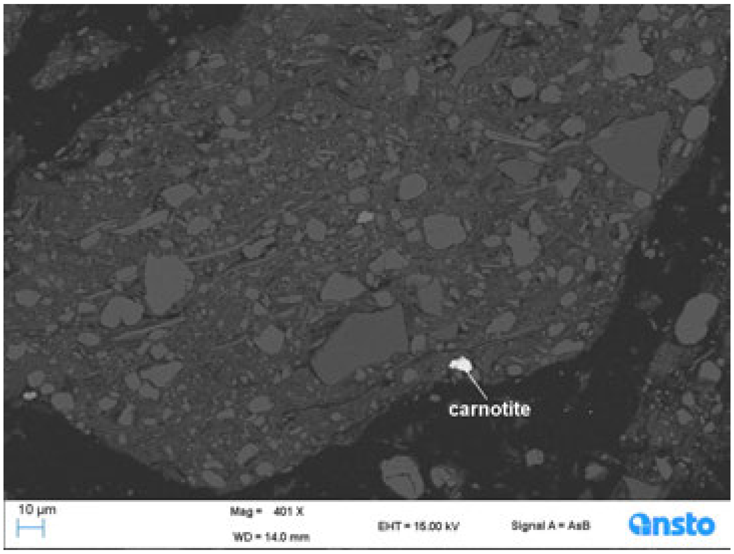

Figure 5: Carnotite grain within the clay rich matrix.

3. ORE UPGRADING AND URANIUM DISTRIBUTION WITH SIZE

Radiometric Sorting

Each ore type was crushed to pass 65 mm and two coarse fractions were examined with regard to their amenability to radiometric ore sorting. Both ore samples were generally of low competency and only a limited fraction of the carefully crushed rock ended up being in the size ranges suitable for industrial radiometric sorting. The rocks in the two coarse size fractions were sorted according to their gamma count rate with the aim of rejecting rocks which contained little uranium.

The Pb-214 count rates were arranged and radiometric sorting profiles produced. An example is shown in **Figure 6**.

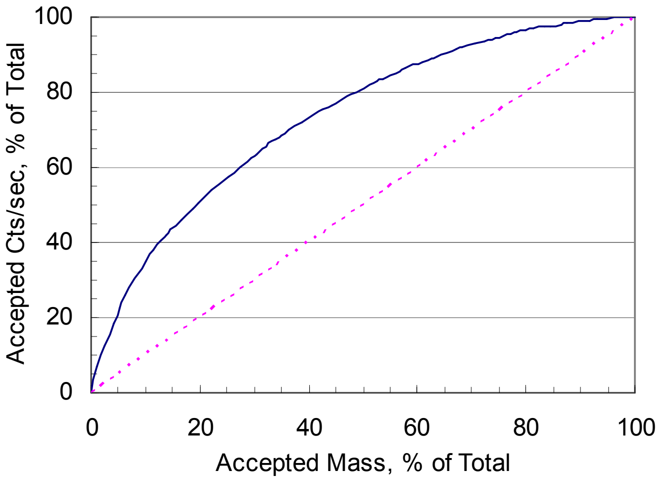

Figure 6: Radiometric sorting profile for -65+40 mm calcrete

The data generated indicated that both ore types could be sorted to some extent. Radiometric sorting would be of more benefit to the processing of weathered bedrock ore but is not likely to be of benefit to the processing of the lower grade calcrete ore, although this would depend on dilution during mining etc. The benefit would be limited by the quantity of ore available for sorting in the required rock size ranges, *i.e.* a high proportion of fines is produced during coarse crushing of ore and this could limit the applicability of radiometric sorting.

Ore Scrubbing

Ore, which had been previously crushed to pass 65 mm, was further crushed to various sizes for size versus uranium determination and for scrubbing tests. Scrubbed slurries were sized and the fractions assayed. An example of the size versus uranium distributions in scrubbed ore is given in Table 4 and shows that the ore is potentially amenable to significant upgrading by scrubbing and size separation (by screening, cycloning, or hydrosizing) depending on the size separation and washing efficiencies. The scrubbing test on weathered bedrock demonstrated that 90% of the uranium could report to the < 150 µm fines, which could represent 30 wt% of the ore fed to the scrubber.

Table 4: Uranium distribution in scrubbed weathered bedrock ore

Size Fractions (mm)	Wt %	Uranium	
		Assay (ppm U)	Distribution (%)
19	4.0	30	0.4
16	3.5	47	0.6
12.7	3.0	28	0.3
6.7	7.9	67	1.8
3.3	5.2	49	0.9
1.7	5.1	51	0.9
0.850	5.4	36	0.7
0.600	4.4	38	0.6
0.300	13.7	31	1.5
0.150	17.6	46	2.7
0.075	9.7	95	3.2
0.038	5.1	187	3.3
<0.038	15.4	1586	83.4
Calculated head	100.0	(293)	100.0
Assay head		232	
Upgraded fraction (<150 µm)	30.2	(871)	89.8

A similar upgrading result was also observed for the calcrete ore in which 90% of the uranium could be retained in 37 wt% of the ore in the <300 µm fraction, and with an increase in grade of 242%.

4. LEACHING

Heap Leach Amenability

Ore crushed to various sizes was subjected to bottle roll tests to evaluate the amenability of the ores to heap leaching. Although the extractions were satisfactory (see Table 5), even gentle handling of the ores during bottle rolling produced fines, which would hinder solution percolation in heap leaching, unless the ores were effectively agglomerated.

Table 5: Bottle roll leach test results

(after 5 weeks at ambient temperature, 0.4 M/0.1 M $Na_2CO_3/NaHCO_3$)

Ore Type	Rock Size (mm)	Leach tail (ppm U)	Uranium Extraction (%)
Calcrete	<6.3	17	78.8
	<12.5	14	81.2
	<25	11	82.9
Weathered bedrock	<6.3	34	84.4
	<12.5	38	79.9
	<25	29	86.2

Agitated Slurry Leaching

Samples of both ore types, after crushing and scrubbing, were screened at selected sizes (resulting from the scrubbing tests described above). The screen undersize was used in agitated slurry leaching tests under a range of leach conditions.

The assays of upgraded ores are given in Table 6.

Table 6: Upgraded ore assays – as used in agitated slurry leach tests

Sample	Al	Ca	Fe	K	Mg	Na	S	Si	Sr	Ti	U_3O_8 (ppm)	V	C
Calcrete (< 300 µm)	4.43	12.8	1.79	1.58	1.31	0.601	1.92	18.4	0.18	0.20	257	0.027	3.02
Bedrock (< 150 µm)	5.05	16.0	2.54	1.36	1.30	0.719	3.67	13.5	0.53	0.28	982	0.043	3.08

Although high uranium extraction was achieved, as shown in Table 7, the net consumption of sodium carbonate/bicarbonate reagents was relatively high. The consumption of carbonate reagents is primarily due to the presence of sulphate minerals in the ore and existing methods to remove these minerals by flotation, before leaching, are being investigated. A small associated loss of uranium is expected due to the intimate association that is observed between a small portion of the carnotite with the sulphate minerals. Preg-robbing of uranium during leaching was observed in most leaches, particularly after 12-24 h, except when RIP was used (resin added after 24 h).

Table 7: Agitated slurry leach test results

Ore Type	Leach Test	T (°C)	Reagent Concentration (M)		U Extraction (%)		
			Na_2CO_3	$NaHCO_3$	12 h	24 h	30 h
Calcrete	slurry + air	60	0.200	0.02	38	64	73
	slurry + air	80	0.200	0.02	91	94	86
	slurry + air + RIP	80	0.200	0.02	64	94	95
	slurry + air	80	0.125	0.02	84	92	93
	slurry + air	95	0.125	0.02	90	83	71
	slurry + no air	80	0.125	0.02	57	93	93
Weathered Bedrock	slurry + air	60	0.200	0.02	16	76	81
	slurry + air	80	0.200	0.02	92	92	90
	slurry + air + RIP	80	0.200	0.02	98	89	92
	slurry + air	80	0.125	0.02	86	91	92
	slurry + air	95	0.125	0.02	92	86	85
	slurry + no air	80	0.125	0.02	73	93	93

Slurry Leach Variables

Leach variables examined included leach temperature, aeration, leach duration, reagent concentration, and resin in pulp.

The effects of leach temperature, duration and reagent concentration are indicated in Figures 7 and 8. Increased temperature from 60 to 80°C increases the leach kinetics but extractions are comparable after 30 h leach duration. RIP after 24 h arrested the decrease in extraction and slighly improved the overall extraction. Removing the aeration did not reduce uranium extraction, because the carnotite contains predominantly hexavalent uranium.

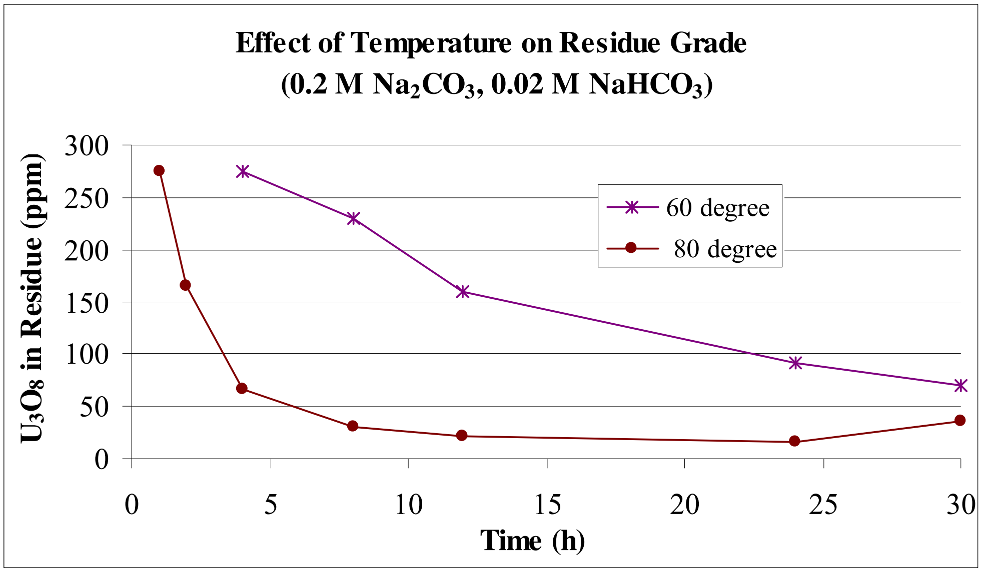

Figure 7: Effect of leach temperature at higher reagent concentration

The composition of leach liquor being used in IX testwork is shown in Table 8. This is not expected to be problematic in IX.

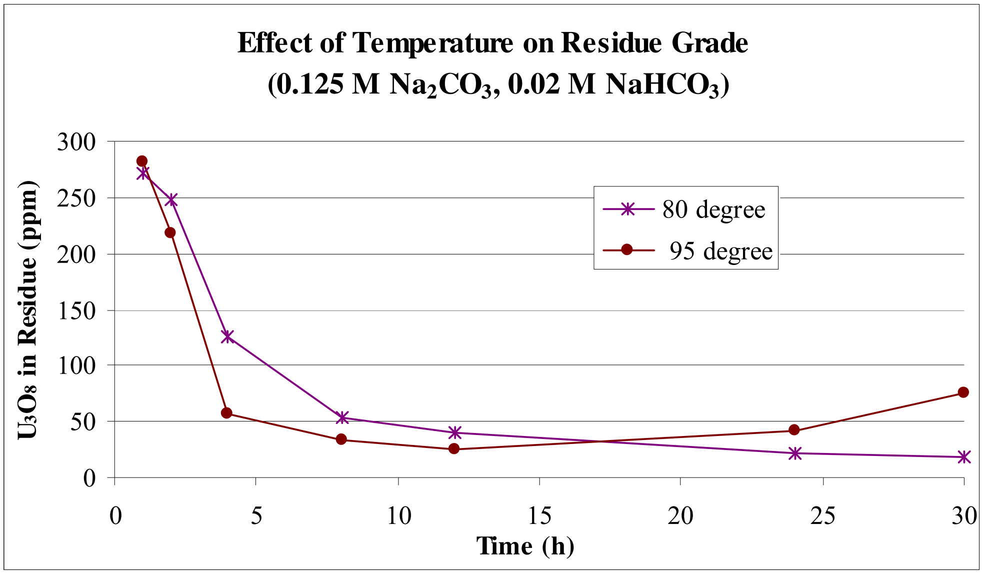

Figure 8: Effect of leach temperature at lower reagent concentration

Table 8: Composition of PLS to ion exchange (element concentrations in mg/L)

Na_2CO_3 (M)	$NaHCO_3$ (M)	pH	Al	Ca	Fe	K	Mg	Mo	Na	P	S	Si	Sr	U	V	Cl
0.40	0.10	10.3	1.07	7.6	1.28	182	0.98	1.4	37600	<2	9770	51	<1	500	86.3	183

Flowsheet options include heap leaching or slurry leaching. A flowsheet which includes slurry leaching is shown in Figure 9.

5. CONCLUSIONS

Metallurgical testwork carried out to date has shown that the Marenica ore:

- is readily amenable to upgrading by scrubbing and sizing;
- can be efficiently processed without significant milling; and
- leaches effectively in carbonate solution.

Testwork is either underway or proposed to examine:

- ore variability;
- means of reducing reagent consumption in slurry leaching;
- the rheological properties of the leached slurry with respect to maximising slurry density, improved agitation and resin screening during RIP;
- water and reagent recovery; and
- ion exchange resin loading / elution and uranium recovery from eluate.

6. REFERENCES

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7. ACKNOWLEDGEMENTS

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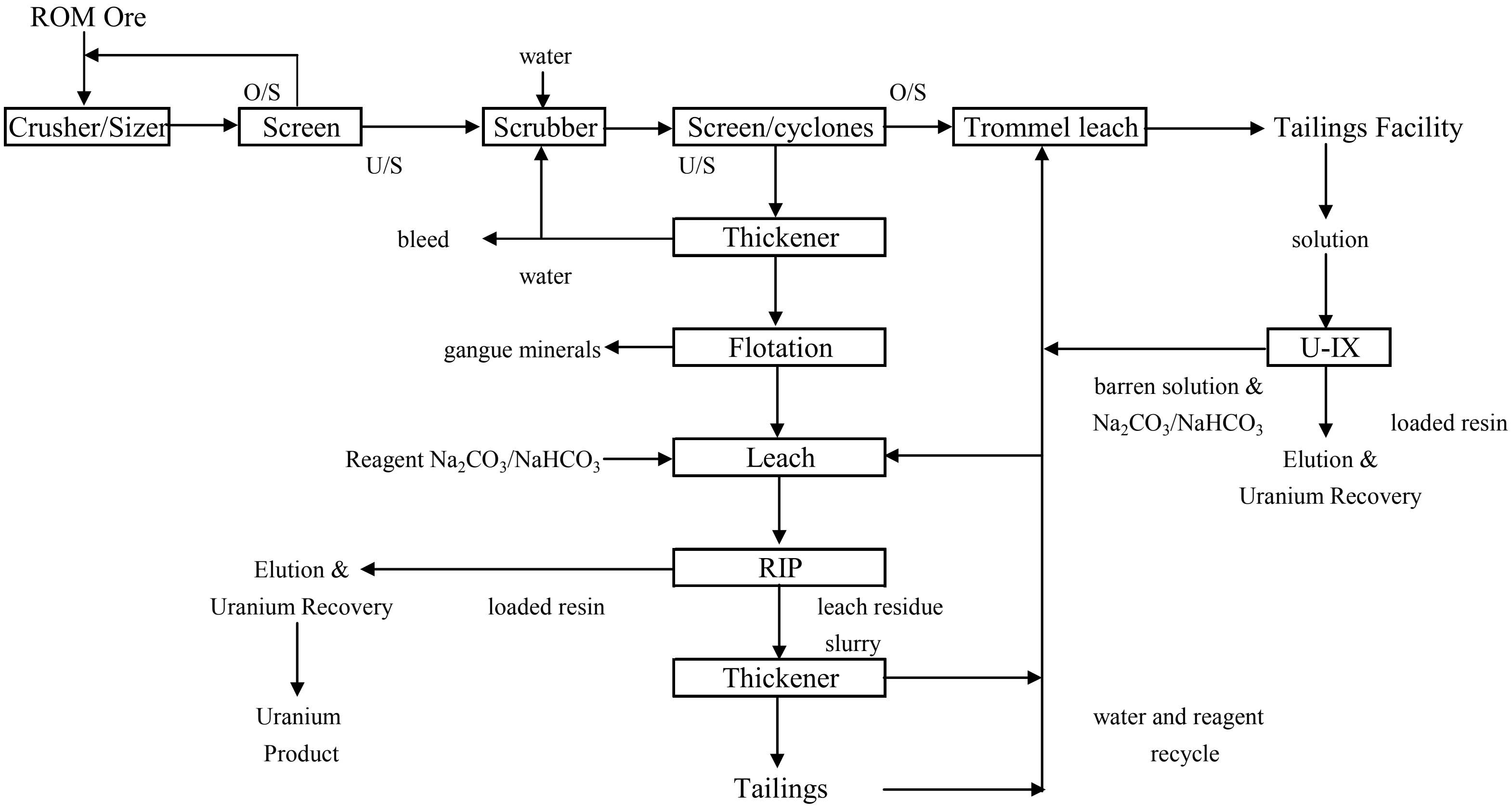

Figure 9: Conceptual flowsheet involving scrubbing, sizing, flotation and slurry leaching

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URANIUM

SOLVENT EXTRACTION

ANALYSIS AND TROUBLESHOOTING IN URANIUM SOLVENT EXTRACTION CIRCUITS

By

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CONTENTS

1. INTRODUCTION

A thorough review of the challenges experienced in uranium solvent extraction (USX) circuits due to impurity ingress would likely take more space than is permitted in the usual publications. Mindful of this~~,~~ as well as the confidentiality concerns of some of the mining companies where the issues have been found and resolved, each challenge and solution is treated separately, and without name. Some of the issues discussed may not be specific to one mine or uranium operation, but rather may be generic in nature.

It is reminded that each uranium leach, IX and or SX operation is somewhat unique in that the PLS generated from leaching will be influenced primarily by the ore and gangue mineralogy, site water quality and water balance issues specific to that site. Therefore the ideas and philosophy outlined in this paper serve to provide a generic approach that can be potentially applied and adapted to any site or project.

2. SOME MILESTONES RELATED TO USX

1951	First Ion Exchange plant - West Rand Consolidated Mines, South Africa.
1956	First USX plant using DAPEX process (with D_2EHPA), Kerr McGee, USA.
1957	General Mills Chemicals develops Alamine® 336.
1958	Kerr McGee converts from DAPEX to AMEX process using Alamine 336 for improved selectivity.
1960's	First phase expansion of USX industry. Many process innovations from 1960's to 1970's.
>1960's	Gradual acceptance that atomic energy can be used for clean energy production drives new project development.
1973	Oil crisis drives U price higher; new projects established.
1979	USX industry at its peak, with more than 18 mills around the world using Alamine 336 (about ¾ of Western uranium production).
1979	Three Mile Island incident.
1986	Chernobyl incident. Industry goes into long contraction, with few exceptions (eg, Olympic Dam and several Canadian plants are commissioned).
Mid 2000's	Awareness of reducing uranium stockpiles drives uranium price higher, spurring new project exploration and expansion. The USX (and IX) industry starts to recover.
2010	Consensus gradually dawning that the world needs alternative energy sources. Many new nuclear power plant reactors in construction. Attitudes towards nuclear energy becoming more positive.

3. COGNIS AND USX

Cognis is a mid-tier specialty chemical company which evolved from Henkel's Chemicals Group in the late 1990's. The mining chemicals division of Cognis originated from General Mills Chemical Inc which was involved, with many other organisations, in developing the USX process starting in the late 1950's. The same GMCI chemists and engineers went on to invent the copper solvent extraction process in the 1960's. Their descendants today continue to work in the copper and uranium solvent extraction areas, manufacturing the extractants, and helping clients to solve their process issues.

4. URANIUM SOLVENT EXTRACTION WITH TERTIARY AMINES

The process of USX by tertiary amines has been described in many previous publications (refs.2-7) and so only a brief description will be provided here.

Following leaching the Pregnant Leach Solution (PLS) containing the dissolved uranium values is contacted with an organic phase consisting of a hydrocarbon diluent, a long-chain tertiary amine, and usually a third-phase modifier such as isodecanol. Extraction of uranium into the organic phase occurs, usually, in four countercurrent stages with very high recoveries typically attained.

The loaded organic may be scrubbed of impurities in the subsequent scrubbing stage(s) if necessary, and the uranium is then stripped from the organic phase into a purified liquor, again, usually in four countercurrent stages. There are several stripping processes that can be employed depending upon localised preferences. The uranium is recovered from the pregnant strip liquor, again by various precipitation techniques, to produce a high purity uranium oxide concentrate to ship to the nuclear fuel converters.

Both the USX process efficiency and the product quality can be affected by the presence of impurities in the leach liquor, since:

- Impurities present in the PLS can interfere with the chemical or physical aspects of the SX process.
- Tertiary amine extractants in the protonated form function as ion exchangers and are not perfectly selective for the uranium anions over other anions which are present in the PLS. The tertiary amines are however more selective for uranium than the quaternary amine functionality employed in ion exchange resins and this is why tertiary amine solvent extraction has often been used to purify the concentrated eluant produced from a uranium ion exchange plant.

PLS impurities may be either organic or inorganic in nature. Where they are the cause of process problems, methods must be sought to minimise their effects. With sufficient information available to the design engineers prior to plant and process construction, suitable treatment methods may be incorporated in the project design phase. However, that information is not always available and, during the course of mine life, process conditions may change (due to ore or water source changes, for example). I n any case, the problem whether potential or actual requires identification before a remedial solution can be implemented

5. IMPURITY TRANSFER

5.1 TRANSFER MECHANISMS

As in most metallurgical processes, the separation step is never complete nor is it totally efficient. Unwanted impurities are almost always carried along with the loaded organic phase. The impurities can be transferred from the PLS into the final product by either physical entrainment of the PLS (and crud) in the organic phase~~,~~ and/or chemical transfer. The concentrations of some impurities can buildup in the organic phase. In either case, the impurities may cause process or product purity challenges in which case it becomes important to determine which transfer mechanism is dominant in order to devise a solution to the impurity transfer problem. For example, usually, a study of the concentration ratios of impurities in the PLS vs the concentration ratios in the strip liquor can highlight which elements are being entrained in the organic phase, and which are being co-extracted and subsequently concentrated. An example is demonstrated in the following table.

.

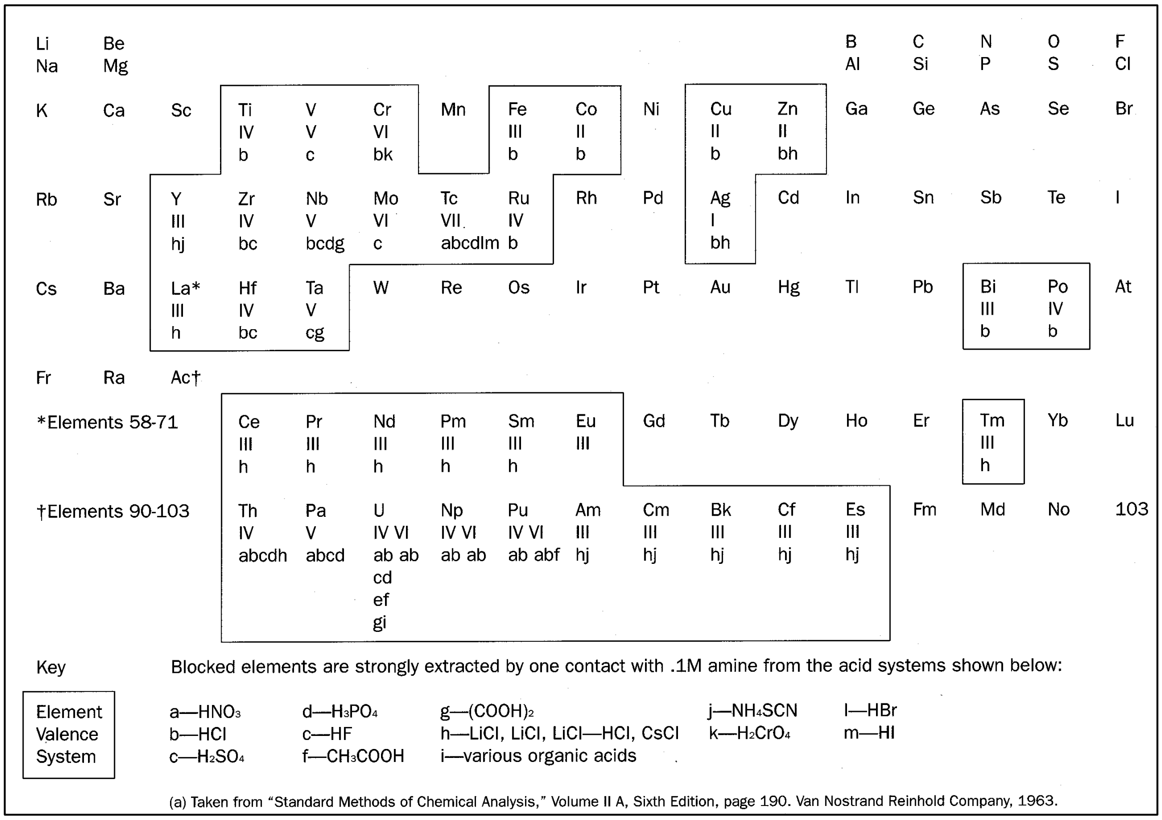
Element (gpl)	Al	Cl	Fe	Mo	Si	U_3O_8	Zr
PLS	3.0	2.5	5.0	0.01	0.20	0.5	0.01
Strip	0.03	5.0	0.05	0.05	0.02	20.0	0.10

Table 1: Sample Analysis of a USX PLS and Loaded Strip Liquor

In this example, elements that are transferred by entrainment of PLS in the loaded organic phase include Al, Fe and Si since their concentrations in the loaded strip liquor are lower than in the PLS. Alternatively, those impurities that are chemically transferred include Cl, Mo and Zr whose concentrations are higher in the loaded strip liquor than in the PLS.

5.2 CHEMICAL TRANSFER

Chemical impurity transfer occurs when the impurities are chemically co-extracted by the tertiary amine extractant and then stripped into the loaded strip liquor in the Strip Stage. The degree of impurity loading often depends upon several factors such as the amine concentration, the operating organic uranium loading, the relative concentrations of extractable values/impurities in the PLS, the phase ratios used in extraction, and more. Some of the elements extracted by tertiary amines are shown below.



Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti IV b	V V c	Cr VI bk	Mn	Fe III b	Co II b	Ni	Cu II b	Zn II bh	Ga	Ge	As	Se	Br
Rb	Sr	Y III hj	Zr IV bc	Nb V bcdg	Mo VI c	Tc VII abcdlm	Ru IV b	Rh	Pd	Ag I bh	Cd	In	Sn	Sb	Te	I
Cs	Ba	La* III h	Hf IV bc	Ta V cg	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi III b	Po IV b	At
Fr	Ra	Ac†														
*Elements 58-71			Ce III h	Pr III h	Nd III h	Pm III h	Sm III h	Eu III	Gd	Tb	Dy	Ho	Er	Tm III h	Yb	Lu
†Elements 90-103			Th IV abcdh	Pa V abcd	U IV VI ab ab cd ef gi	Np IV VI ab ab	Pu IV VI ab abf	Am III hj	Cm III hj	Bk III hj	Cf III hj	Es III hj	Fm	Md	No	103

Key

Blocked elements are strongly extracted by one contact with .1M amine from the acid systems shown below:

Element
Valence
System

a—HNO_3
b—HCl
c—H_2SO_4
d—H_3PO_4
c—HF
f—CH_3COOH
g—$(COOH)_2$
h—LiCl, LiCl, LiCl—HCl, CsCl
i—various organic acids
j—NH_4SCN
k—H_2CrO_4
l—HBr
m—HI

(a) Taken from "Standard Methods of Chemical Analysis," Volume II A, Sixth Edition, page 190. Van Nostrand Reinhold Company, 1963.

Figure 1: Elements extractable by Tertiary Amines (Ref. 8)

This list is not by any means complete, and it may be expected that other elements may also be extracted by tertiary amines depending, for one, upon the aqueous system being treated.

Typically the impurity elements need to be in an anionic form to exchange with the sulphate / bisulphate ion associated with the protonated tertiary amine. These elements are either anionic in nature, i.e. chloride, bromide, fluoride, etc, or others which form anionic species such as zirconate, cobalticyanide, bismuth oxychloride etc.

5.3 PHYSICAL TRANSFER

Physical transfer occurs by entrainment of PLS, or as fine crud / precipitates, carried over in the loaded organic. Useful information on the forms of physical entrainment may be obtained by analysing the plant operation parameters such as PLS and loaded strip liquor assays, organic depth, organic space velocity, crud removal and build up rate, aqueous removal rate from the loaded organic surge tank, etc.

Routine analysis of the loaded organic phase exiting the extraction stages (and/or loaded organic tank) for aqueous (PLS) entrainment can assist in identifying impurity transfer before it becomes problematic. If a significant level of aqueous entrainment is detected (i.e.>100ppm) then preventative measures to reduce it can be implemented once the cause has been identified.

Of interest is that the crud produced in a USX plant in the extraction stages may consist of a high concentration of an impurity element such as silica. Silica can be concentrated at the organic/aqueous interface. Even very small quantities can form significant volumes of siliceous crud. In these cases, entrainment of the crud in the loaded organic phase can cause elevated impurity levels of silica and other impurities in the strip liquor and final product.

6. PHYSICAL ISSUES

Some of the problems encountered in uranium SX circuits may not solely be associated with impurity transfer but could be associated with a change in the behavioral characteristics of the organic phase brought about by the introduction of an unwanted species into the PLS and – subsequently – its transfer into the organic phase.

The predominant physical parameters that can influence the performance of the organic phase include;

- Phase Disengagement Time (PDT)
- Organic Space Velocity
- The presence of silica or solids

Parameters that influence the PDT can be;

- Mixing speed and intensity;
- Viscosity and density of the organic (i.e. temperature, reagent concentration and loading);
- Organic and crud depth in the settler and organic flow rate factors which also affect the organic space velocity.

Therefore, regular checks of the PDT should be made to keep a record of performance changes over time. Routine measurement of the organic depth and a means to control it are recommended as good operating and design practice.

7. ANALYTICAL TECHNIQUES

A variety of analytical techniques are available to the troubleshooter to assist in the identification of problems associated with impurity transfer. Often, both experience and intuition play an important conjunctive role when examining the process problems and the results of analytical work.

Several of the tests employed for process monitoring and control may shed light on the source or reason for impurity transfer, such as routine PDTs and extraction isotherms, etc; and then there are investigative methods, such as PDT matrix, surface tension and viscosity measurements, pH scrubbing and stripping tests, etc. Most of these can be evaluated at the plant site.

Other test methods that may be found to be extremely useful in determining the composition of a circuit organic and the presence of any impurities dissolved in the organic phase may involve techniques more complex than those available at the plant site. These methods typically require instrumentation only available in a specialized laboratory. In addition, often the results of these tests require interpretation where experience will often play a significant role. Some of these are discussed below.

7.1 ON–SITE TESTS

7.1.1 Alamine 336 Concentration and Tertiary Amine Content

It is important to know the concentration of amine present in the organic phase to ensure the desired uranium recovery may be achieved, but without having excess amine available which may promote impurity transfer. It is also important to know if secondary amines are present in the organic.

A series of titrations may be used to determine both the tertiary amine concentration and the secondary amine concentration in the solvent. Typically Alamine 336 is the highest purity tertiary amine reagent commercially available, i.e. >95% and in some cases >99% tertiary amine, with very low levels of secondary amine (</= 0.5%) and zero primary amine.

Minimizing the level of secondary amine in the incoming reagent is desirable since secondary amines tend to be problematic in the USX process as they:

- promote impurity transfer;
- tend to form insoluble complexes/salts, and
- are more prone to reagent degradation than are tertiary amines.

Degradation of tertiary amines in USX circuits often involves formation of secondary amines as either an intermediate in the degradation pathway or as a final product. While the presence of some secondary amine in a USX circuit organic is to be expected, the presence of elevated levels of secondary amines in a USX organic can indicate the existence of some reagent degradation issues that need addressing.

Titration based analytical methods for the determination of Alamine® 336 and secondary amine concentrations in the plant organic are available (ref 9). The concentration of isodecanol – the third phase modifier – may also be determined by titration.

Since the tertiary amines break down first to secondary amines and then to primary amines, it may be expected that primary amines should be present in the circuit organic. In actual fact, Cognis has yet to find any evidence for the presence of primary amines in the circuit organic. Either the degradation pathways do not lead on to primary amines or the primary amines are water soluble enough that they very quickly wash out of the circuit organic.

The above mentioned procedures involve the use of perchloric acid as the titrant. If perchloric acid is used as a titrant, the end point of these titrations can be determined by an indicator end point method or by a potentiometric method. Many labs find the use of titrimetric methods involving perchloric acid to be undesireable from a safety standpoint due to the explosive nature of many perchlorate salts and organic compounds. While Cognis has used this method for more than 50 years without incident, the use of perchloric acid requires rigid attention to laboratory safety procedures and strict laboratory hygiene. Recently, Cognis has carried out some work to show that perchloric acid can be successfully replaced with HCl. The overall shape of the potentiometric curve with the HCl is not quite as clean as with the perchloric acid. As a result, the HCl method is less precise but it is certainly adequate as a plant control method.

A key point in successfully carrying out these titrations is to make sure that the circuit organic sample is completely stripped and also deprotonated. Protonated amine will not titrate resulting in lower than expected results. Cognis has a Blue Line Bulletin describing a procedure to ensure that the organic is completely stripped and contains no residual aqueous strip solution. The presence of any aqueous strip solution will result in excess consumption of acid titrant resulting in higher than expected results. The use of wax treated filter paper to remove entrained aqueous is, in such cases, required.

The titration procedure is the preferred method for determining the concentration of amine in the USX organic. Gas Chromatographic (GC) methods have been investigated as a replacement for the titration procedure. The use of GC for these quantitative analyses is problematic. Alamine 336 is a mixture of 4 different amines which will breakdown to yield 3 different secondary amines. In a GC, these amines all give different response factors relative to typical internal standards. The response factors also are non-linear making it very difficult to develop a consistently accurate method. The presence of hot active glass and metal surfaces can also lead to thermal breakdown of the amines in the GC. These surfaces must be maintained as completely passivated by silylation prior to analysis. The circuit organic samples must also be completely stripped prior to GC analysis. Any loaded salts will be deposited in the injection port over time and help to catalyze breakdown of the amines.

In the absence of titration methods the maximum uranium uptake of the organic can be routinely evaluated against both the plant PLS and also a synthetic PLS (the “maximum load”). The synthetic

PLS will provide a consistent reference point to back-calculate the approximate amine concentration. Whilst the plant PLS maximum load value can indicate any potential issues with uranium loading due to other problematic impurities in the PLS such as chloride, nitrates, etc.

7.1.2 Phase Disengagement Time Tests

The simplest way for the plant personnel to assess the physical performance of any SX process is to conduct routine and regular PDT tests. Standard Cognis quality control tests employing a standard baffled beaker and turbine may be used to assess phase separation behavior. Contacting the plant PLS and organic phases together and timing (and observing!) the phase disengagement characteristics can tell one much about the health of the SX process. These tests should be conducted under both organic continuous (OC) and aqueous continuous (AC) mixing conditions. The plant solutions should also be checked against their synthetic or virgin counterparts, i.e. synthetic QC PLS and virgin organic containing fresh amine and isodecanol in clean diluents.

A retarded OC PDT can indicate that there are contaminants or impurities in the organic phase whereas a slow AC PDT will tend to indicate that there are impurities in the aqueous phase that are restricting the coalescence of the organic droplets, such as silica, flocculants, or fine aqueous wetted solids.

If it is suspected that impurities are present in the organic phase a laboratory regeneration test can be conducted and the regenerated organic then subject to PDT tests. A difference in behaviour between the regenerated organic and plant organic will confirm the presence of a contaminant.

7.1.3 Viscosity

Whilst not a procedure commonly used at plants, tracking the viscosity with temperature and reagent concentration / uranium loading of the organic phase can provide some useful reference data should issues with PDT arise. This reference library can indicate if the change in viscosity has been rapid or gradually occurring and may assist with troubleshooting the plant performance. Viscosity can simply be measured by using a low cost, relatively simple falling ball type viscometer.

7.1.4 Scrub and Strip tests

In USX circuits using ammonia/ammonium sulphate scrub and strip aqueous systems there are a number of scrub and strip stages operating in series with a rising pH profile as the organic moves downstream. It is not possible to exactly simulate a multistage SX circuit with a pH profile in a batch laboratory test. However there are some tests which can be carried out to determine if the plant circuit is operating in the manner for which it was designed.

Scrub Circuits

A (500 ml minimum) sample of plant loaded organic or of loaded organic which has already been scrubbed with dilute sulphuric acid is contacted at an O/A of 1 in a baffled beaker. The turbine is started in a way that produces aqueous continuous mixing. The pH of the aqueous is measured. Ammonia/ ammonium sulphate at the plant design concentration is then added to bring the pH of the aqueous up to 2.5. The mixing is continued at this pH for 3 minutes. A small sample of aqueous and organic are withdrawn from the beaker and analysed for uranium and the impurity elements which need to be scrubbed from the organic. Further ammonia/ammonium sulphate is added to bring the pH up to 2.6 and a further sample of emulsion is taken. This process is repeated using 0.1 pH steps until the pH is in the range 2.8- 2.9. From the analytical data it is possible to see how effective the scrubbing process is and what pH values should be targeted in order to scrub impurities from the organic.

Strip Circuits

A (500 ml minimum) sample of plant scrubbed loaded organic is contacted in a beaker at O/A 1, aqueous continuous, with barren ammonium sulphate from the ADU precipitation circuit. After three minutes mixing the pH is measured and a sample of the emulsion is withdrawn for analysis of the organic and aqueous for uranium. Aqueous ammonia (100 g/l) is added to increase the pH by 0.2 to 0.25 units and the process is repeated. By continuing the test to cover the pH range of the strip circuit it is possible to determine the optimum pH profile for stripping.

Obviously these scrub and strip batch tests can also be used to evaluate the effect of ammonium sulphate concentration on the scrub and strip stages.

7.2 LABORATORY ANALYTICAL TESTS

Whilst the above methods are useful in pointing the investigator towards the cause of the problem, a range of analytical techniques using specialised instrumentation are often required to supplement the site tests. A combination of the observations from both sets of techniques would then be utilized to try and assess the source of the problem. These techniques include, but are not limited to:

- Gas Chromatography (GC);
- Infrared Spectroscopy (IR);
- Mass Spectroscopy (MS).

The problems with the use of GC to carry out quantitative analysis of USX circuit organics has already been addressed. GC is a useful tool however for qualitative analysis. It is useful for determining the relative ratios of the various tertiary amines and secondary amines present in a circuit organic. For example, this can be useful information in helping to interpret the nature of degradation analysis. The composition of Alamine 336 is very uniform. If the amine is being degraded by the presence of an oxidant in the aqueous phase, the lower molecular weight amines will tend to be selectively degraded and this shift will be observable in the overall distribution of the various amines. The retention times of various alternative degradation products relative to those of the Alamine 336 components is also known. The presence of degradation products such as unsaturated amines, nitrosoamines, etc result in a characteristic GC “fingerprint” of peaks that can quickly help to pinpoint the nature of the problem.

Combining GC with Fourier Transform Infrared Spectroscopy (GC-FTIR) results in a very useful tool in analysizing circuit organics. The components of the circuit organic sample are separated by the GC and the individual peaks are then passed through the FTIR. The combination of the retention times of the peaks under known conditions as well as the IR spectra allow one to identify the components. The combination of GC with MS can be used in a similar fashion to the GC-FTIR. Chemicals have characteristic breakdown patterns in the MS which can be used in identifying them.

Contaminants may be present in such small quantities that it is difficult to get useful analytical data. One way to obtain a more concentrated sample, especially of materials which have an acidic proton, is to essentially regenerate the organic by contacting it with aqueous base (pH 11-13). The contaminants as salts will often be either extracted into the aqueous or form a dark viscous third phase. Use of a caustic 10-15% ethanol solution will often improve extraction of the salts of contaminants into the aqueous phase. Neutralization of the aqueous and/or third phase with sulphuric acid to a pH of 4-5 will result in freeing up the contaminant so that it can be collected in a concentrated form for study.

8. DETERMINATION OF URANIUM MAXIMUM LOADING AND EXTRACTION ISOTHERMS

8.1 MAXIMUM LOADING

Alamine 336 in its protonated form extracts uranium via an ion-pairing type ion exchange mechanism. The theoretical uranium maximum loading for 1 v/v% Alamine 336 for the uranyl sulphate species is as follows:

Hexavalent (predominant)	$UO_2(SO_4)_3^{4-}$	1.43 g/l U_3O_8	(or 1.21 g/l U)
Tetravalent (rare)	$UO_2(SO_4)_2^{2-}$	2.86 g/l U_3O_8	

In practice the maximum loading is not achieved when extracting uranium from acid sulphate solutions. The inevitable presence of sulphuric acid and in particular the bisulphate anion HSO_4^- results in some of the potential uranium sites being occupied by the bisulphate and sulphate anions. This depresses the value of the uranium maximum loading. Other competing anions such as chloride and nitrate will also co-extract with uranium and depress the uranium loading. Therefore the equilibrium loading of anions on the organic in contact with a PLS containing sulphuric acid and an extractable anion such as chloride will be:

Total anion loading is proportional to: $[UO_2(SO_4)_3^{4-}] + [HSO_4^-] + [Cl^-]$

It is not uncommon for the plant uranium maximum loading to be around 75% - 80% of the theoretical maximum loading or approximately 1.0 g/l U_3O_8 per 1.0 v/v% Alamine 336 and in the presence of high chloride or nitrate concentrations it may be less than 50% of the theoretical value. It should be noted that the uranium maximum loading versus plant PLS corresponds to the point of maximum crowding by uranium of impurity anions. In practice uranium solvent extraction circuits do not operate under uranium maximum loading conditions. At the lower uranium loadings experienced in plant operation, the crowding effect will be reduced and the concentration of impurity anions as compared to uranium anions on the organic will be higher than at the maximum loading value.

Because most USX circuits operate at high A/O values it will be necessary in the laboratory to use repeated batch contacts at high A/O values in order to determine the maximum loading of all the potentially extractable anions. Both the organic and the aqueous in equilibrium with the organic should be analysed for uranium, sulphate and any other anions being extracted.

8.2 ISOTHERM DETERMINATION

Where competing anions are present it is necessary to determine the uranium and competing anion concentrations in the organic and aqueous phases over a wide range of O/A ratios. The concentrations of contaminating anions such as zirconates which can affect the physical operation of the SX circuit and report as an impurity in the final product should also be measured even though these anions are seldom present at concentrations high enough to noticeably depress the uranium extraction.

9. PLS CLARITY – SOLIDS

Where solids are present in the PLS there is almost certainly always an interaction with the organic phase when the two phases are contacted in the extraction mixers. (This applies to mixers in other section of the SX circuit also).

Solids occur in the PLS due to incomplete clarification of the leach liquor and since this is never totally efficient there are always some solids present in the PLS.

The organic phase contains both a charged species – the protonated amine – and usually an alcohol modifier, both of which can interact with suspended solids: the amine through electrostatic forces, and the alcohol through hydrogen bonding forces. The degree of interaction depends upon both the nature and the amount of the solids involved.

Thus, whenever an unclarified PLS contacts an amine you can expect to see some crud generated, which in mild cases will be responsible for impurity transfer, and in extreme cases for shutting down the plant until removed.

Typically, design specifications call for less than 20ppm solids in the PLS, although on occasions solids levels can and do exceed several hundred ppm and in extreme cases several thousand ppm. During such extreme events, many operators will choose to bypass or shutdown the SX process until the PLS clarity returns to normal levels. This preventative action can save many hours of process disturbance and increased operating costs. In some cases, it minimises the risk of having to shutdown the SX circuit for a lengthy period of time to clean out the crud and solids accumulation that results.

10. PLS CLARITY – SILICA

Silica has caused problems in most USX plants the world over, especially in agitation leach plants where the dissolution of silica is promoted by the high surface area of the milled pulp. High acid concentrations and temperatures in the leach process promote silica dissolution. In the USX plant silica rapidly precipitates from solution at the organic/aqueous interface when the aqueous phase contacts the USX organic; in so doing it produces crud.

When crud is formed in the extraction section it usually migrates throughout the organic phase taking PLS impurities with it. The crud may become so voluminous that the plant will have to be stopped and the organic phase removed.

Silica is known to self-coagulate and precipitate from solution. It is important if silica is considered to be a potential problem that precautions to evaluate and treat silica be properly considered. One project in the 1970’s failed to adequately take this into account. They shipped leach solution overseas for testing, during which process the dissolved silica present in the PLS precipitated and failed to report in the subsequent test program. The plant was designed and built and immediately encountered significant crud issues, so limiting plant production rate. At significant expense a second plant was designed and installed to allow the project to attain design PLS throughput rates.

Ore mineralogy often affects the quantity of dissolved silica in the PLS. The presence in the ore of chlorite, for example, which is more easily leached than silica, will always tend to promote crud formation and several plants have been adversely affected in this way. Appropriate control measures and ore blending are often required to ameliorate the situation.

Whenever dissolved silica is present in the PLS, crud production is always more severe when the plant is operated in Aqueous Continuous (AC) mode. Thus, it is usually a rule of thumb that all USX circuits should operate in Organic Continuous (OC) mode to minimise the harmful effects of dissolved silica. Due to the design of the process equipment, one plant found that in order to maintain design recoveries it was unable to operate in OC mode, and thus had to suffer higher organic loss due to entrainment and crud generation, and some associated impurity transfer, due to the need to operate in AC mode.

In many cases when either solids or silica are present in the PLS in troublesome amounts it may be difficult for the plant operators to hold organic continuity in the mixers. Under these conditions, it is often required to increase the mixer O/A ratio, sometimes substantially, in order to regain control of mixer phase continuity. In extreme cases, this may require complete cessation of aqueous flow for a while which is always preferable to a complete plant shutdown due to a major crud event.

11. ADDITIVES

11.1 Coagulants

Wherever silica becomes a significant issue, the use of silica coagulants should be investigated. The coagulant is often added to the clarifier ahead of SX, and the coagulated silica is flocculated with the clarifier solids. Neutral charge coagulants like polyethylene glycol ethers are the best type for use ahead of USX circuits in view of the ion exchange process involved. Adding ionically charged species ahead of SX may result in physical (PDT) problems downstream.

11.2 FLOCCULANTS

Many USX plants have experienced process difficulties due to poor phase disengagement as a result of incorrect flocculant selection or with overdosing. When flocculant addition is suspected of causing problems in the USX circuit or where flocculants are being screened for possible use ahead of USX, then laboratory PDT batch tests can be used to evaluate the flocculant type. Typically the choice is between non ionic, anionic and cationic polyacrylamides. The flocculant is added to the aqueous phase and the phase is mixed before adding to the test beaker. If a flocculant has a detrimental effect on the phase separation rate then the use of this flocculant in the uranium plant should be avoided.

Questions often arise as to what level of flocculant addition should be tested. This is a difficult decision to make as the bulk of the flocculant added to the solid liquid separation and clarification circuits is adsorbed on the solids and does not usually report to the USX plant unless the clarifier misbehaves or overdosing occurs. In addition there is the possibility that residual flocculant in the raffinate may recirculate and may build up in the PLS. A strategy which Cognis has used is to add the flocculant at ten times the anticipated addition rate. If this addition rate shows no harmful effect in the phase separation test then this flocculant may be regarded as being potentially harmless. If however it substantially changes the phase separation rate then the flocculant is potentially harmful and further tests must be carried out to determine the longer term effect of flocculant type and concentration on phase separation behaviour.

The golden rule with plant flocculant addition is to select the flocculant type carefully and not to overdose. The addition point is also worthy of consideration, as it helps if the PLS is clarified upstream of the USX plant and before a PLS settling / storage pond to provide some time for any silica to coagulate and for flocculated solids and residual flocculant to settle out of the PLS.

At times, unusual problems may be associated with flocculant addiition. One plant in USA found that its organic strip point was increasing – inexplicably – over time, so causing higher raffinate values and lower uranium recoveries. Temporary relief was obtained by increasing amine concentration, but this was a costly exercise and a remedy needed to be found. Based upon the local circuit and processing conditions a number of theories were expounded regarding the cause – presence of molybdenum, amine degradation, etc. by a variety of experts. After exhaustive investigations by General Mills chemists it was concluded that a guar-based flocculant used in the process was in part responsible for the stripping issues. Once the flocculant was removed the plant slowly returned to normal operation.

This was somewhat of an unusual case brought about by the unique chemistry of the plant in question. Frequently in the past, guar-based flocculants have been very successfully employed as filtration aids when filter circuits have been used in the solid/liquid separation stage of the process prior to SX.

12. ORGANIC ACIDS (AND OTHER SX REAGENTS)

If organic acids are present in the PLS they can substantially interfere with uranium extraction and stripping performance, since often their corresponding mechanisms may be competitive. Organic acids may occur in several ways: they may derive from carbon in the ore which converts to organo-soluble specie during leaching; they may occur as decomposed vegetation particularly when previously milled tailings are reprocessed, or they may occur due to the plant design.

Organic acids can affect USX operation in several ways. They can severely impact upon the phase separation rate eventually leading to complete plant shutdown until the problem is isolated and treated. They can reduce amine loading capacity since the (often) anionic organic specie are extracted by the amine and do not strip. Or in one or two special cases the organic species may load uranium during stripping resulting in transfer of uranium back into the extraction section, and lowering plant recovery.

Determination of the cause may be a complex task, and usually continuous regeneration of the plant organic is required at high pH to remove the unwanted species.

13. ZIRCONIA

Tertiary amines extract zirconia along with uranium into the organic phase and, if present in the loaded organic which is presented to the stripping stage, will strip into the loaded strip liquor and report to the final product as a contaminant. Zirconia is a penalty element in uranium concentrates and should always be removed if possible in the scrubbing stage, intermediate between extraction and stripping. It may usually be removed by pH adjustment to around pH 2.5 – 3, but it frequently comes out of solution as a ultrafine, loose, crud which may require special operating practices to be instituted to keep the process running. The impact of zirconia on final product purity may be minimised by allowing some uranium to circulate around the final scrub stage, so displacing zirconia by crowding effects.

14. CHLORIDE

Chloride is quite strongly extracted by tertiary amines – competing for loading sites on the organic with the desired uranium values. Chloride may derive from the ore minerals, the ore moisture, the site make up water and/or the sodium chlorate oxidant that is sometimes used in the leaching process.

The presence of chloride in the PLS can result in the formation of anionic complexes such as $Fe(Cl)_4^-$ and these can also be extracted by tertiary amines.

In the past, an upper limit of chloride in the PLS of around 2 gpl was considered realistic, but higher levels have more recently been found to be tolerated if sufficient extractant concentration is employed and the scrub stages are operated appropriately.

Although chloride is less easily scrubbed than zirconia, again, like zirconia, chloride transfer to final product may be partially regulated by the recycle of uranium in the scrub stage. Fortunately, chloride presents less of issue in the final uranium precipitation product, as evidenced by some plants which employ a chloride ion exchange strip process for tertiary amines, as do some of the IX processes.

15. NITRATE

Nitrate is strongly extracted by amines and in some cases may degrade the amine. In some early SX circuits this proved problematic because they were employing a nitric acid strip of IX resin prior to SX in an Eluex plant. All nitrate strip Eluex circuits were converted to acid sulphate strips.

In two cases nitrates are known to have resulted in degradation of the tertiary amine to a secondary nitrosamine. In the first case in fact it took some years to identify the cause, but in both cases the degradation was associated with an Eluex circuit design, not an Amex circuit. Conversion to nitrosamine changes the amine to a form which does not protonate, nor therefore does it extract any species in a SX circuit. Usually, nitrosamine formation is thus accompanied by a fairly rapid loss of uranium loading on the organic phase with an associated increase in uranium raffinate values. Continued addition of tertiary amine to the circuit may be required on a daily basis to maintain reasonable extraction levels, so leading to a significant elevation of processing costs until the appropriate control measures are taken.

Fortunately, nitrosamine is readily detectable by GC examination of the circuit organic phase. Nitrosamine formation is usually associated with the presence of several conditions: acid; nitrate; a high Eh; and perhaps chlorides (which are thought to help catalyse nitration).

16. OXIDATION POTENTIAL

Tertiary amines are stable under most process conditions like temperature, acidity, and alkalinity, however at high oxidation potential degradation of the tertiary amine to a secondary, and then possibly a primary amine, will occur. There have been several industrial examples – most commonly seen if there are strong oxidants present that can be extracted into the organic phase, like in the extraction of vanadium(+5), a strong oxidizing agent.

Exposure of tertiary amines to strong oxidants such as H_2O_2 will result in conversion of the amine to the corresponding amine oxide. In the presence of ferric ion, the amine oxide is converted to an alkyl aldehyde and the corresponding secondary amine. This chemistry occurs very rapidly, essentially within the time of mixing the organic and the aqueous phases. Even brief exposures can result in significant degradation of the amine in the circuit.

17. VANADIUM

If vanadium is present in the uranium leach liquor, one can use control of the Eh of the solution to separate the uranium from the vanadium. So long as vanadium is present in the +4 state, it will not be extracted by a tertiary amine. Vanadium(+5) is readily extracted. Uranium is 100% converted to the +6 state at an Eh of 320 mV in acidic sulphate systems. Vanadium(+5) is rapidly reduced to the +4 state by ferrous ion. If any iron is present in the PLS and the Eh is less than about 600 mV, all of the vanadium will be present as the +4 and the uranium can be selectively extracted away from the vanadium. Once the uranium is recovered, one can adjust the Eh of the raffinate to above about 720 mV and successfully extract the vanadium as a polyvanadate species.

As noted above, these polyvanadate species are strong oxidants and circuit organics used to extract vanadium reflect that fact. Cognis has analyzed a number of these circuit organics and they all exhibit a similar pattern. These organics contain some tertiary amine, lots of secondary amine, some unsaturated tertiary amine, and N,N-dialkyl formamide. The relative amounts of these components present are typically 1:1.5 to >10:0.1:0.02. The exact pathway by which these products are generated is not clear. It is thought that the V(+5) first converts the tertiary amine to an unsaturated tertiary amine which can then be rearranged to an imine which hydrolyzes to give secondary amine and an alkyl aldehyde. Alternatively, the double bond in the unsaturated amine is oxidized to give the dialkyl formamide and a shorter chain alkyl aldehyde. The dialkyl formamide could potentially hydrolyze to the secondary amine and formic acid. There does not appear to be any preference with regard to the tertiary amine used. Higher molecular weight amines appear to be attacked about as readily as the lower molecular weight amines suggesting that the oxidant is the polyvanadate species itself and the attack is occurring in the bulk organic phase.

Chagnes and co-workers have published some work on the role of vanadium(+5) in oxidizing Alamine 336 in an organic phase. Their investigation was carried out on synthetic solutions. They propose that the alcohol solvent modifier plays a key role in the oxidative attack on the amine and is itself oxidized to a carboxylic acid. This is not consistent with our findings. In circuit organic samples where isotridecanol is used as the solvent modifier, we find that the isotridecanol is present in the organic phase in about the concentration we would expect to find it based on addition rates and we find no evidence of the corresponding carboxylic acid even in very low concentrations. The chemistry occurring in the circuits appears to be significantly more complex than that under laboratory conditions.

Cognis has seen circuit organics where the organic contains little or no tertiary amine with significant levels of secondary amine and the N,N-dialkyl amides being present. These circuits seem to extract and transfer vanadium almost as well as fresh organic. Given these observations, it is suggested that one should not add fresh amine to a vanadium circuit if there are other amine circuits also operating at the site. If you are operating a uranium circuit also, one should only add fresh amine makeup to the uranium circuit and use uranium circuit organic as diluent and reagent makeup for the vanadium circuit. Fresh tertiary amine is relatively rapidly degraded in the vanadium circuit.

18. MOLYBDENUM

Molybdenum can be particularly troublesome if not identified early on in the life of the project, and even today – after many years of experience – it can present surprises. Molybdenum is present in many uranium deposits and is dissolved along with the uranium during leaching. Molybdenum co-extracts with the uranium from acidic sulphate leach liquors, and separation of the molybdenum from the uranium can be somewhat problematic. Molybdenum is readily stripped along with the uranium using sodium carbonate or ammonia/ammonium sulphate resulting in a uranium product that is not particularly desirable with regard to further downstream processing. The preferred option is to strip with acidic chloride which allows one to selectively strip the uranium away from the molybdenum (14,15).

Over time the molybdenum will build in concentration on the organic to the point where the loading capacity for uranium is reduced and eventually to the point where the solubility of the molybdenum species in the organic phase will be exceeded resulting in precipitation of a variety of amine-molybdenum complexes as a sticky third phase or "goo". This third phase will accumulate in the settlers at the interface and in the bottom of the settlers reducing settler volume and plugging interstage piping. These precipitates may be orange, green, blue or gray in color. The concentration of molybdenum on the organic can be controlled by scrubbing a bleed stream of the stripped circuit organic with an aqueous sodium carbonate solution from which the molybdenum can be recovered as a marketable product.

The molybdenum species present in an aqueous solution is dependent on the pH of the solution, the redox potential, and the presence of ions such as phosphate, silicate, arsenate, etc (15,16). One takes advantage of this variability in stripping of molybdenum from the amine. At typical extraction pH's (1 to 2), molybdenum is present as some type of polymolybdate which is preferentially extracted into the organic. At pH's >8, molybdenum is present predominantly as molybdate which is not as readily extracted. The combination of the deprotonation of the amine as well as conversion of the polymolybdate to molybdate helps to drive the sodium carbonate stripping process. In dilute sulphuric acid solution at pH's < 7, molybdenum(+6) will exist as a series of poly molybdenum oxides such as $Mo_7O_{24}^{-6}$ and $Mo_8O_{26}^{-4}$. Due to the large size of these anions and relatively low charge density, they are readily extracted into the organic phase. If heteroatoms such as phosphorus or silicon are present in solution, heteropolymolybdates can be formed. An example of a typical polyphosphomolybdate is $PMo_{12}O_{40}^{-3}$ where the molybdenum is all in the +6 oxidation state. It transfers into the organic phase as a complex with three protonated amines. Due to the large size of the anion and the relatively low number of protonated amines associated with it, it has limited solubility in the organic phase. If one or two of the molybdenum atoms are present as the +5 species, the protonated amine complex is even less soluble and more prone to precipitate out as a green complex.

Where molybdenum is an issue, one can minimize the problem by ensuring that the molybdenum is all present in the +6 oxidation state and using a diluent with a higher aromatic content.

19. THORIUM

Following an oxidising sulphuric acid leach uranium will be present in the leach solution as U (+6) sulphate ions $UO_2(SO_4)_3^{4-}$ and thorium as Th (+4) sulphate $Th(SO_4)_3^{2-}$. Both these anions can be extracted by amine based extractants. Fortunately the relative extraction of uranium and thorium varies with the type of amine used and this variation is the basis of the solvent extraction circuits which have been proposed for uranium/thorium separation.

Thorium currently has little or no commercial value. However for a leach solution containing soluble uranium and thorium it is not possible to simply extract the uranium and to reject the thorium to the raffinate. Firstly the raffinate contains valuable sulphuric and ferric ions and must be recycled to leach. This will also recycle thorium and the thorium content in the leach solution will build up to unacceptable levels.

Also thorium cannot be rejected into the environment. Therefore any uranium solvent extraction circuit treating a solution containing appreciable quantities of thorium must also incorporate a thorium recovery (removal) circuit which produces thorium as a stable compound which can be stored in tailings dams or in land fill.

In addition thorium is a penalty contaminant in uranium yellow cake. Therefore the uranium solvent extraction circuit must incorporate both extractant composition purity and loaded organic scrubbing to ensure that thorium is substantially removed from the uranium organic prior to uranium stripping.
Most of the uranium/ thorium solvent extraction circuits descried in the literature rely on the differences between the extraction of thorium and uranium from acid sulphate leach solutions by various amines. It should be noted that few of the circuits proposed have been commercialised. The relative extraction of uranium and thorium from a pH 1 sulphate solution containing~ 1.0 g/l of uranium and thorium by various amines is given below.

The Extraction Coefficient is $[M]_{org} / [M]_{aq} = EC$

Amine type	Trade name	EC U	EC Th
Primary	Primene JM	5-30	>20,000
Secondary	Amberlite LA-1	80-120	5-15
Tertiary	Alamine 336	140	<0.03

Table 2: Extraction coefficient of Uranium (VI) and Th (IV) by various Amines (10)

20. COBALT AND GOLD

In some South African uranium circuits – which were usually tacked onto an existing gold plant – the uranium loading capacity was seen to decline over time, so resulting in higher raffinate values and uranium losses.

This was especially evident in uranium plants that incorporated an Eluex circuit, and after much exhaustive investigation by many parties it was found the loss of loading was associated with cobalticyanide poisoning of the ion exchanger – with resins being more adversely affected than solvent based systems. Various formulae have been proposed for the cobalt species involved – $[Co(CN)_6]^{3-}$, $[Co(CN)_4.2H_2O]^{3-}$ for example – and a divalent Co species $[Co(CN)_5 H2O]^{3-}$.

Complete deprotonation of the amine allowed its re-use in extraction, and in some circuits deprotonation revealed the presence of a gold-sulphur-cyanide complex in the strip aqueous (regeneration aqueous) solution; gold thiocyanate. Whilst this was first seen as a problem as it decreased uranium loading capacity, the solution proved much more useful (and profitable) than most of the issues discussed above, because it was found that gold could be recovered from the regeneration aqueous solution. This was implemented at several plants in South Africa in the 1970's with many ounces per month of gold being recovered in the uranium SX circuit.

It is interesting that not all South African Gold/Uranium plants experienced any significant gold loading on the USX organic. Since the aurocyanide complex is not stable in acid, to extract gold you first had to make thiocyanate and then to form the acid stable $Au(SCN)^{2-}$ anion. Thiocyanate was produced in the leach but not all plants produced much thiocyanate and it seemed to depend on the amount of pyrite present and the leach conditions. A forward leach probably favoured thiocyanate formation whereas a reverse leach may not have done so. Also, plants which added acid plant calcine to the uranium leach – whose main feed was gold plant tails – seemed more likely to produce thiocyanate since the calcine contained quite a lot of gold as it was formed from a float concentrate which concentrated the pyrite, gold and uranium.

21. BIOLOGICAL ATTACK

Over the course of history humankind has developed a liking for alcohol, and so it is not unsurprising that such attractions can occur naturally. A large solvent extraction plant some time after start-up experienced an unexplained loss of the third phase modifier isodecanol, and after exhaustive investigations it was found that the isodecanol was being consumed by fungus. Switching to an aromatic diluent enabled the circuit to operate without any isodecanol present and eliminated the problem.

22. CONCLUSIONS

Uranium recovery from acid leach liquors usually involves extraction and purification with either an ion-exchange resin or a tertiary amine, typically Alamine® 336, or in some cases, with both. Whichever recovery route is selected, process efficiency and product purity are invariably affected by the presence of impurities in the leach liquor since the extractants themselves are not altogether selective for uranium. These impurities may be either organic or inorganic in nature, and if problematic, methods must be sought to minimise their impact.

However, this information is not always available and, during the course of mine life, process conditions can and do change (i.e. due to ore and / or water quality changes,). In such cases, the problem needs identification, preferably at the mine site, before a remedial solution can be implemented.

Uranium solvent extraction is a mature process but still today may offer (unpleasant) surprises if appropriate impurity control measures are not taken during the plant design phase.

It is always advisable to conduct a thorough assessment for the presence of impurities in the leach solution and their potential impact upon the solvent extraction process. Much experience in tackling issues brought on by impurity transfer has been obtained over the years, but surprises can still occur. It is up to the metallurgical design engineer to minimise this risk.

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INNOVATIVE DESIGN IN TWO RECENT SOUTH AFRICAN URANIUM SOLVENT EXTRACTION PLANT INSTALLATIONS

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CONTENTS

1. INTRODUCTION

Australia-based Pacific Minerals Processing in association with M C Process of South Africa have in recent times designed and installed two uranium solvent extraction (USX) plants in the Witwatersrand basin region of South Africa. Prior to the design, extensive research was undertaken into the operational challenges facing uranium solvent extraction plants, and an attempt was made to provide solutions to these by incorporating novel process innovation and material of construction selection into the designs. Furthermore, construction, erection and process challenges experienced at the first USX plant led to further refinements and improvements in the design of the second plant.

Valuable experience has been gained that can be utilised to provide cutting-edge designs of mid-tier size SX plants for uranium and other metals.

Innovations incorporated into the design and construction of the two plants include the following:

- The use of a single pumper-mixer tank with no false bottom to provide pumping and mixing for a single stage, utilising a new SX pumper-mixer impeller: the Constant-Q Impeller to provide all requisite pumping and mixing for a stage, at a tip speed of below 215 m/min;
- The design of the distribution channel between pumper-mixer tanks and settlers;
- Simple organic to aqueous (O:A) ratio control in the provision of height and level adjustability of the aqueous weirs and easy, visual adjustment of recycle percentages in both aqueous and organic weirs;
- The design of the organic weirs: resulting in a reduction in organic losses due to misting and 'the waterfall effect', and reduced air entrainment in the organic;
- The use of vacuum-infused pure fibreglass-reinforced polyester (FRP) as the sole material of construction of SX settlers; and
- The use of Ross Pots to facilitate accurate pH measurement and control where necessary, preventing the pH probe from coming into contact with organic fluids.

2. USX PLANT DETAILS AND PROCESS PARAMETERS

2.1 EZULWINI PLANT (OWNED BY FIRST URANIUM CORPORATION)

The Ezulwini mine is located near Westonaria in the Gauteng province of South Africa, about 55km southwest of Johannesburg. The USX plant was commissioned successfully to C4 level (hot commissioning, with organic) in three weeks during April 2009, and has since been operating and producing satisfactorily. Plant details and process parameters are shown in Table 1.

	Ezulwini plant	**Mine Waste Solutions plant**
Uranium plant configuration	Atmospheric leach, counter-current decantation (CCD), ion exchange (IX), SX, ADU precipitation	Atmospheric leach (pressure leach design for later phase), CCD, IX, SX, ADU precipitation
SX equipment	Mixer-settlers	Mixer-settlers
SX configuration	4 Extraction stages (and 1 after-settler); 3 Scrub stages; 4 Strip stages (and 1 after-settler); 1 Organic Regeneration stage	4 Extraction stages (and 1 after-settler); 3 Scrub stages; 4 Strip stages (and 1 after-settler); 1 Organic Regeneration stage
Pumper-mixer tank dimensions	1.5m Ø, 1.7m H	1.5m Ø, 1.7m H
Settler dimensions	6.7m L x 2.2m W x 1.2m D	6.7m L x 2.2m W x 1.2m D
PLS flowrate	14.6m^3/h	Design 14.6m^3/h
PLS U_3O_8 grade	5.0g/l	Design 4.0g/l – 5.0g/l
Scrub solution flowrate	3.5m^3/h	Design 2.9m^3/h
Organic flowrate	17.6m^3/h	Design 14.6m^3/h
OK Liquor U_3O_8 grade	6.5g/l	Design 6.5g/l

Table 1: Plant details and process parameters of both USX plants

2.2 MINE WASTE SOLUTIONS PLANT, FORMERLY CHEMWES (OWNED BY SIMMER & JACK MINES)

The Mine Waste Solutions tailings treatment plant is located near Stilfontein in the North West province of South Africa, about 180km southwest of Johannesburg. The USX plant was commissioned successfully to C3 level (cold commissioning, and full circuit operation with water only) – the contractual battery limit – in three weeks by mid-February 2010, and is presently pending hot commissioning. Plant details and process parameters are shown in Table 1.

3. PUMPER-MIXER TANK DESIGN AND THE CONSTANT-Q IMPELLER

3.1 PUMPER-MIXER TANK DESIGN

Through use of the innovative new Constant-Q Impeller (as discussed in section 3.2), the need for a false bottom in the pumper-mixer tank has been eliminated. Instead, due to the geometry of the Constant-Q Impeller, a slight conical section is included in the base of the tank, and this impeller then provides both the requisite pumping and mixing necessary for the USX plants.

There is a distributor attached to the bottom of the pumper-mixer tanks, into which up to four inlets may be connected (accounting for one organic feed, one aqueous feed, one recycle line and one other). These streams are all drawn upward, with the cylindrical portion of the four-way distributor acting as the orifice in a conventional false-bottom configuration, as shown in Figure 1.

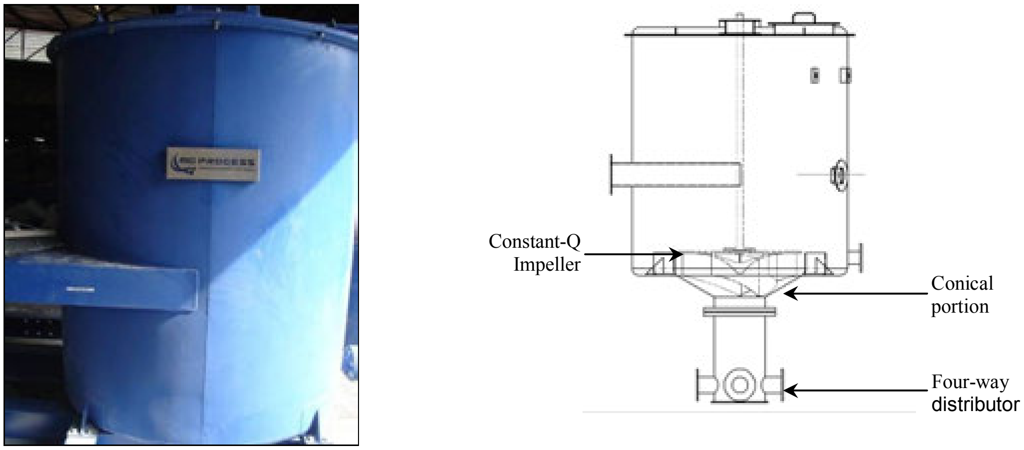

Figure 1: Pumper-mixer tank, with four-way distributor (on the right)

The tank is fitted with baffles, and an internal overflow weir at the top end of the tank for the mixed-phase fluid flow discharge into the settler. The design prevents short-circuiting through the pumper-mixer tank, ensuring that adequate residence time is allowed for mass-transfer between the two phases.

The tank lid has a facility for conductivity probes to be inserted, and a flanged connection for the attachment of a Ross Pot to facilitate pH measurement and control where appropriate.

3.2 THE CONSTANT-Q IMPELLER

From the earliest days of solvent extraction, a particular form of pumper impeller has been employed to effect suction of aqueous and organic streams into a pumping tank, creating head and in effect, working like a pump. The most common design of impeller used for this purpose is known as the General Mills or Holmes and Narver pumper, produced by, *inter alia*, Lightnin Mixers, who produce this as the R300 type impeller. General defining features for this type of impeller are six straight blades situated radially on the underside of a horizontal disc (semi-shrouded), where the height of each blade is constant and equal to 0.125 times the impeller diameter, and the associated orifice diameter (the diameter of the hole in the centre of the false bottom in a pumping tank) is between 0.33 and 0.37 times the impeller diameter, as per Mular *et al* (5).

In the late 1970s a double-shrouded impeller known as the Davy BB (both the upper and lower surfaces of the impeller vanes covered by flat discs) with eight curved blades in a manner analogous to a pump impeller was introduced. The impeller was typically positioned 33% of the wetted internal height of the pumper from the tank floor and was fed via a draft tube. The draft tube diameter was typically 0.5 times the impeller diameter, and the blade height was around 0.15 times the impeller diameter, according to Mular *et al* (*ibid*) and Taylor and Jansen (10).

In 1986 Lightnin Mixers introduced the R320 semi-shrouded impeller, with six curved blades extending from the centre to the periphery of the underside of a flat disc. This had the benefit of reducing turbulence and shear, with lower power consumption for given head and flow.

In almost every mixer-settler solvent extraction plant above, the pumping of solution has involved the use of either straight or curved-bladed pumping impellers over a false bottom with an orifice. Using the Constant-Q impeller, an almost-constant displaced volume is achieved over the outer 60% of the impeller blade, as shown in Figure 2. This has allowed the achieving of both the pumping required to move the design flowrate of fluid and the mixing required to effect sufficient mass transfer between phases. This is done with a single impeller, in a single pumper-mixer tank, and without the use of a false bottom.

The graphs displayed in Figure 2 are obtained by taking concentric 1mm slices of a single impeller blade of a Constant-Q Impeller and a R300 impeller. Both the Constant-Q and R300 impellers had overall diameter 870mm (as installed at the two USX plants discussed), a blade starting point at 150mm from the centre of the impeller, a single-blade radial length of 400mm, and rotating at 100rpm. Blade height of the R300 was 0.125 times the overall impeller diameter, while blade height of the Constant-Q impeller was read from the mechanical construction drawings.

Displaced volume Q_i (m^3/h) is calculated from angular velocity v_i (m/h) and area A_i (m^2) as shown in Equation 1, for index *i* taken from 1 to n, and radial distance of the concentric 1mm slice r_i (m) runs from the internal blade radius at 0.150m for i=0 to the outer blade radius at 0.400m for i=n.

$$Q_i = v_i \cdot A_i \qquad (1)$$

The angular velocity v_i is calculated by Equation 2, where ω (revolutions/h) is the rotational speed of the impeller

$$v_i = r_i \cdot \omega \qquad (2)$$

Since ω is the same for both impellers, velocities v_i may be calculated for a corresponding array of radii r_i, and since areas A_i are implicitly defined by r_i (Equation 3) with h_i the height of the i^{th} slice, and *w* the constant slice width of 1mm, an array of flowrates Q_i are obtained for a given r_i. These can be plotted as shown in Figure 2.

$$A_i = h_i \cdot w \qquad (3)$$

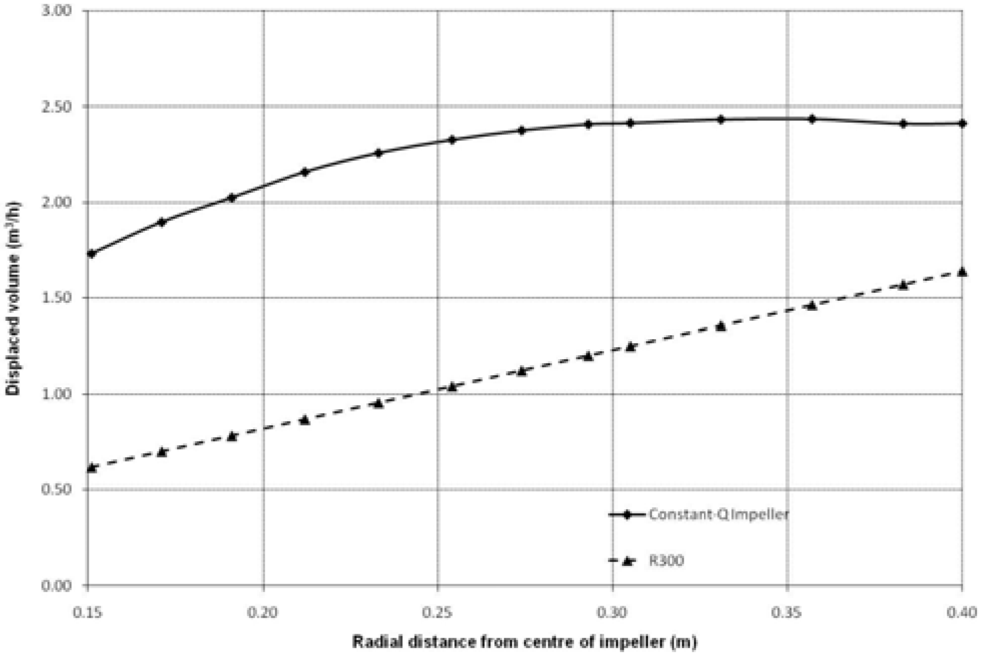

Figure 2: Displaced volume versus radial distance for the R300 and Constant-Q Impeller

4. SETTLER FLOW PATTERNS AND OPTIMISATION

4.1 DISTRIBUTION CHANNEL MODIFICATIONS AND DEAD ZONES

In most mixer-settler SX plants, the pumper tank overflows into one or many mixing tanks to achieve a desired degree of residence time for mass transfer, and the final mixing tank overflows into the settler through a rectangular distribution channel. The dimensions of this distribution channel are typically less than those of the side of the settler to which it is connected. This is especially true in SX plants with large settler geometries, and this is attempted to be addressed by distribution manifolds, as can be seen in modifications like those in the Bateman Reverse Flow Mixer-Settler™. For elements like uranium, where the settler geometry is typically more modest, this can be addressed more directly. The disadvantage of having a rectangular distribution channel discharging into a settler of dimensions less than those of the distribution channel is that dead zones may be experienced, and the sudden expansion of fluid as it enters the settler can inhibit or delay the commencement of coalescence.

To address the issue of dead zones in both the Ezulwini and Mine Waste Solutions USX plants, a distribution channel was developed that results in a gradually expanding cross-sectional area through which the mixed-phase flows. The arrangement is shown in Figure 3. The benefits of this modification are two-fold: firstly, since the area of the distribution channel inlet into the settler is gradually increasing, rather than suddenly expanding, the velocity of the fluid decreases gradually, and coalescence begins in the distribution channel; and secondly, since the inlet into the settler occupies a larger area, the dead zones and eddy currents formed in the settler are minimised.

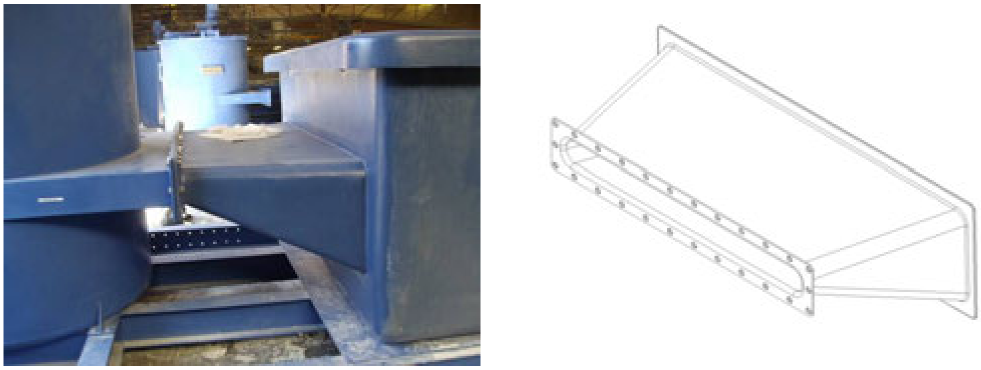

Figure 3: Distribution channel showing increasing area from pumper-mixer tank to settler

Using the current mixer and settler geometry for the Mine Waste Solutions USX plant, if utilising the standard practice of maintaining the mixer tank diameter as the width of the distribution channel, the distribution channel width would occupy 1.500m / 2.200m = 68.2% of the width of the settler. After the modification described above was implemented, the distribution channel width increased to 2.012m at the settler inlet, or 91.5% of the width of the settler.

This modification to the distribution channel into the settler has effectively reduced dead zones and eddy currents and facilitated earlier commencement of coalescence than often experienced in mixer-settler SX plants of similar geometry.

4.2 COALESCENCE AND THE USE OF PICKET FENCES

A further benefit that may be attributable to the distribution channel design, and the reduced inlet velocity generated as a result thereof is the reduced requirement for picket fences.

It is immediately apparent from the preceding section that the design of the inlet distribution channel to the settler has resulted in a reduced inlet velocity to the settler. It follows that not only has coalescence begun at an earlier stage in the settler than conventionally experienced, but that this reduced inlet velocity to the settler would have an impact on the settling and coalescing characteristics of the fluid in the settler.

In the design of both USX plants, at Ezulwini and Mine Waste Solutions a single coalescing picket fence per settler was supplied, with facility made in each for either moving the one picket fence to another of the four total locations, or inserting a second or third picket fence, depending on the operational requirements of the USX plant. At the time of writing, the Ezulwini USX plant has been operating for eleven months since its commissioning in April 2009, and the single picket fence supplied into each of the fourteen settlers has proved adequate in providing sufficient coalescing. Acceptable levels of entrained aqueous in the exiting organic phase, and organic in the exiting aqueous phase are present as a combined result of the distribution channel design and single coalescing picket fence.

Another factor taken into consideration in the design of the picket fences supplied for both the Ezulwini and Mine Waste Solutions USX plants is the option to replace the pickets with (in the case of Ezulwini) or to insert between the adjacent fibreglass coalescing plates (in the case of Mine Waste Solutions) standard packing to further improve coalescing in the settler. The need for this additional coalescing could only be determined during operation of the USX plants.

There is therefore significant flexibility inherent to the design of the picket fences supplied for both the Ezulwini and Mine Waste Solutions USX plants, from a single coalescing picket fence in one of four locations, to a maximum of four sets of coalescing packing per settler, using the framework from the supplied picket fences.

4.3 ORGANIC TO AQUEOUS RATIO CONTROL AND PHASE CONTINUITY

The Ezulwini and Mine Waste Solutions USX plants both have the same settler configuration: four Extraction mixer-settlers with a coalescing after-settler, three Scrub stages, four Strip mixer-settlers with another coalescing after-settler and a single Regeneration stage.

Desired phase continuity was discussed and agreed upon during the design phases of both projects, and the settlers and associated piping were designed accordingly. For ease of manufacture, the settlers were almost identical in construction, with only weir modifications varying dependent on the section of the USX plant into which the settler was to be used, however, the piping changed significantly depending on the desired phase continuity. Generally, if a phase was desired to be continuous in a mixer-settler, an adjustable portion of that phase would be recycled to the pumper-mixer tank of that settler. There are three outlets from each aqueous and organic weir: two of the three are used to convey the fluid to the next stage, while the third is used either to recycle a portion of the fluid back to the pumper-mixer tank, or is blanked off when this fluid is not required to be recycled.

The fraction of the total process stream to be recycled, either aqueous or organic, is determined by utilising a splitter plate: since the overflow from either the aqueous or organic weir is completely level (and is ensured to be so during commissioning) a physical barrier in the weir effectively splits the flow into the weir into a recycle fraction determined by the ratio of the length of the weir edge on the side of the recycle pipe to the overall length of the weir edge. This results in the benefit that, should the flowrate of either aqueous or organic fluctuate or change for whatever reason, the fraction of a stream reporting to the recycle will remain constant, as opposed to configurations where recycle flowrates are determined by valves, which would require continual adjustment to achieve the same result.

The ratio of an organic stream able to be recycled can thus, based on the settler and weir geometry, be selected to be one of the following: 10.0%, 20.0%, 30.0% or 40.0% of the organic flow overflowing the organic weir as shown in Figure 4, and the ratio of an aqueous stream able to be recycled can thus be selected to be one of the following: 15%, 24%, 33% or 42% of the aqueous flow overflowing the perimeter of the aqueous weir as shown in Figure 5.

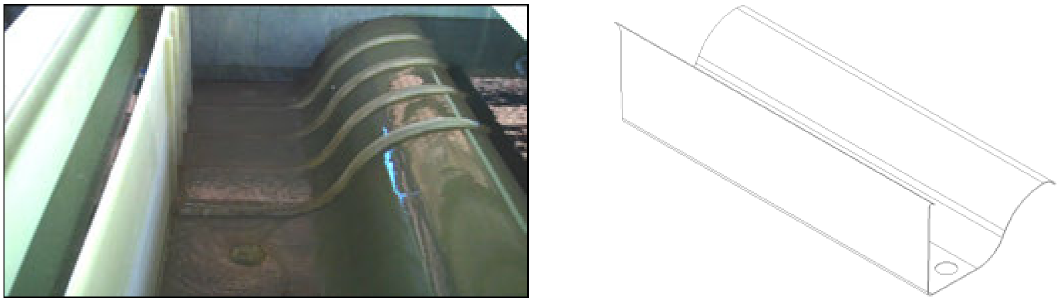

Figure 4: Organic overflow weir, showing guides for organic splitter plate (not inserted)

Figure 5: Aqueous overflow weir, showing guides for aqueous splitter plate (inserted)

In order to account for both minor construction inconsistencies and varying organic to aqueous (O:A) ratios, the aqueous weirs of all settlers were made fully adjustable, with adjustments possible at all four corners of the aqueous weir, from a height equal to that of the organic weir (used in the extract and strip after settlers) to operating levels 150mm to 200mm below that of the organic weir (used in other settlers at O:A ratios of between 1:1 and 1.2:1). This adjustability allows the aqueous weir to be made perfectly level during commissioning, but also realises two further benefits: firstly, this allows for differing O:A ratios to be catered for with minimal modification, and secondly, this allows for different flowrates to be accommodated – should the feed stream to the USX plant increase significantly, the head experienced over the organic weir will increase, requiring adjustment to the aqueous weir height to compensate.

The adjustment mechanism on the aqueous weirs installed in the settlers at Mine Waste Solutions has an adjusting nut welded onto a threaded rod at each corner of the weir, which, by turning, will raise or lower the weir with no need to come into physical contact with the process fluid.

Provision of adjustability of the aqueous weir also presented challenges. For the Ezulwini plant, PTFE bellows were installed between the outlet stubs of the aqueous weir and the pipe stubs in the settler, to allow for flexibility and adjustability of the aqueous weir height, as shown in Figure 6. These bellows were, however, easily damaged and torn from handling during commissioning, and replacement of the bellows *in situ* proved to be difficult. This was addressed in the design undertaken for the aqueous weir height adjustability provided for the Mine Waste Solutions plant, where the pipe stubs from the aqueous weir were lengthened, and the stubs rising from the floor of the settler were reduced in diameter and fitted with nitrile rubber O-rings, as shown in Figure 7. This provided a good seal, preventing undercutting of the aqueous weir, while still allowing adjustability of the aqueous weir height.

Phase continuity is monitored constantly at two points in the USX plants under consideration: in the final extract mixer (the aqueous discharge of which is fed into the extract after-settler), and in the final strip mixer (the aqueous discharge of which is fed into the strip after-settler) through use of conductivity probes, since aqueous continuous media are conductive, while organic continuous media are not. The conductivity reading is transmitted to the control room, where a phase inversion will trigger an alarm, and signal to the operator to vary the recycle flows to re-establish the desired phase continuity. This can be remedied as described in Gupta and Singh (2) and others.

Figure 6: PTFE bellows installed at Ezulwini for aqueous weir height adjustment

Figure 7: O-rings installed in the aqueous weirs of the Mine Waste Solutions plant.

5. ORGANIC LOSSES

Of the many mechanisms that result in organic losses in SX plants, volatilisation due to misting ('the waterfall effect'), evaporation and crud formation were addressed to varying degrees by design innovations made on the Ezulwini and Mine Waste Solutions plants. These are discussed in the following sections.

5.1 MISTING AND THE WATERFALL EFFECT

A significant cause of organic losses (and fire risk) in SX plants is from organic volatilisation caused by the organic stream falling into the organic collection weir, prior to either being transferred to the next mixer, or recycled back to the pumper-mixer tank from which it was discharged. Having empty organic weirs, with a sharp edge over which the stream falls is a feature encountered on many SX plants, and this has historically been addressed to some degree by raising the level of organic in the weir – typically by restricting the flow leaving the organic weir. This modification alone has resulted in significant organic savings on several SX plants: Skorpion Zinc, for example, targeted an organic loss of 3.8kg per tonne of Zinc produced, but was achieving a 10kg/t loss prior to raising the liquid levels in the organic weirs. After raising the organic level, the solvent losses dropped to 6.8kg/t as per Musadaidzwa and Tshiningayamwe (6)

The innovation installed in both the Ezulwini and Mine Waste Solutions plants was to profile the organic overflow weir in such a way as to ensure that the organic stream could not crash into a pool of organic, but instead flow gently down to the outlet pipes, as shown in Figure 8. Thus, irrespective of the flow of organic leaving the settler, and whether the organic weir is full or empty, the generation of organic mist as a result of 'the waterfall effect' in the settler is eliminated almost entirely.

Figure 8: Organic overflow weir, showing smooth flow and no air entrainment

A further benefit of the profiling of the organic weirs in these USX plants was that air entrainment into the organic phase is significantly reduced since the organic stream flows gently once discharged into the settler. This has an added benefit of reducing crud formation.

5.2 EVAPORATION

Due to the large surface areas of organic solvent that are the trademark of mixer-settler SX plants, and due to the volatile nature of the solvents that are mostly used in these plants (high-flashpoint diluents notwithstanding), evaporative losses of solvent are a concern and cost that cannot be safely ignored. Factors exacerbating these evaporative losses are, *inter alia*, elevated temperature and wind speed. These have been addressed in the Ezulwini and Mine Waste Solutions plants.

Firstly, the USX plants are both situated below roofs, preventing direct sunlight shining onto the mixers and settlers. This limits the daytime maximum temperatures experienced by the fluids, limiting the vaporisation of organic – since vaporisation of organics is more pronounced at higher temperatures. This also protects the mixers, settlers and ancillary equipment like impeller motors, pH and conductivity probes and the associated analysers from the elements. As an unrelated benefit, having the bunded SX area under roof minimises rainwater dilution of the spilled process fluids in the sump, thereby reducing the quantity of water pumped back into the SX circuit.

Secondly, all settlers in the USX plants are covered with fibreglass lids, and there are many reasons behind this: minimising evaporation of organic is a significant benefit, but this also ensures that dust ingress, as well as other debris (such as grass, insects, birds, hard-hats etc.) which also lead to crud formation is kept to a minimum. Covering the settlers completely has an associated potential hazard, however, in that the vapours that will form in the enclosed air space between the organic surface and the lid cannot readily escape, and could present a fire risk. For this reason, care should be taken to ensure that no ignition source is created in the periodic inspection into and/or removal of these lids.

5.3 CRUD FORMATION

Mechanisms of crud formation in solvent extraction plants are many, and can include, *inter alia*, the presence of solids, high shear in the pumping or mixing stages and excessive air entrainment as per Ritcey, 2007 (8) and Rydberg *et al* (9). Solids ingress into the SX plant is addressed through having the pumper-mixer tanks as well as the settlers completely covered, and although inspection hatches were installed, these are kept closed during normal operation. Further, all storage tanks for regenerated organic solution, organic regeneration solution, loaded strip solution and barren strip solution are all covered with lids to prevent solids ingress.

Excessive shear in the mixed phase is minimised when pumping and mixing by ensuring the pumper impeller tip speed is not overly high, and that the impeller blades are designed such that sharp edges presented to the fluid while mixing are minimised. Jergensen (3) provides a maximum pumping impeller tip speed of 400m/min as a guideline, while Aguilar and Cortina (1) provide common operating tip speeds of between 270m/min and 350m/min for pumping impellers. The Constant-Q Impeller is running at Ezulwini at a tip speed below 215m/min, providing sufficient pumping and mixing for all pumper-mixers. Also, consider the R300 impeller with straight blades situated radially on the underside of a flat disc, presenting a 90° impeller discharge angle and relatively high shear, and the R320 presenting a 27° approximate discharge angle, while the Constant-Q Impeller presents only a 23.9° discharge angle to the fluid, and hence reduced shear and consequent emulsion formation.

Air entrainment is particularly problematic in solvent extraction plants, especially when introduced to mixed phases – as in the case of the pumper-mixer tank, or into the organic phase in the organic overflow weir – from where air bubbles may not disengage from the fluid before being transferred to the next stage. As mentioned in the previous section, the organic weir has been redesigned from the conventional rectangular box-type to having a profiled lip, ensuring that, whether the flow of organic over the edge of the weir is fast or slow, or whether the weir is full or empty, there is virtually no entrainment of air in these organic streams.

6. MATERIALS SELECTION AND CORROSION

6.1 SETTLERS

The Ezulwini USX settlers were manufactured from mild steel, and then lined internally and externally with fibreglass. While this method of construction has been proved consistently in the industry, and equipment properly fabricated, manufactured and maintained will give excellent service, there remains a risk of the ‘cancerous core’ of mild steel being exposed to corrosive fluids in the event of a pinhole or other defect in the fibreglass coating, and thereafter corroding undetected until potentially catastrophic failure.

It was this concern that led to investigation into alternative materials of construction for the settlers at the Mine Waste Solutions plant. Vacuum infusion of composites has been used in a variety of industries for a number of years, and while Ritcey, 2006 notes the use of FRP as a lining material of settlers in a few SX plants (7) and Taylor and Jansen (10) note the use of self-supporting FRP in several plants, the introduction of vacuum-infused pure FRP into solvent extraction seems to have been overlooked. Detailed structural Finite Element Analysis (FEA) was conducted on a vacuum-infused pure composite settler. The settler was designed in accordance with EN13121 and BS4994, and indicated acceptable mechanical properties for use in the SX environment, as shown in Figure 9. Chemical resistance was addressed through utilisation of the same Derakane 470 resin used elsewhere in the Mine Waste Solutions plant as a resistance barrier on the external surfaces of the settler. EN13121 calls for a minimum 2.5mm barrier layer, which was exceeded throughout the surface of every settler.

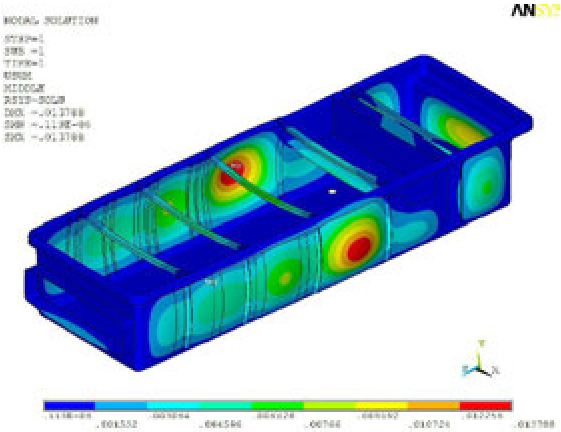

Figure 9: FEA model of settler, showing maximum expected deflection well within parameters allowed by EN13121.

Vacuum infusion of the resin results in a fully competent, strong, smooth-surfaced product with no air voids anywhere in the construction. The final completed settler was attached to the pumper-mixer tank, secured to its base frame and moved into position as one unit, shown in Figure 10.

Figure 10: Completed mixer-settler assembly being placed at Mine Waste Solutions

7. PH CONTROL

7.1 pH PROBES AND THE ROSS POT

pH control in the Strip section of uranium circuits is important to optimise stripping, while preventing ammonium diuranate (ADU) precipitation in the settlers, and Mackenzie (4) presents a suggested pH profile to be followed in the Strip section. Measurement of pH in these plants, however, presents a challenge since, at the time of design, pH probes available were intolerant of significant quantities of organic fluids. It was necessary to design these Ross Pots from first principles, since no drawings or technical data on Ross Pots were available in the literature, despite being manufactured and used relatively recently in solvent extraction plants.

The need for the development of a Ross Pot was in response to the requirement to provide accurate and rapid measurement and control of pH in a pumper-mixer tank, while preventing the pH probe from coming into contact with organic fluids. The Ross Pot does this by taking a small slip stream of the fluid in the pumper-mixer tank; throttling the flow of this stream to facilitate settling in the Ross Pot; allowing this mixed phase stream to settle – and aiding this settling by passage through a lamellar pack; allowing the organic to rise on one side of a dividing plate and overflowing into a common overflow weir; allowing the aqueous to sink and underflow the dividing plate; measuring the pH in this aqueous stream – now free from organic; allowing the aqueous stream to overflow into the opposite side of the common overflow weir; and returning the recombined stream back to a feed pipe to the same pumper-mixer tank from which the stream was taken. The installed Ross Pot and rendering are shown in Figure 11.

At Ezulwini, the Ross Pots have been giving good service, with a time delay of around 2 minutes between the injection of ammonium hydroxide (into either of Strip pumper-mixer tanks 1, 2 or 3) or sodium hydroxide solution (into the Regeneration pumper-mixer tank) and the registering of a pH increase with the associated pH probe. The reading is not instantaneous due to the necessarily low flowrate of solution into the Ross Pot, set by the inlet valve shown in Figure 11: too high a flowrate could result in insufficient separation being experienced, with organic contamination of the aqueous (aqueous contamination of the organic is of no concern here); while too low a flowrate creates an unnecessarily long delay time between the injection of a reagent and the detection of the subsequent pH change by the probe, which could lead to process control inefficiencies.

Since the commissioning of the Mine Waste Solutions USX plant, however, pressurised pH probes have become available that may tolerate organic to a greater degree than those available prior to commissioning, and further research into this technology may prove beneficial.

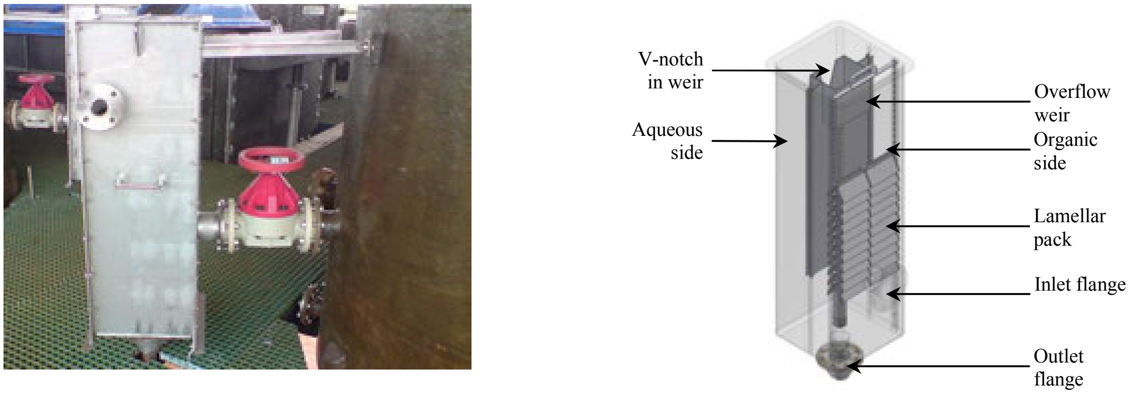

Figure 11: Ross Pots at Ezulwini showing pH probe flange (probe removed) and schematic

8. CONCLUSION

Pacific Minerals Processing (Pty) Ltd and M C Process (Pty) Ltd have made significant progress in addressing many of the challenges posed by mid-scale mixer-settler solvent extraction plants in general and uranium mixer-settler solvent extraction plants in particular.

The innovative Constant-Q Impeller, gradually expanding distribution channel between pumper-mixer tank and settler, adjustable aqueous weir, readily adjustable organic and aqueous recycle fractions, profiled organic weir, use of pure composites in a vacuum-infused settler, and use of Ross Pots to measure and control pH have all realised definite improvements to various elements of USX plant design, as installed at the Ezulwini and Mine Waste Solutions USX plants in South Africa.

9. ACKNOWLEDGEMENTS

The authors wish to thank First Uranium Corporation and Simmer & Jack Mines, Limited for permission to include information relating to their Ezulwini and Mine Waste Solutions solvent extraction plants in this paper.

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USE OF 2,6-DI-TERT-BUTYL-4-METHYLPHENOL (BHT) ADDITIVE FOR DELAYING THE CHEMICAL DEGRADATION OF SOLVENT DURING URANIUM RECOVERY FROM ACIDIC SULFATE MEDIA

by

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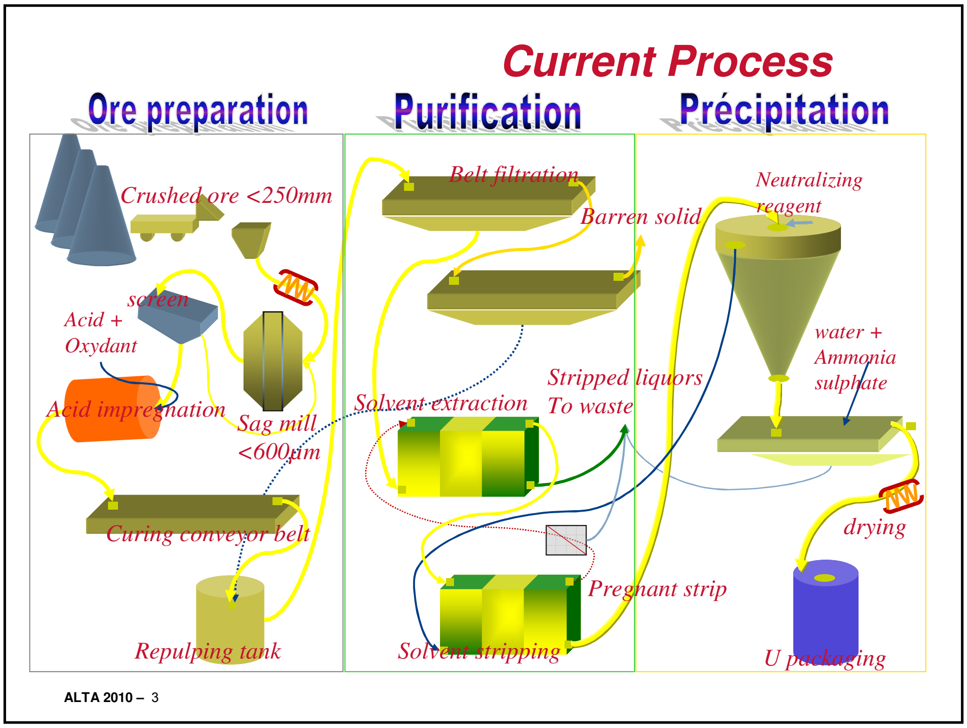
Presentation Layout

1. *Background*
2. *Objective*
3. *Solvent degradation*
4. *Solvent protection*
5. *Conclusions and recommendations*
6. *Future work*



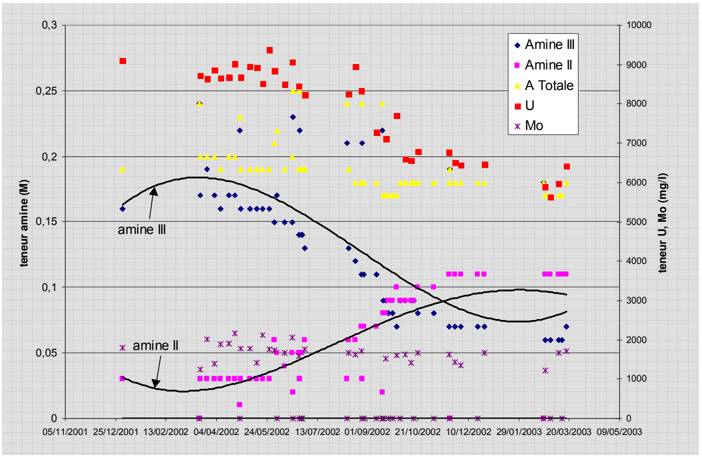
Current Process

ALTA 2010 – 3

Research Motivation

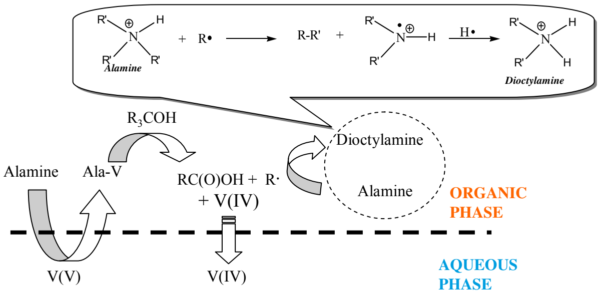
ALTA 2010 – 4

Solvent Profile



- Loss of extractant
- Reduced productivity
- Higher operating costs

Degradation Mechanism



- Radical theory proposed by research team
- Fe^{3+}, Mo^{6+} and Cr^{6+} are also capable of inducing similar oxidations.

Solution: Protect solvent against radicals using a chemical additive (e.g. BHT) ⟶ Objective

Study Approach

☑ Objective established : protect the solvent with BHT

- Experimental approach using 2 stages
  - Stage 1: Induce solvent degradation
  - Stage 2: Protect the solvent using BHT

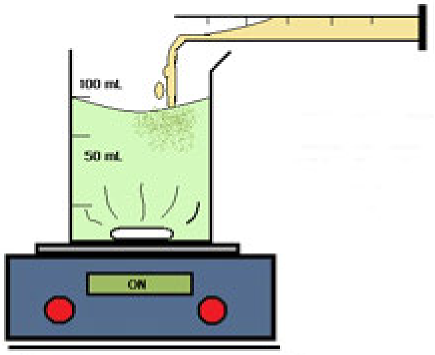
Solvent Degradation

Step 1: Solvent degradation via $NaNO_2$

- 50 mL water
- Sodium nitrite

- Magnetic stirring
- 10 mL H_2SO_4 9M

- 50 mL new solvent
** Kerosene (80%)*
** Tridecanol (10%)*
** Tert. amines (10%)*

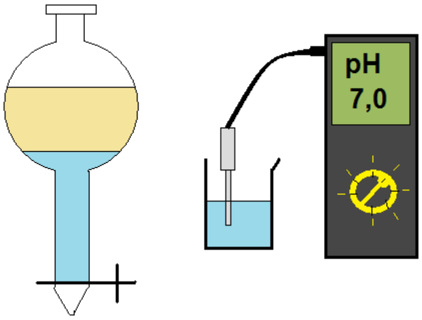


Solvent Degradation

Step 2: Solvent washing

- 300 mL carbonate solution (60 g/L)
- 2 contacts

- Distilled water washing until neutral pH attained

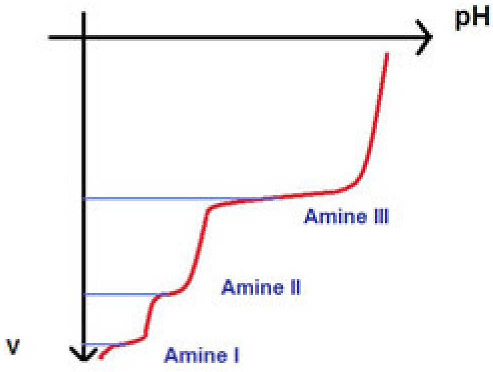


Solvent Degradation

Step 3: Solvent amine speciation analysis

- pH titration of amines using Perchloric acid

- Rates of degradation and recovery



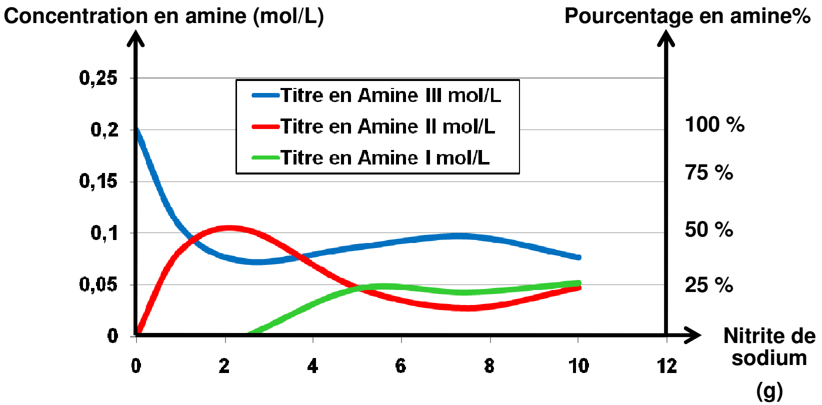
Solvent Degradation

Step 4: Experimentation

Test N°	$NaNO_2$ (g)	H_2O (mL)	Concentration (g/L)
1	0	50	0
2	1	50	20
3	2,5	50	50
4	5	50	100
5	7,5	50	150
6	10	50	200

Solvent Degradation

Step 5: Results



Degradation confirmed !!!

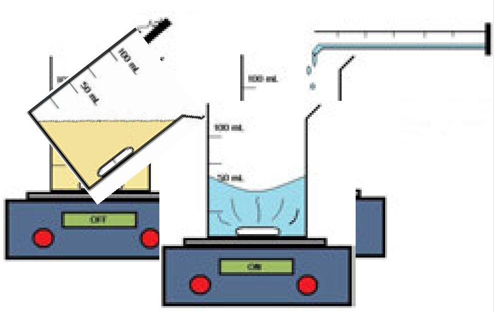
Solvent Protection

Step 1: Methodology

- Preparation of degradation solution
- Preparation of solvent protection using BHT
- Solution mixing

Solvent washing

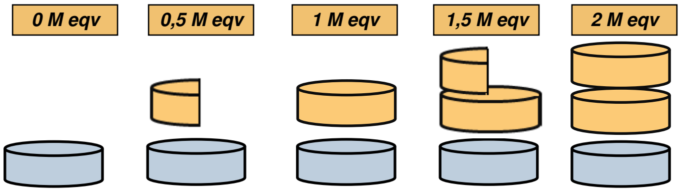
Solvent titration



Solvent Protection

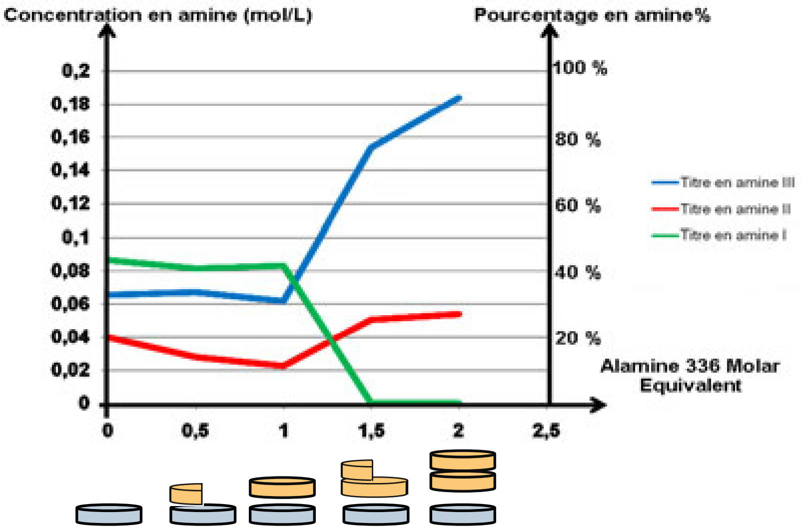
Step 2: Experimentation

Test N°	1	2	3	4	5
BHT (g)	0	1.21	2.42	3.63	4.85
Solvent (mL)	50	50	50	50	50
H_2O (mL)	50	50	50	50	50
$NaNO_2$ (g)	10	10	10	10	10
H_2SO_4 (mL)	10	10	10	10	10



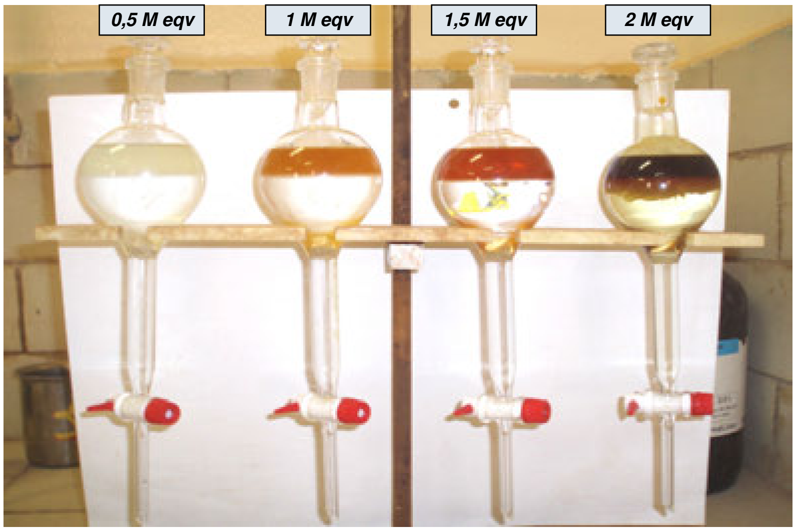
Solvent Protection

Step 3: Results



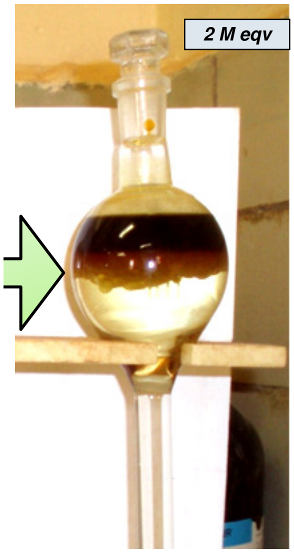
Solvent Protection

Step 3: Results (continued)



Solvent Protection

Step 3: Results (continued)



Assessment :

- Amine protection evident at >2 M eqv.

- Generation of degradation products and 3rd phase formation

Unknown effects

CONSEQUENCE :
Partial solvent loss (5 - 10%)

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5. Conclusions and Recommendations

☑ Confirmation of the degradation theory as proposed by the research team

☒ Solvent protection by the BHT additive is effective *however* it also generates cruds that causes solvent loss!

➔ Evaluate other reagents that are less susceptible to degradation

6. Future work

➢ Changing ore-body (lower Mo/U) suggests this route may no longer be necessary, other options are now being explored . . .

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- **Jacques THIRY**

RECOVERY OF URANIUM FROM THE IRON-RICH PHOSPHORIC ACID OF ARAFURA

By

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CONTENTS

1. INTRODUCTION

Arafura Resources is an Australian based mineral exploration and development company currently developing the Nolans Rare Earths-Uranium project.

Raw Phosphoric Acid (PA @ 18% P_2O_5) to be obtained by Solvent Extraction (SX) from the leach solution of Nolans ore is expected to contain ~100 mg/L U and ~8 g/L Fe. It was clear that the acid has to be purified before being concentrated to a salable product.

While most extractants remove either Fe alone (removal of Fe from the PA is well known in the phosphoric acid industry and is usually done by Alamine 336 or similar, in a process named “amine wash”), or both U and Fe, the challenge was to remove both metals, with Uranium to be recovered separately as a valuable product

This paper describes the work carried out in an effort to find a solvent that could extract both U and Fe and from which, they can be recovered in two separate, distinctive steps.

2. LABORATORY TESTS

2.1 REMOVAL BY DEHPA

DEHPA has been ruled out as one common extractant with separate stripping steps since it is known to be poisoned by Fe and no acidic stripping can remove it from the solvent.

This leads to either a two-stage process using two solvents:

- Quantitative extraction of the Fe by the standard amine wash process.
- Application of DEHPA for uranium removal after Fe was removed to a level low enough (< 50 ppm) that it will not poison the DEHPA.

Or finding an optimal process in which

- simultaneous removal of both metals from PA occurs, followed by
- selective stripping of them is possible.

Then, Fe rich solution could be disposed of, while the U rich strip solution could be utilized.

For process simplicity reasons, it has been decided that efforts should be put into finding a common extractant for both U and Fe from which these ingredients could be stripped separately.

A few solvents have been considered and their mixtures were tested during the test work described **herewith, to compose the optimal solvent.**

2.2 SIMULTANEOUS EXTRACTION OF U AND Fe FROM PA AND SEPARATION BY SELECTIVE STRIPPING, USING A SUITABLE SOLVENT

2.2.1 Removal of Fe using DEHPA and DEHPA+Alamine 336 mixture

Initially, a feasibility test of extraction and re-extraction of the ferric ion *from neutral solution,* by two solvents: 15% DEHPA and a mixed solvent with 5% DEHPA, 5% Alamine 336 and 5% TBP in aliphatic Kerosene (Cleansol 63L), was performed.

The aqueous solution contained 1.5 g/L Fe, as $Fe_2(SO_4)_3$ or as $FeCl_3$.. The stripping was done with 10% Na_2CO_3 solution. Both the extraction and stripping tests were done at phase ratio of 1:1. The strip solution, that contained Fe precipitates, was mixed at phase ratio 1:1 with 200 g/L H_2SO_4 solution, to dissolve the solids. The results are given in Table 1:

Table 1: Distribution of Fe between aqueous and organic phase

Test	Aqueous Feed	Solvent	Fe (g/L)	
			Raffinate	Strip Solution
1	$Fe_2(SO_4)_3$ solution	DEHPA	0.0006	0.86
2	$FeCl_3$ solution	DEHPA	0.0018	0.94
3	$Fe_2(SO_4)_3$ solution	Mixed	0.73	0.6
4	$FeCl_3$ solution	Mixed	0.7	0.68

As expected, with DEHPA all of the iron was extracted, and most of it was stripped with the Na_2CO_3 solution. The novel result of this test is ***the feasibility of stripping the ferric ion from DEHPA with Na_2CO_3.*** It is important to recall that ferric ion cannot be stripped from DEHPA with a strong acid.

With the mixed solvent the extraction was inferior, and only about 50% of the iron was extracted. On the other hand, the stripping was (by mass balance) almost quantitative.

2.2.2 Simultaneous Removal of Fe And U with a Blend of DEHPA+Alamine 336 Solvent

The Mixed Solvent contained 5% Alamine 336, 5% DEHPA and 5% TBP in aliphatic kerosene;

The aqueous phase contained about 100 ppm U, 1.5 g/L Fe and 14% P_2O_5. It was contacted with the solvent at two O:A phase ratios: 1:1 and 10:1, at $T=50^oC$.

The organic phase of the 1:1 contact was stripped with an equal volume (1:1) of 90 g/L of Na_2CO_3 solution. The organic phase became colorless and an orange solid precipitate was clearly visible in the aqueous phase.

The aqueous phase was diluted 1:1 with 200 g/L H_2SO_4 solution, and the orange solid dissolved completely.

The results are given in Table 2:

Table 2: Concentration of Fe and U in the aqueous phase using mixed solvent`

Sample	P_2O_5 (%)	HCl (%)	U (mg/L)	Fe (g/L)
Feed	14.2	1.39	96	1.55
Raffinate of O:A=1:1	13.7	1.69	69	1.09
Raffinate of O:A=10:1	12.8	0.07	22	1.47
Strip solution	n.d.	n.d.	30	0.23

The recovery of U is acceptable – about 80% at limiting conditions of O:A=10. The recovery of the iron was rather poor. Apparently all the extracted iron and U were stripped with the Na_2CO_3.

The test was repeated with another solution**.** This time the solvent was 10% Alamine 336, 10% DEHPA and 5% TBP. The aqueous phase had similar concentration of U, Fe and H_3PO_4, but about 4 times more HCl. The results are given in Table 3:

Table 3: Concentration of Fe and U in aqueous phase using mixed solvent

No.	Stream	O:A	P_2O_5 (%)	HCl (%)	U (mg/L)	Fe (g/L)
1	Feed		14.2	5.0	119	0.75
2	Raffinate	1	13.8	4.9	76	0.01
	Strip solution	1	0.5	-	33	0.66
3	Raffinate	1	14.5	4.3	43	0.01
	Strip solution	1	-	-	37	0.61
4	Raffinate	10	13.0	3.0	19	0.01
	Strip solution	1	-	-		
5	Raffinate	5	14.1	2.6	24	0.007
	Strip solution	1	-	-	10	0.46
6	Raffinate	10	13.2	2.0	14	0.03
	Strip solution	1	-	-	7	0.59

At limiting conditions, i.e. O:A phase ratio of 10, the extraction of U remained about 80% but the extraction of Fe climbed near to 100%. Apparently the high concentration of HCl is essential in order to achieve high recovery of Fe that is known to be extracted as $FeCl_4^{2-}$.

2.2.3 Simultaneous Removal of Iron and Uranium with FEU Solvent

After preliminary trial-and-error experiments, a combined proprietary solvent, nicknamed FEU, was developed. It was tested with the following aqueous feed: 14% P_2O_5, 6.4% HCl, 7 g/L Fe, 100 ppm U.

The comparison of the extraction of metals with the proprietary solvent and with other solvents is given below. The extraction was done at O:A= 1:1 phase ratio.

Only aqueous phases ("raffinate") were analyzed.

Table 4: Concentration of Fe and U in raffinate using various solvents

No.	Solvent	P_2O_5 (%)	HCl (%)	U (mg/L)	Fe (g/L)
1	10% Alamine 336, 10% DEHPA, 5% TBP	13.0	6.4	69	1.34
2	5% Alamine 336, 15% DEHPA, 5% TBP	13.7	5.3	40	3.4
4	FEU	13.6	4.6	12	1.7

It can be seen that the extraction of U with the FEU is far better than with the combination of DEHPA and Alamine, whereas Fe extraction is similar or better.

2.2.4 Effect of Acidity

Increased concentration of HCl improves significantly the extraction of both Fe and U. Apparently the Fe is extracted as a complex with chlorides (e.g. $[FeCl_4]^-$).

The results in Table 6 demonstrate this point:

Table 5: Extraction of Fe and U from PA with FeU at various concentrations of HCl

PA (feed)				Raffinate (out)					
HCl (%)	P_2O_5 (%)	Fe (g/kg)	U (mg/L)	Fe (g/kg)	% Fe Removal	D_{Fe}	U (mg/L)	% U Removal	D_U
2.8	16.2	6.1	55	5.3	12	0.22	28	49	1.24
6.0	13.7	4.0	49	2.2	45	1.2	8	84	6.4
10.2	11.3	3.2	44	0.062	98	71	3.5	92	14

D is the distribution coefficient, defined as the concentration of the species in the solvent divided by its concentration in the aqueous phase (in any consistent units).

The results show that the **extraction of both metals is efficient only at high (>6%) concentration of HCl.**

2.2.5 Stripping

The new solvent may be stripped with DI water, acidic water or an alkaline solution.

Stripping tests were performed by cross-current stripping of loaded solvent, that contained 7.8 g/L Fe and 350 mg/L U. Each test was done at O:A phase ratio of 5:1.

Tests no. 1-5 have been carried out with DI water, while no. 6, with a 100 g/L Na_2CO_3 solution.

Table 6: Stripping of Fe and U from loaded FEU with various aqueous solutions

No.	Aqueous Phase (experimental)			Solvent (calc.)	
	Fe (g/L)	U (mg/L)	pH	Fe (g/L)	U (mg/L)
1	11.8	6	~0	5.5	350
2	11.1	7	0.2	3.3	350
3	8.1	28	0.5	1.6	340
4	3.6	63	1.0	0.9	330
5	0.63	280	1.45	0.8	280
6	0.04	1300	>10	~0	~0

It has been observed that when the pH increased above 1.0 phase separation is slower and that stripping of U significantly improves. When DI water was substituted by 1% HCl, the phase separation was excellent and both phases were clear. The stripping of U was very low, while the stripping of iron was similar. The isotherm for Fe stripping with water is presented in Fig. 1:

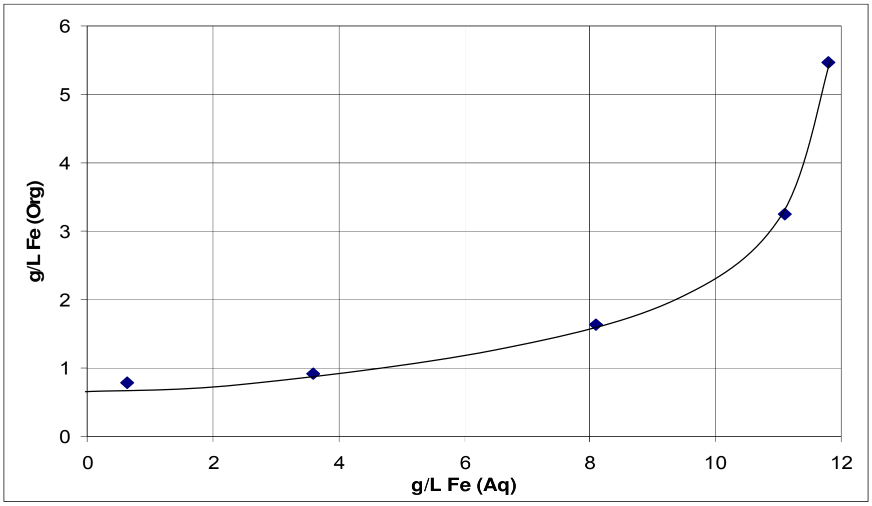

Figure 1: Stripping isotherm of Fe^{+++} with water

With Na_2CO_3 the stripping of both the U and the residual Fe is efficient, but they both precipitate in the resulting stripping solution and create crud with part of the solvent. At pH > 5.5, a lot of orange-brown colloidal precipitate appeared. Phase separation became slower as the pH increased. At pH 7, the mixture did not separate appreciably after 30 minutes.

Therefore **the stripping should be a two stage process**: first with diluted HCl, to remove most of the iron, followed by diluted Na_2CO_3, to recover the U. The stripping with Na_2CO_3 is expected to be followed by precipitation of solids, mainly the residual iron.

3. BENCH SCALE MS PILOT

The FEU solvent was tested in the bench-scale MS pilot.

The aqueous feed contained 12.6% P_2O_5, 6.3-8.1% HCl, 3.7 g/L Fe and 39 mg/L U.

The aqueous phase to the first stripping was DI water, and later was substituted by 1% HCl. The aqueous phase to the second stripping was 50 g/L Na_2CO_3 in DI water.

The pilot contained 6 stages: 2 for extraction, 2 for stripping with water/acid and 2 for stripping with 50 g/L Na_2CO_3. There was no optimization of the number of stages, and probably *one stage is sufficient for the alkaline stripping.*

The flow-sheet of the bench scale appears in Fig. 2.

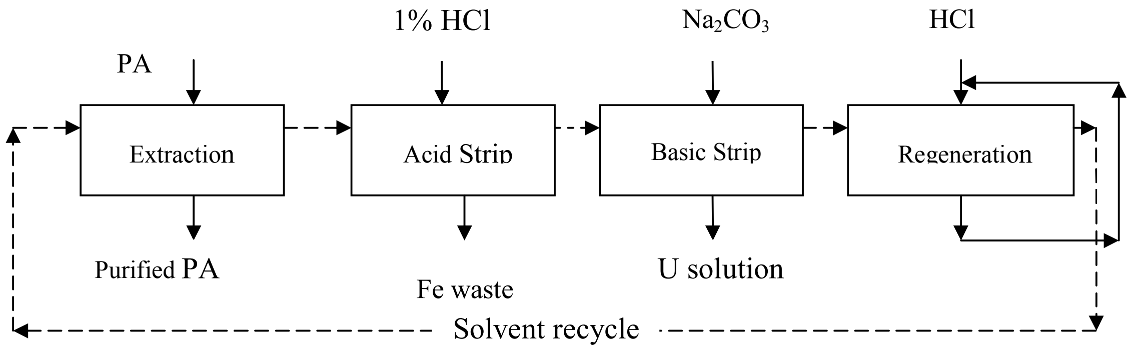

Figure 2: Flow-sheet of the bench scale Pilot

Only the outlets of the aqueous phases have been analyzed. The results are given in Table 7.

Table 7: Bench Scale MS Pilot for Removal of Fe and U from PA

Extraction			1st Stripping (DI/1% HCl)			2nd Stripping (50 g/L Na_2CO_3)		
O:A	Fe (g/L)	U (mg/L)	O:A	Fe (g/L)	U (mg/L)	O:A	Fe (g/L)	U (mg/L)
1	0.04	n.d.	1	5.45	1.5	1	0.009	57
1	0.02		1	2.73		1.5	0.67	
1	0.17	1.5	2	6.2	2.4	3	0.03	124
1	0.18	3.2	2	6.5	3.7	3	0.004	169
1	0.13	<1	2	6.6	<1	3	0.013	103
1	0.29	<1	2	7.0	<1	3	0.005	100
1.5	0.76	<1	2	8.0	<1	3	0.013	98
1	0.13		2	4.8		4	0.025	142
1	0.17		2	7.0		4.5	0.012	124
1	0.12	<1	3	8.4	<1	4.5	0.025	125
1	0.005	<1	3	5.4	<2	6	0.008	126
1	0.02		3	6.6		6	0.01	150

The concentration of P_2O_5 in the raffinate was about 12% (similar to the feed), while in the acidic strip solution, 0.3 - 0.7%.

The initial concentration of HCl was 8.1% and later it was decreased to 6.3%. No significant difference between the extraction of either U or Fe was observed, concluding that apparently 6% HCl in the PA is sufficient for the process. The concentration of HCl in the raffinate, after removal of the metals, was similar to its concentration in the feed.

The solvent after the second/alkaline stripping was full of crud. It had to be washed with HCl solution in order to remove the floating solids and receive a clear regenerated solvent.

4. PILOTING IN BPC

Full scale piloting of the recommended process was done using Bateman Pulsed Columns (BPC) for extraction and first stripping, one MS for the second stripping and one MS for solvent regeneration. The configuration was identical to that shown in Fig. 2.

According to the bench scale MS, the following steps were carried out:

1. Extraction of both metals using the FEU solvent.
2. Stripping of the loaded solvent (LS) with 1%-2% HCl to remove Fe.
3. Stripping of the partially stripped solvent with 50 g/L Na_2CO_3 to remove U and the residual Fe.
4. Regeneration of the solvent with 16% HCl, to break crud and remove entrained metals.

4.1 EXPERIMENTAL SYSTEM

The process was carried out continuously in a **combination of 2 BPC and 2 MS.** Steps (1) and (2) were carried out in 40 mm BPC and (3) and (4) – in MS. The entire process was carried out at 40°C.

4.1.1 Mixer-Settlers (MS)

The MS units are made from PVDF and equipped with efficient air agitators.

The mixer is 16 cm in diameter and 15 cm deep, i.e. 2 L volume.

The dimensions of the settler are 16*35*26 cm, i.e. its volume is 15 L.

About 10 L of solvent are needed for each MS.

4.1.2 BPC

Both columns are 40 mm in diameter with 2 decanters 80 mm in diameter. The height of the extraction column was 4 m, and of the stripping one – 5. Both columns are equipped with mechanical pulsator.

4.2 RAW MATERIALS

Feed solution: Raw phosphoric acid (PA) obtained from earlier stages of the process, contained 11% P_2O_5 and 2.5% HCl.

It was further acidified to 10% HCl, by using 31% technical HCl; the resulting feed contained 8.5% P_2O_5, 10.5% HCl, ~40 mg/L U and 2.5 g/L Fe.

Solvent: The proprietary FEU blend was used.

First stripping: 1% HCl was prepared by adding 30% HCl to DI water.

Second Stripping: 50 g/L Na_2CO $solution_3$ was prepared by addition of anhydrous Na_2CO_3 to DI water.

Regeneration solution: 16% HCl was recycled in closed loop during the entire test.

4.3 OPERATION

In order to work in a closed loop, the flow rate of the solvent in all 4 units was equal. The test lasted 8 hours. The frequency in both columns was set to 1 Hz (60 spm) and the amplitude to 15-20 mm.

4.3.1 Extraction

The results of the run are given in Table 8.

Table 8: Results of Extraction in BPC

Flux $m^3/m^2/h$	Feed (L/h)		U_{Aq} (mg/L)	Fe_{Aq} (mg/L)	Remarks
	Aq.	S			
26	14.5	18.9			Start; O:A=1.3
33	17.6	23.4	n.d.	1	
38	23.4	23.4	n.d.	2	O:A=1
38	23.4	23.4	2	2	
30	23	15	1		O:A=0.65
30	23	15	n.d.	140	
38	23.4	23.4	n.d.	28	O:A=1

Remarks:

The dispersion was O/A (the aqueous phase was the continuous phase).

The holdup was 10-14% along the column.

The initial O:A phase ratio was 1.3. As the results showed good extraction during the run, the solvent flow rate was decreased by 30%, working at phase ratio of 1.

The losses of P_2O_5 in the process are small (~1%).

The results show that the solvent can remove both Uranium and Iron from the feed with no losses of H_3PO_4. The flux in the column was excellent: up to 38 $m^3/m^2/h$.

4.3.2. Acidic Stripping

In this column the flow rates had to follow suit with the extraction, therefore the flux was obviously lower than the maximum achievable flux.

The average holdup was 15%.

The results of the run are given in Table 7:

Table 7: Results of Acidic Stripping in BPC

Time	Flux ($m^3/m^2/h$)	Feed (L/h)		U_{Aq} (mg/L)	Fe_{Aq} (mg/L)	Remarks
		Aq.	S			
11:00	19	6.3	18			Start, O:A=3
11:40	25	7.9	23.4			
13:10	25	7.9	23.4			
13:30	25	7.9	23.4	3	4000	
14:15	25	7.9	23.4			
15:00				4	4400	
16:00	25	7.9	23.4			h=3m
18:00	25	7.9	23.4			
19:00	20	7.9	15	6	5600	O:A=2.1

The operation was smooth: the column was operated at a flux of 25 $m^3/m^2/h$ and the flow could have easily been increased. Both phases were clear and apparently the entrainment was negligible.

The stripping itself was excellent, and almost all of the iron was stripped, while only ~10% of the U was lost in the aqueous stream.

4.3.3 Alkaline Stripping and Regeneration

The solvent flow rate in both MS was constant and equal to the flow rate in the extraction column. The aqueous O:A was constant: 5 in the basic stripping and 2 in the regeneration. Most of the time the flow rates were 4.8 L/h in the stripping and 12 L/h in the regeneration. The aqueous phase in the regeneration was run in a closed loop.

The hydraulic behavior of the second stripping with Na_2CO_3 was problematic, as could have been expected from the laboratory and bench scale tests. An emulsion was created, even when very mild mixing was applied, and the MS needed long residence time to separate it. The resulting flux was below 1 $m^3/m^2/h$ and the residence time in the settler was 30 minutes. This number cannot be used for scale-up, as there is no geometrical similarity between the pilot and the industrial settler, but it means that a low flux should be anticipated.

The regeneration was easy, and the opaque solvent from the 2nd stripping left the regeneration settler quite transparent. It proves that the regeneration of the entire solvent stream is a must.

Though it was run in a closed loop during 7 hours, the acid concentration dropped only slightly, from 16% to 15% HCl. Most of the U from the solvent was recovered in the stripping.

5. ANALYSIS OF RESULTS

The results prove that the performance of the FEU solvent is excellent, and it enables full recovery of U with minimum Fe contamination, as well as the removal of the Fe to any required level.

The allowed concentrations of Fe and U in the concentrated purified PA (PPA, 61.5% P_2O_5)) are about 2 g/L and 100 mg/L respectively. Accordingly, the allowed concentration of Fe and U in the product removal pilot (8.5% P_2O_5) should be 0.25 g/L Fe and 14 mg/L U respectively.

The average results of the continuous run in the bench scale show practically full recovery of U, down to 1 mg/L and lowering the concentration of Fe to 0.1 g/L Fe.

In the full scale pilot tests, the results were even better, and the Fe dropped to 1-2 ppm, while the U was below the detection limit. It proves that this process may recover both metals to any required level.

Extraction was easy and no problems of phase separation were detected. It may be carried out in 2 MS or in one BPC. In MS O:A phase ratio of 1:1 was applied. Changing the phase ratio to 1:1.5, i.e. decreasing the solvent by 33%, more than doubled the concentration of Fe in the PA. In a 4 m high BPC the results were superior, and **O:A phase ratio of 1:1.5 is sufficient.**

The first stripping, when done with acidic solution, was easy and efficient. It removed above 99% of the iron at O:A phase ratio of 3:1, both in the MS and BPC. This is the recommended phase ratio for the process. 3 meters of column were found sufficient. No problems of crud, phase separation or turbidity were observed.

The second stripping, with Na_2CO_3, is very efficient too, but more problematic. At O:A phase ratio of 4.5:1 it recovered practically all of the U and the remaining Fe. Further decrease of the flow rate of the aqueous solvent, down to O:A of 6, is detrimental and is not recommended. In the final pilot a phase ratio of 5 was applied.

The main problems of this process are crud formation in the second stripping stage (probably caused by precipitation of iron and other impurities) and slow phase separation. The solution to these problems that was verified in the pilot is to contact the stripped solvent with 16% HCl solution. The entire stream of the solvent should be treated this way.

6. CONCLUSIONS AND RECOMMENDATIONS

1. An efficient process for recovery of Uranium and removal of Iron from phosphoric acid (PA) that contains HCl, using one proprietary solvent named FEU, was developed.

2. The process takes place in four batteries: extraction, acidic stripping, alkaline stripping and regeneration. The extraction battery consists of two MS or a Bateman Pulsed column (BPC). The acidic stripping is carried out either in 2 MS or a single BPC. The second (alkaline) stripping and the regeneration are done in a single MS each. The heights of the columns, at a diameter of 40 mm, are 4 m for extraction and 3 m for stripping.

3. The process can recover all the Uranium and reduce the concentration of Iron in the PA to very low levels.

4. More than 99% of the iron and less than 10% of the uranium is stripped in the first (acidic) stripping. Accordingly, <1% of the iron and >90% of the U is stripped in the second (Na_2CO_3) stripping.

5. The losses of P_2O_5 in the process are very low (~1%).

6. The barren solvent must be regenerated with medium strength HCl.

GIBBS ENERGY MINIMISATION FOR PROCESS SIMULATIONS AND AN EXAMPLE IN URANIUM SOLVENT EXTRACTION

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CONTENTS

1. INTRODUCTION

Mass and energy balance simulations form an integral part of metallurgical process design, from concept level studies through to detailed design. To build an efficient process plant, that maximises production with least capital and operating costs, an accurate model of the flows and the chemistry involved in the process is indispensable for all but the simplest of processes. For existing operations, a mass and energy balance is essential for optimisation of the existing process. Also, the consequences of proposed modifications to the process can be assessed quickly, before purchasing any new equipment. In an engineering study, a mass and energy balance is usually created at the concept level, with limited detail, and expanded in the later study phases to contain more detail of both the chemistry and the minor process flows. The selection of tank and pond volumes, pipe diameters, materials of construction, power requirement for motors, and most other design parameters rely on accurate predictions of the conditions that the plant will encounter through the life of the resource.

A mass and energy balance model, as with all models, will always be a simplified representation of reality. The level of detail with which a process is simulated need only be enough for the purpose for which it is being created. As an example, the chemical phenomena occurring in the high temperature and pressure soup of an HPAL autoclave need not be modelled unless they are relevant to the design of the autoclave or downstream processes. The precise reaction or mechanism is usually irrelevant in this case, provided the distribution between phases and the oxidation states of the elements is adequately characterised. While valid in many instances, this philosophy is an easy one to apply irresponsibly. When forming a process design criteria, previous experience from engineers will often be agreed upon as the basis for critical design parameters, but these figures may be biased towards similar, but not identical processes, where a critical factor has not been considered that may drastically affect the result. Future phases of work, and testwork, should hopefully decrease the risk associated with this, but in some cases, the outcome could be disastrous. In this case, had the model been more predictive and less biased towards past experiences, alarms warranting investigation may have been triggered much earlier in the process design.

2. THEORY

Gibbs energy (G), is defined as G = H – TS, where H and S are enthalpy and entropy respectively and T is temperature. At constant pressure and temperature, chemical reactions are spontaneous in the direction of decreasing G[i]. At chemical equilibrium, no reaction is spontaneous, therefore G is at minimum. The equilibrium composition of a mixture of reactants, at a given temperature and pressure, is the mixture of products which produce the lowest value of G. Mass must of course be conserved, so the moles of each element is the same in the reactant mixture as in the product mixture.

The technique of Gibbs energy minimisation to estimate the equilibrium composition for a given set of species is enabled by many process simulation packages, including OLI Systems Stream Analyser[ii], FactSage[iii], Aspen Plus[iv], METSIM[v] and HSC Chemistry[vi] among many others. The software packages have varied levels of sophistication, with some able to predict the behaviour of non-ideal solutions at elevated temperature and pressure. Gibbs energy minimisation has been used to characterise many pyrometallurgical systems[vii,viii]. FactSage is now usually favoured for pyrometallurgical calculations due to its comprehensive databases of molten and solid solution phase equilibria. In hydrometallurgy, OLI Systems Stream Analyser is often favoured for its ability to simulate non-ideal behaviour in concentrated solutions of most aqueous chemical species. The application of Gibbs energy minimisation to solvent extraction is limited due to the lack of available data for the enthalpy and entropy of loaded organic species. Several efforts have been made to determine the Gibbs energy of metal complexed organic extractants from experimental data[ix,x,xi], but the technique is not usually employed by engineering firms during solvent extraction circuit design or existing circuit simulation.

Solving for minimum Gibbs energy is an example of a constrained optimisation problem, for which there are many computational methods available. A simple method of minimising Gibbs energy is described elsewhere[xii]. This method is used by HSC Chemistry to approximate the equilibrium composition of a mixture of selected components. As an example, for the assumed gas species: CO_2, H_2O, CH_4, O_2, CO and H_2, reacting 1 mol of O_2 with 1 mol of CH_4 at 500°C and 1 bar produces the mix of species shown in Table 1. The product mixture is calculated without needing to define any chemical reactions.

Product	mol
CO_2	0.575674
H_2O	0.766929
CH_4	0.342603
O_2	9.01E-28
CO	0.081723
H_2	0.547865

Table 1: Simplified product composition calculated by HSC Chemistry when reacting 1 mol of CH_4 with 1 mol of O_2 at 500°C and 1 bar

In this example, soot (graphite, C) is omitted as a possible reaction product so it is ignored in the calculations. Had it been included, the resulting product composition would have been significantly affected. Comparison of the predicted compositions, with soot allowed and without soot allowed is shown in Table 2.

Product	Without Soot (mol)	With Soot (mol)	Difference (%)
CO_2	0.575674	0.542709	6%
H_2O	0.766929	0.842541	10%
CH_4	0.342603	0.297331	13%
O_2	9.01E-28	1.03E-27	15%
CO	0.081723	0.072041	12%
H_2	0.547865	0.562797	3%
C (solid)	-	0.08792	-

Table 2: Product composition calculated by HSC Chemistry when reacting 1 mol of CH_4 with 1 mol of O_2 at 500°C and 1 bar, with and without soot formation allowed

It is therefore extremely important to know which species are likely to form when setting up an HSC Gibbs minimisation problem as incomplete speciation may give erroneous results.

It is also possible to calculate the isenthalpic product temperature and equilibrium composition by using the StreamH function in HSC's Excel Add-In in conjunction with Excel's goal seek function to set the product enthalpy to equal the reactant enthalpy. For example, if 1 mol of CH_4 and 1 mol of O_2 is reacted with 5 mol of H_2O gas, with each reactant at 25°C, for constant enthalpy, the product temperature is 1059°C and the product mixture is shown in Table 3.

Product	mol
CO_2	0.629898
H_2O	5.370102
CH_4	2.15E-07
O_2	1.91E-12
CO	0.370102
H_2	1.629897

Table 3: Simplified product composition calculated by HSC Chemistry when reacting 1 mol of CH_4 with 1 mol of O_2 and 5 moles of H_2O at constant enthalpy (reactants at 25°C, products at 1059°C) and 1 bar

3. HURDLES FOR GIBBS ENERGY MINIMISATION MODELLING

The modelling of chemical reactions in metallurgical process models is usually based on either testwork data, or some form of previous experience. Predictive tools such as Gibbs energy minimisation ('free energy' minimisation: FEM) are infrequently used in metallurgical process plant design. There are two main reasons for this:

- There is less likelihood, or at least a lower perception of likelihood, of errors being made when testwork data is used. It is hard to argue with experimental data and past experience.
- The cost, or perception of cost, both in man-hours and to project schedule, associated with complex simulation methods is often prohibitive in metallurgical studies.

The first reason is clearly a valid one. The complex suite of chemical species encountered in hydrometallurgical process streams will often behave in unexpected ways. The solubility of calcium in mixed sulphate solutions at varied pH, for example, has long been the bane of process engineers encountering gypsum scaling in places where they wouldn't have hoped to see it. Pyrometallurgists encounter molten, immiscible phases containing many more than the three or four elements usually shown on conventional phase diagrams. Trace elements can affect the melting point of each phase. The relationships between phase equilibria, for molten systems containing more than four elements, are difficult to predict. It is no wonder that when a mining company employs an engineering consultancy to develop a mass and energy balance model of their future or existing process plant, testwork, or existing plant data, generally settles the nerves more than the predictions of a computer-savvy engineer.

The second, cost related, reason why FEM is not often used for metallurgical process plant design, is explored in the following section.

4. JUSTIFYING AND ENABLING GIBBS ENERGY MINIMISATION

There are many instances when the chemistry involved in a metallurgical process can be accurately predicted from first principles, especially when thermodynamic equilibrium can be assumed:

- Gas phase reactions at elevated temperature will often be at chemical equilibrium and the behaviour will often be close to ideal. Here, FEM can be used to predict the gas composition accurately.
- The composition of many aqueous streams in hydrometallurgical refineries is often limited to a small number of elements due to selectivity in upstream solvent extraction or ion-exchange processes. The chemistry of such chemical systems may be well documented in the literature, and accurately predictable by such tools as OLI Systems Stream Analyzer, FactSage, or HSC Chemistry.
- The extraction and stripping of metals by solvent extraction can in simple cases be accurately predicted by FEM, if the entropy and enthalpy of the extractant and the metal complexed extractant molecule is known, or can be calculated from literature data.

- The selective complexation of metal ions to ligands such as ammonia or cyanide can also be predicted by FEM.
- Many vapour / liquid equilibrium systems are accurately characterised in the literature and can be simulated with accuracy for a range of temperatures and pressures.

In each of these cases, FEM can be used to produce mass and energy balance data with confidence of accuracy. Validation from testwork and previous experience should still remain an important part of the review process, but in this way, there are two sets of data arrived at independently that can be compared for consistency: a calculated set and an anticipated set. FEM generates a new, independent, set of information. If the predicted values don't agree with the anticipated values from previous projects, further investigation may discredit the anticipated values which could otherwise have been accepted unchallenged. Conversely, if the Gibbs model proves to be incorrect, the lessons learnt by explaining the deficiencies in the predictive model could prove invaluable to the project by increasing the fundamental knowledge of the engineers involved.

The two software packages most commonly used in industry until 2007 for steady state metallurgical mass and energy balance models were SysCAD (ProBal), and METSIM. Typically, a new model would be created from scratch for every metallurgical plant modelled in either of these packages. While there are many similarities in technology between process plants around the world, every process plant in the world is unique, due to subtle variations in ore body mineralogy. Setting up a model in both METSIM and SysCAD generally first involves setting up the thermodynamic data of chemical species to be encountered in the process. The model structure (tanks, reactors, chemistry etc) would be constructed after this. While it is possible to copy sections of a model from one model to another, when a new model has similarities to an old model, the time and difficulty involved often makes it seem easier to rebuild the model section from scratch. The implications of this are that if a complex, predictive model is built for one process plant, it would usually be rebuilt from scratch for every subsequent process plant to use the same technology. The inefficiencies of such a situation would decrease the appeal of such a model.

IDEAS (Bronze) is a modelling package, similar in many ways to both METSIM and SysCAD. Chemical species are defined, then the model's structure is built. The model can output stream information to Excel in much the same way as SysCAD and METSIM. One point of difference between the packages is copy and paste functionality. IDEAS allows you to select parts of a model and duplicate them, either in the same or in a different model. If the chemical species in the different models aren't identical, there may be difficulties in copying the chemical reactions or some of the settings in the model structure relating to chemical species or elements, but overall, duplicating past work is made significantly easier by the IDEAS software. It follows that if a complex, predictive model is constructed in IDEAS, it is relatively easy to distribute it into as many subsequent models as desired. This reduces the cost impact of the development of predictive models in metallurgical simulations. A section of a model, with complex controls or predictive algorithms, can be built, and stored in a library of complex models, to be used as needed for future studies without significant rework. Time spent on improving the graphic user interface, or other features, to improve the usability for future clients, can now be cost effective because the work need not be repeated again at a later date.

METSIM already contains an FEM object. It uses the Gibbs data entered in the component properties library. Most of the components in the METSIM component library already have Gibbs correlations, but the author recommends that they be validated with another source such as HSC Chemistry before being applied with confidence. In some instances accuracy in a tight temperature range may be desired, so the broad correlations applied to components in METSIM may need “tweaking” for higher accuracy at the desired temperature. The METSIM FEM object operates quickly and accurately, both for adiabatic calculations and for isothermal mode (with calculated enthalpy loss or gain). Chemical reactions do not need to be specified. The object instead solves for the minimum free energy, constrained to the chemical components defined in the model, with conservation of mass for all elements.

IDEAS does not currently have the capacity to do FEM calculations; however as chemical component data can be imported from HSC Chemistry, all the data required to do this already exists in the software, so there is scope for future programming to allow this to happen if there is a need in the industry. It is possible to run FEM models through IDEAS indirectly, by linking IDEAS to Excel through continuous dynamic data exchange (DDE), where a spreadsheet has been set up using HSC Chemistry's Gibbs minimisation array user-function through the HSC 6 Excel Add-In feature. This method is not ideal, because reaction chemistry is still required and links between output composition setpoints and chemical reaction extents need to be established. The benefit with IDEAS however, as previously mentioned, is that after setting the model up once, it need not be repeated in the future.

For single point, or simple correlations that do not require integration into a full mass and energy balance model, the software packages: FactSage for pyrometallurgical processes, or OLI Stream Analyser for hydrometallurgical processes, can be used to calculate the equilibrium in complex, non-ideal multiphase systems. Output data from these packages can also be used to develop simplified correlations to be used in a full mass and energy balance model in another package like METSIM, IDEAS or SysCAD.

5. URANIUM SOLVENT EXTRACTION EXAMPLE

Solvent extraction is the most common extraction route for uranium from sulphuric liquor. One of the most common organic extractants used for the extraction of uranium is Alamine® 336, an octyl / decyl tertiary amine manufactured by Cognis[xiii], usually diluted in kerosene.

Estimating the effect of operating parameters such as the organic to aqueous flow ratio, pH, uranium concentration, extractant concentration, etc, on the equilibrium of the system, is usually achieved by a testwork program. Such testwork requires representative samples of the aqueous uranium feed liquor and usually several weeks of laboratory testing. The benefit of a generic model that could predict to reasonable accuracy the behaviour of a solvent extraction circuit operating under a wide range of conditions is evident. Unfeasible circuit options could be eliminated during the early phases of a desktop study before any money was spent on testwork. Multiple flowsheet scenarios could be examined quickly at low cost. For existing operations, the model could be of use for troubleshooting, or for examining the likely effect of modifications to process parameters before trialling them in reality.

The purpose of the work described in this paper is to demonstrate that a relatively simple model can be prepared in Microsoft Excel combined with HSC Chemistry software, using few experimental correlations gathered from the literature, that can predict the behaviour of uranium in an Alamine® 336 solvent extraction circuit at any pH, to a degree of accuracy high enough for preliminary design work, based on Gibbs energy considerations alone.

Justification for the speciation selection, and the method used to approximate the thermodynamic data required for Gibbs energy minimisation modelling is presented in the following sections.

5.1 AQUEOUS SPECIATION

There are numerous chemical species present, both in the aqueous and organic phases, during the loading and stripping of uranium that affect the performance of the solvent extraction process. All such species should be taken into account to improve the reliability of the model. The predicted speciation, present in sulphate solutions of uranium with ammonia and sulphuric acid used for pH control, was determined using OLI Stream Analyser software. The H^+ databank was used and redox chemistry was excluded. The aqueous species considered are shown in Table 4.

H_2O	$(UO_2)_2(OH)_2^{2+}$	OH^-
UO_2SO_4	$(UO_2)_3(OH)_5^+$	$SO4^{2-}$
H_2SO_4	H^+	$UO_2(SO_4)_2^{2-}$
NH_3	HSO_4^-	UO_2^{2+}
$UO_2(OH)_2$	NH_4^+	UO_2OH^+
NH_4SO4^-	SO_3	

Table 4: Aqueous species present in H_2O / UO_2SO_4 / H_2SO_4 / NH_3 system

The database included with HSC Chemistry 6.1 includes enthalpy and entropy data for all components in Table 4 except $NH_4SO_4^-$. The OLI results suggest that this specie is a major constituent so the component was added to a custom HSC database and enthalpy and entropy of formation data were approximated from results obtained by OLI. The estimated HSC database parameters for $NH_4SO_4^-$ are:

$$H = -1042.4 \text{ kJ/mol}$$

$$S = 127.7 \text{ J/(mol.K)}$$

The parameters for $NH_4SO_4^-$ may not be correct, but they result in similar predicted concentrations of $NH_4SO_4^-$ in the HSC Gibbs calculations for the system being examined at both 25°C and 50°C, and thus are fit for the current purpose.

HSC version 6.0 and above has an Excel Add-In feature that allows equilibrium calculations to be set up in Excel. It is a relatively simple model based on an early Gibbs minimisation technique[xiv], that uses the enthalpy and entropy data from the HSC database to estimate equilibrium composition at a given temperature and pressure. Currently, there is no way of incorporating activity coefficients into the model, but Outotec is currently working on including this in future versions of the software. By using Excel, this allows the flexibility of using the "goal seek" feature to achieve target pH (approximated as $-\log[H^+]$) by adjusting H_2SO_4 or NH_3 input to the system. Equilibrium compositions at any pH can thus be estimated.

Results from OLI were validated against HSC by comparing the outputs for a 0.1M solution of UO_2SO_4 with trace NH_3, with H_2SO_4 adjusted to achieve 3.0 for $-\log[H^+]$ in the HSC output. The results are presented in Table 5. Note that HSC cannot predict the activity of the H^+ ion, so calculated "pH" from HSC data is only approximate.

HSC Species	Input mol	HSC Output mol	OLI Output mol
$H_2O(l)$	5.55E+01	5.55E+01	5.55E+01
$UO_2SO_4(a)$	1.00E-01	8.42E-02	6.01E-02
$H_2SO_4(l)$	4.69E-04	2.70E-15	2.14E-17
$NH_3(a)$	1.00E-07	5.78E-14	4.03E-14
$UO_2(OH)_2(a)$		4.01E-09	3.37E-09
$(UO_2)_2(OH)_2(^{+2}a)$		2.69E-04	5.40E-04
$(UO_2)_3(OH)_5(^{+}a)$		3.35E-07	2.31E-07
$H(^{+}a)$		1.00E-03	1.33E-03
$HSO_4(^{-}a)$		5.38E-04	7.64E-04
$NH_4(^{+}a)$		9.96E-08	9.28E-08
$NH_4SO_4(^{-}a)$		4.12E-10	7.23E-09
$OH(^{-}a)$		1.03E-11	1.33E-11
$SO_4(^{-2}a)$		6.51E-03	2.06E-02
$UO_2(SO_4)_2(^{-2}a)$		4.62E-03	9.48E-03
$UO_2(^{+2}a)$		1.06E-02	2.92E-02
$UO_2OH(^{+}a)$		5.96E-05	7.24E-05
pH		unknown	3.009
$-\log[H^+]$		3.000	2.877

Table 5: OLI and HSC predicted aqueous species for 0.1M UO_2SO_4 at approximately pH = 3

The concentration of aqueous SO_3 calculated by HSC was erroneously high. OLI predicts it to be present in very low concentrations under all solvent extraction pH conditions. This specie has thus been excluded from the HSC model. The results in Table 5 show that the HSC Gibbs energy minimisation model agrees reasonably well with OLI for all other species and is thus suitable for an approximation of the aqueous phase behaviour.

5.2 ORGANIC SPECIATION

Unlike the aqueous phase, which contains common, well characterised species, Alamine® 336 and the organic complexes present during uranium loading and stripping are not well characterised. Enthalpy and entropy data for trinonylamine (N,N-dinonyl-1-nonanamine) is included in the HSC 6.1 database. While Alamine® 336 is a mixed octyl / decyl ternary amine (R3N), it will be assumed that Alamine® 336 has the same properties as trinonylamine due to their similar molecular structure. All complexed forms of Alamine® 336 will be assumed to be complexed forms of trinonylamine.

The species listed in Table 6 are the assumed constituents and data for these species are required to model the organic phase. The kerosene diluent is assumed to have the composition of decane for simplicity, but remains an unreactive component so this assumption does not affect results.

The majority of the available literature data is for experimental results at 25°C. To model the effect of temperature, both enthalpy and entropy data would be required. The model created in this current study is limited to 25°C so Gibbs energy is reduced to being a function of component enthalpy only.

$C_{10}H_{22}$	Kerosene
R_3N	Alamine® 336
R_3NHHSO_4	Protonated Alamine® 336 bisulphate
$(R_3NH)_2SO_4$	Protonated Alamine® 336 sulphate
$(R_3NH)_2UO_2(SO_4)_2$	Alamine® 336 uranyl complex #1
$(R_3NH)_4UO_2(SO4)_3$	Alamine® 336 uranyl complex #2

Table 6: Assumed organic speciation

5.2.1 Acidification

Before the extraction stage, the amine is acidified with sulphuric acid according to reactions (1) and (2) to ensure that no contaminating anions are loaded onto the organic prior to uranium extraction.

$$H_2SO_4 + R_3N \leftrightarrows R_3NHHSO_4 \tag{1}$$

$$H_2SO_4 + 2\ R_3N \leftrightarrows (R_3NH)_2SO_4 \tag{2}$$

Reactions (1) and (2) produce two distinct acidified organic species that are present in varied proportions depending on the equilibrium conditions. Reaction (1) is also responsible for the stripping ability of concentrated sulphuric acid on loaded organic.

The acid loads onto the organic as pH is decreased. Below a certain pH, the acid saturates the organic and the proportion present in the aqueous phase increases. The distribution of acid between the aqueous and organic phase was studied by Yakubu and Dudeney[xv]. For the Gibbs minimisation model to accurately predict the acidification behaviour of Alamine® 336, two species: $C_{27}H_{57}NHHSO_4(l)$ and $(C_{27}H_{57}NH)_2SO_4(l)$ were added to a custom HSC database and enthalpy data for both species was adjusted until the Gibbs model output was as close as possible to the Yakubu and Dudeney results. The results are presented in Figure 1, where acid in organic is the sum of molar concentrations of both acidified organic species from (1) and (2) and acid in aqueous is the sum of the sulphate, bisulphate and undissociated H_2SO_4.

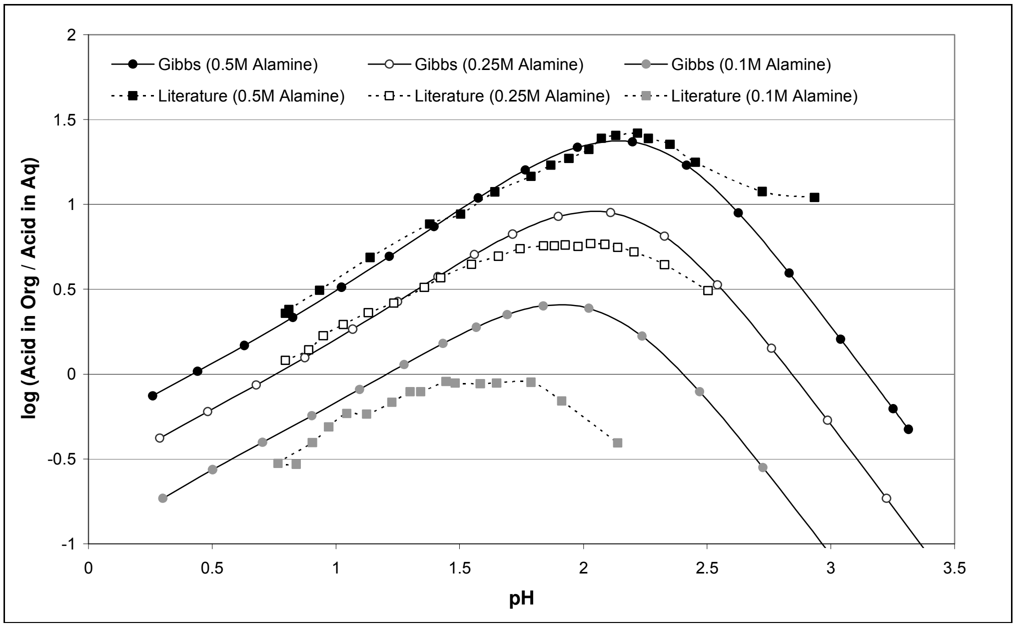

Figure 1: Comparison of Gibbs minimisation model and literature data for the acidification of Calamine® 336

The results show good agreement at low pH but deviate at higher pH, especially at the lowest Alamine concentration of 0.1M.

5.2.2 Uranium extraction

Uranium is loaded onto Alamine® 336 as an anionic complex. It has been demonstrated[13] that there are two predominant uranyl complex species present in the loaded organic: $(R_3NH)_4UO_2(SO_4)_3$ and $(R_3NH)_2UO_2(SO_4)_2$. The predominant complex was found to be $(R_3NH)_4UO_2(SO_4)_3$ under most uranium extraction conditions, implying that 4:1 Alamine® 336 : uranium molar ratio is required for near-complete extraction. It is interesting to note that the existence of the aqueous anionic species $UO_2(SO_4)_3^{4-}$ is questionable[xvi,xvii] so the formation of $(R_3NH)_4UO_2(SO_4)_3$ appears unlikely to follow reaction (3).

$$2\,(R_3NH)_2SO_4 + UO_2(SO4)_3^{4-} \leftrightarrows (R_3NH)_4UO_2(SO4)_3 + 2\,SO_4^{2-} \qquad (3)$$

Mechanism (4) or (5) appears most likely.

$$2\,(R_3NH)_2SO_4 + UO_2(SO_4)_2^{2-} \leftrightarrows (R_3NH)_4UO_2(SO4)_3 + SO_4^{2-} \qquad (4)$$

$$2\,(R_3NH)_2SO_4 + UO_2SO_4 \leftrightarrows (R_3NH)_4UO_2(SO4)_3 \qquad (5)$$

Similarly, for the formation of $(R_3NH)_2UO_2(SO_4)_2$, the reaction mechanism is likely to follow (6).

$$(R_3NH)_2SO_4 + UO_2SO_4 \leftrightarrows (R_3NH)_2UO_2(SO4)_2 \qquad (6)$$

The species $(C_{27}H_{57}NH)_2UO_2(SO_4)_2(l)$ and $(C_{27}H_{57}NH)_4UO_2(SO_4)_3(l)$ were added to a custom HSC database. Uranium extraction data from the Yakubu and Dudeney study[xv] was plotted for a range of Alamine® 336 concentrations vs pH. The enthalpy parameters for $(C_{27}H_{57}NH)_2UO_2(SO_4)_2(l)$ and $(C_{27}H_{57}NH)_4UO_2(SO_4)_3(l)$ were varied until the Gibbs model most closely approximated the experimental results. The results are presented in Figure 2.

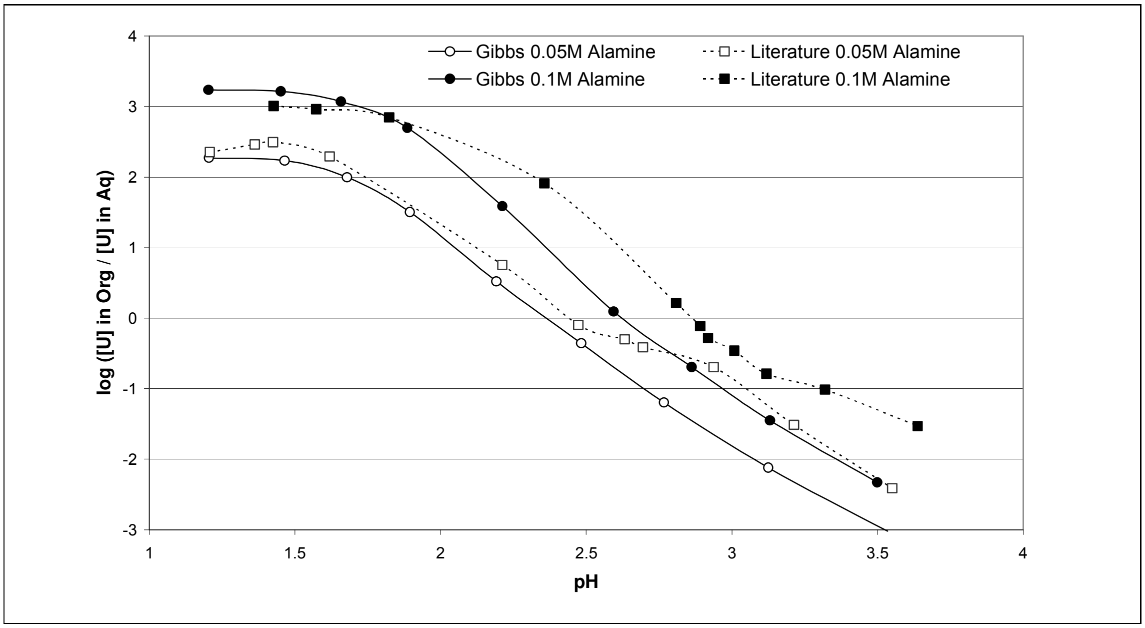

Figure 2: Comparison of Gibbs minimisation model and literature data for the uranium loading behaviour on Calamine® 336

The Gibbs model agrees reasonably well with the literature data although the Gibbs model predicts lower than anticipated uranium loading at pH > 2.

5.2.3 Testwork validation

A testwork program was recently completed for a uranium mining client. The pregnant leach solution is exceptionally clean of contaminant metal anions, so this testwork was considered ideal for the validation of the Gibbs model. The extraction isotherms from the testwork were compared with predicted results from the Gibbs model, comprised of the aqueous and organic species defined in Sections 5.2.1 and 5.2.2.

Extraction isotherms were prepared for three concentrations of Alamine® 336 with varying initial U_3O_8 concentration in aqueous feed. The organic solutions were made up using fresh Shellsol, isodecanol and Alamine® 336. Each isotherm was prepared using eight equilibrium points by varying the organic to aqueous ratio.

The individual data points for each series were calculated using the Gibbs model, using goal-seek in Excel to achieve the target pH (assuming pH = -log[H+]) for each data point by adjusting sulphuric acid in the feed. The testwork and Gibbs model isotherms are presented in Figure 3 although axis values are hidden due to confidentiality constraints.

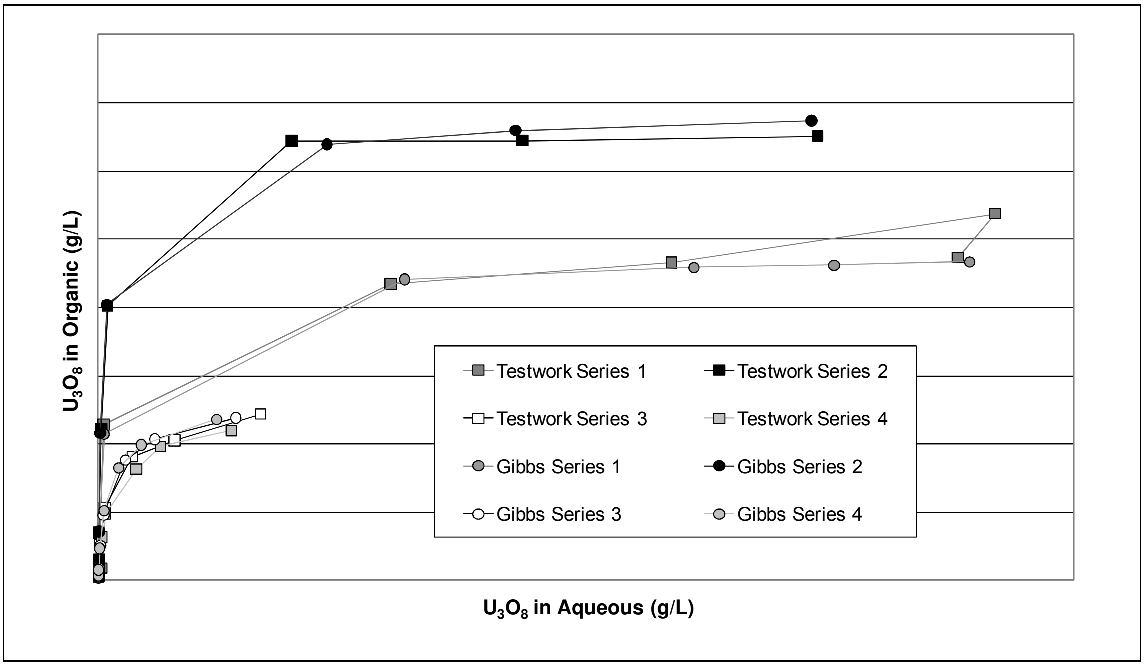

Figure 3: Testwork and Gibbs minimisation extraction isotherm results

The predicted isotherms agree exceptionally well with the testwork results for all testwork series. By using relatively little literature data, it has been possible to create a generic solvent extraction model for the solvent extraction of uranium by Alamine® 336. Testwork extraction isotherm results were predicted to high accuracy by the Gibbs model.

Gibbs energy minimisation could be used during the early phases of an engineering study, to generate first-pass isotherm predictions before the execution of a testwork program. Such a model could be developed for other solvent extraction systems, using other extractants, with predictive speciation for more than one metallic loading element.

For an existing solvent extraction plant, operating with a consistent leach solution composition, the Gibbs model could be improved by customising it for the plant conditions. Specie thermodynamics could be adjusted to increase the model's accuracy for a specified leach solution. The more accurate model could be used to evaluate plant "what if" scenarios quickly and at low cost.

6. OTHER OPPORTUNITIES FOR GIBBS ENERGY MINIMISATION MODELLING

6.1 REDUCTION OF SULPHIDE ORES BY SYNGAS

Coal or other hydrocarbon fuels can be decomposed in a gasifier to produce a gas containing large proportions of H_2 and CO. This "syngas" could be used for the reduction of metal sulphide concentrate in a fluid-bed. The decomposition of the hydrocarbon in the gasifier can be assumed to be at equilibrium and can hence be modelled by FEM. For hydrocarbon FEM modelling, Aspen Plus is often used, however in this example, it is desirable to optimise the syngas composition and temperature for downstream metallurgical requirements. METSIM or IDEAS would therefore be selected as the ideal modelling package. The gasification and downstream metallurgical process would be simulated in an integral model.

The reduction of sulphide ores by H_2 and CO is not an equilibrium process. The solid phases present in the reduced ore will not be at thermodynamic equilibrium. The gas phase however will be near equilibrium while at the temperatures encountered in the fluid bed. Known solid phase reaction extents could be hard coded into the model, with the resultant offgas equilibrated by the FEM object, improving the energy balance of the model.

6.2 ACID PLANT SIMULATIONS

One of the example models provided with METSIM is a Lurgi sulphuric acid plant model that makes use of the FEM object to simulate the acid plant converter stages. Modelling the converter section of an acid plant requires FEM to calculate the SO_2 to SO_3 conversion during each stage. The heat balance of an acid plant is critical to the sizing of the coolers.

6.3 NICKEL SMELTING AND CONVERTING

There are many excellent papers in the literature about using Gibbs energy minimisation to calculate furnace thermodynamics for nickel smelting and converting. Tan and Neuschütz[viii] developed a complex model for the smelting of high-grade nickel matte, for the Outokumpu flash-smelting process and the INCO flash-smelting process. The model considers 16 elements and the activity coefficients of the components are derived from literature data. Model predictions agree exceptionally well with measured data. Kellogg[xviii] developed a model for the thermochemistry of nickel matte converting which uses Margules parameters to model non-ideal solution thermodynamics for the Ni-O, Ni-O-S and Ni-Fe-O-SiO_2-CaO systems.

The use of these types of models in engineering studies remains limited. Typically, a simple METSIM model, with rudimentary and highly simplified reaction chemistry is used to develop a mass and energy balance. The benefit of having a comprehensive Gibbs energy minimisation furnace model, to evaluate the effect of process changes, could be enormous for existing operations. Metal losses, offgas SO_2 content, and fuel consumption could be optimised more effectively. The reduction of greenhouse gas emissions has never been as relevant as it is today. Decreasing fuel consumption will aid smelter operations to meet their increasingly stringent greenhouse gas emission targets as well as reduce their operating cost.

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URANIUM

PROCESS DESIGN

CONSIDERATIONS AND METHODOLOGIES FOR THE DESIGN OF GASSED AGITATED CSTR'S

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CONTENTS

1. INTRODUCTION

Processing of ores via a hydrometallurgical route requires agitated tanks. The main task of these agitated tanks is the suspension of solids to avoid any accumulation or deposition which could have severe consequences for continuously operated plants during long periods of operation.

Applications in continuously stirred tank reactors (CSTR's) range from simple suspending duties, as can be found in the crystallization of aluminum hydroxide in alumina plants, up to three phase mixtures involving an additional gas phase. Figure 1 shows a cascade of crystallization vessels each having a size of approximately 5000 m³. For this application a homogeneous distribution of the solids is required to ensure enough pressure head available for overflow into the next vessel. More demanding agitation conditions can be found in bioleaching or neutralization applications. Even at high specific power input levels, agitators installed in such tanks will often need to be operated at low shaft speeds. For gassed applications one especially has to consider impellers operating under very 'special' conditions. For certain atmospheric leaching reactors a further design consideration is the temperature. To achieve a fast leach result the reaction temperature could range close to boiling conditions, which leads to increased gas evolution since the added gas will saturate with water vapor. Therefore, conventional design methods should be applied with caution. These challenging processes in addition to the physical plant scale demands requires further considerations in defining the mechanical design of the agitators and its impellers.

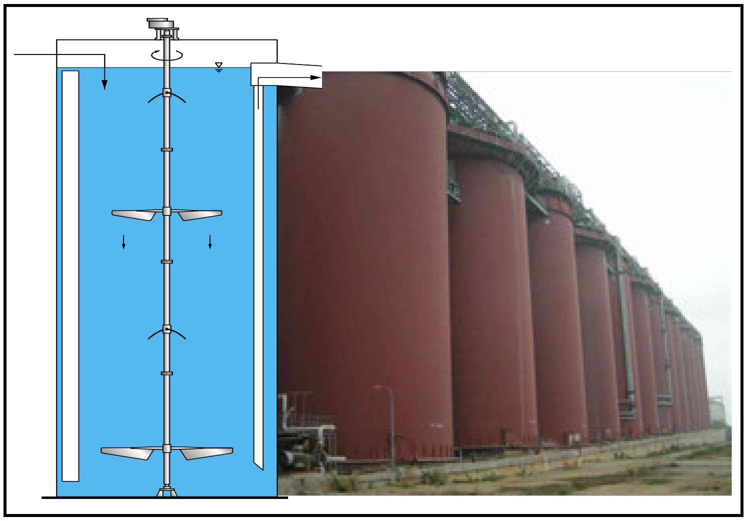


Figure 1: Continuous stirred tank reactors 5000 m³.

Besides the specific knowledge of designing agitators for these demanding condition, the possibility to run lab tests for 'out of the range applications' at appropriate scaled down conditions with original products or a model system is very important.

This paper presents model options in approaching the design of the agitators for these challenging systems. The impact on the mechanical design is considered and the influence of auxiliary features such as sparger design is addressed. Lastly the results from lab. measurements confirming the suitability of the described methods for CSTR's are discussed.

2. SOLIDS SUSPENSION

As any of the other basic mixing tasks ‘solids suspension’ is governed by natural laws, which must be known by the engineer to design an agitator. Besides being able to describe the solids behavior in a fluid the objective of the mixing process has to be known, i.e., which degree of homogeneity is required or sufficient. For some applications, for example tanks with a bottom discharge, off-bottom suspension could be adequate. More stringent specifications for the homogeneity of suspension have to be made for a continuously operated vessel with an overflow. Many information and design guidelines on ‘solids suspension’ can be found in literature [1, 2, 3, 4].

To design an agitator for slurries the physical properties of the substances have to be taken into account. With this information the free-settling velocity of a single particle is calculated which then allows the determination of the hindered settling velocity due to the presence of numerous particles. Assuming that all solid particles are distributed uniformly, and all simultaneously begin to settle, they release a settling power. The agitator must provide a power input to counteract this settling power. The agitator power always amounts to a multiple of the settling power and depends on the impeller type applied.

For simple suspending tasks as is the case for the crystallization of aluminum hydroxide, specific power inputs are relatively small since the hindered settling velocity is only 0.001 m/s. A typical motor size for a 4500 m³ crystallizer is about 75 kW. This motor power is sufficient to achieve a homogeneous solids distribution using a multiple stage impeller design. Requirements get more demanding for bigger particle sizes in the range of 500 to 1000 μm meaning higher hindered settling velocities of 0.075 m/s. Some examples are found in leaching vessels for uranium ores. For typical tank sizes of approximately 1500 m³ even at motor sizes of 250 kW only off-bottom or just suspended conditions can be achieved. For such demanding applications EKATO advises testing with original products or through model simulation.

Impeller designs used to suspend solids are typically hydrofoil types, as an example the EKATO VISCOPROP. Compared to a standard pitched blade turbine with its simple blade geometry hydrofoils require 2.3 times less power to achieve the same degree of homogeneity. The main difference between these impeller types is that the VISCOPROP transfers a bigger portion of the power input into axial pumping which is required to keep solids in suspension. Figure 2 shows a comparison of the axial flow velocities and flow field induced by these impeller types. As can be seen by the size of the indicated area the flow velocities using a VISCOPROP are much higher explaining its better suspending performance.

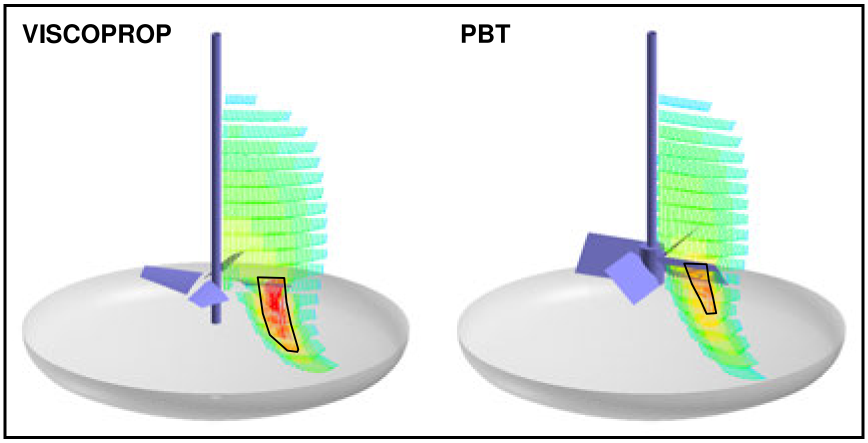


Figure 2: Flow field induced by a VISCOPROP and a standard pitched blade impeller.

3. SOLIDS SUSPENSION AT GASSED CONDITIONS

The mixing task of ‘simple’ solids suspension gets more complex if an additional basic mixing task gets involved; the dispersion of a gas in the liquid (‘gassing’). The function of the agitator in this three-phase system is then to suspend solid particles and disperse gas simultaneously. One typical example is a bioleach process where air has to be dispersed to achieve sufficient interfacial area for oxygen to be transferred from the gas phase into the liquid phase while at the same time keeping the ore particles suspended. In this three-phase medium the liquid forming the continuous phase, while gas and solids are present as disperse phases, requires special attention for the agitator design since the presence of the gas fundamentally alters the liquid phase flow field. The assumption of design principles deduced in the corresponding two-phase system is an unreliable reference for the three-phase agitator design [5, 6, 7].

The main reason causing concern is that sedimentation of suspended particles occurs at gassed conditions if a critical air flow number is exceeded. This is due to a change in the impeller’s effective power number and therefore power input at gassed conditions. In addition the gas changes the flow field below the impeller which reduces the circulation flow or pumping rate of the impeller. This inevitably leads to reduced flow velocities and partial settling of the solid particles. A further increase of gas flow rate under otherwise constant operating conditions will eventually fully compromise the dispersing capacity of the impeller which then becomes flooded. The flooding will cause most of the solid particles to settle [8, 9].

Due to the additional mixing task of gas dispersion hydrofoil type of impellers are typically not applied anymore. Figure 3 shows the power requirements to achieve off-bottom suspension for different impeller types at increased dimensionless gas rates Q_g [10].

$$Q_g = \frac{\dot{q}_g}{n \cdot D^3}$$

where q_g is the actual gas feed rate, n the shaft speed and D the impeller diameter.

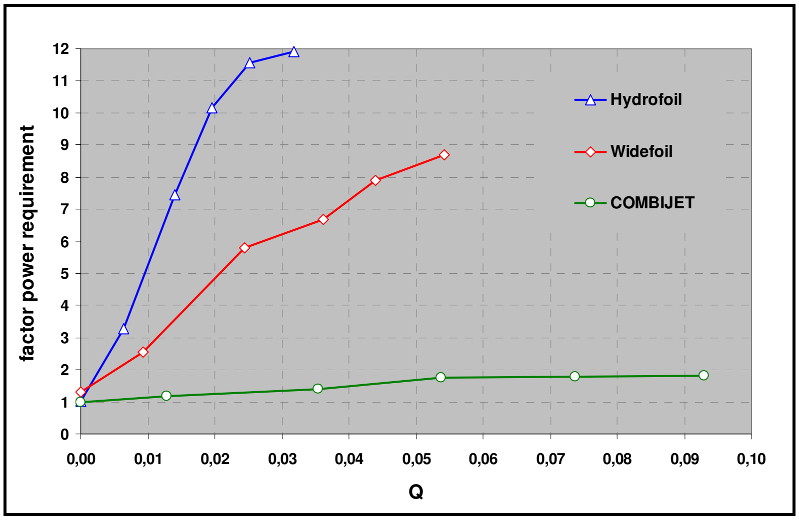


Figure 3: Power requirement to achieve off-bottom suspension at gassed conditions.

As can be seen from figure 3 hydrofoils require the lowest power input to achieve off-bottom solids suspension at ungassed conditions (Q = 0). At even quite low gassing rates the power demand increases drastically. Widefoil type of impellers, e.g., the EKATO ISOJET-B, require a slightly higher power input at ungassed conditions but exhibit better behavior at increased gas feed rates. The flow field and axial flow velocities of an ISOJET-B are shown in figure 4. As an adapted hydrofoil impeller this impeller variant applies the strong axial flow required to suspend solids. Due to an increased blade area it can handle a quite high amount of gas as well.

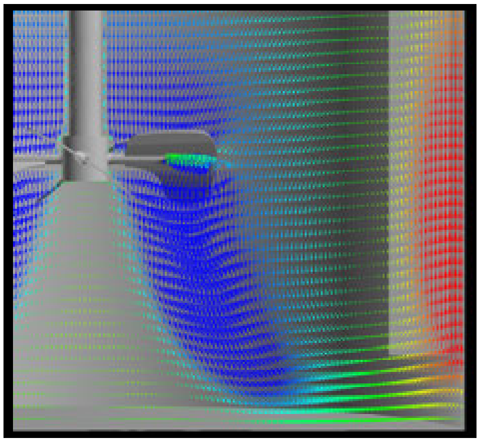


Figure 4: Flow field and axial flow velocities of a widefoil ISOJET-B impeller.

The best behavior of all compared impeller types is offered by the patented EKATO COMBIJET which is a combination of the proprietary gas dispersing EKATO PHASEJET and widefoil ISOJET-B impellers. Its special blade shape creates primarily a strong radial flow but at the same time inducing an axial flow leading to good gas dispersion. As for the PHASEJET the blades of the COMBIJET are shaped to decrease the size of gas cavities at the low pressure side which ensures a stable performance and gas dispersing capability across a wide range of operating conditions. As can be seen in Figure 3 its power requirements at ungassed condition is comparable to the widefoil impeller types but shows a substantially reduced power requirement at all measured gas feed rates. A big advantage for this application is obviously that the pumping capacity at gassed conditions is more stable than for the hydrofoil or widefoil impeller types.

Figure 5: The patented EKATO COMBIJET impeller.

Wong [16] compared different impeller types in slurries over a wide range of gas flow rates and gives a model to predict the increase in shaft speed to achieve just suspended conditions. Y. Zhu [8] in his paper proposes to correlate the ratio of the gassed n_{jsg} to ungassed n_{js} just suspended speed by the following modified equation

$$RJSS = \frac{n_{jsg}}{n_{js}} = 1 + m \cdot Q_{js}{}^{x}$$

$$Q_{js} = \frac{\dot{q}_g}{n_{js} \cdot D^3}$$

where m and x are constants.

The constants in above equation can be fitted to excellently correlate with the data measured by EKATO for all impeller types.

Measurements of the flow velocities for different types of impellers further explain the different suspending behavior at gassed conditions. As described before a reduced pumping rate will result in decreased flow velocities below a gassed impeller. Figure 6 shows the relative flow velocities as function of the ratio of the sparged air to the agitator power input. For a widefoil type of impeller the flow velocity is still about 45 % of its initial flow velocity, and is much higher than for a pitched blade turbine (PBT 6) or hydrofoils which drop below 20 %. The COMBIJET (ECJ 6) shows a more stable flow behavior; at a comparable power input ratio it achieves 85% of its initial flow velocity.

Besides the better gas handling capacity of the COMBIJET it offers the further advantage of a much higher flooding limit compared to the other impeller types. At comparable conditions about 2.7 times the gas rate can be added before flooding occurs.

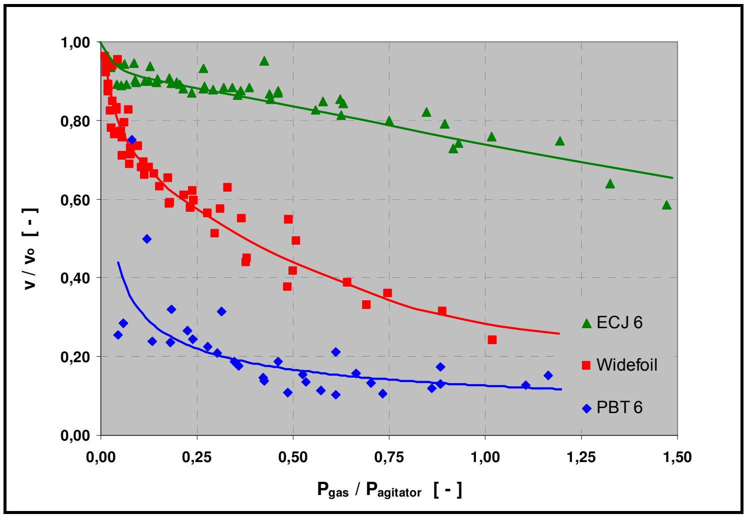


Figure 6: Flow velocities for different impeller types at gassed conditions.

4. SOLIDS SUSPENSION AT GASSED AND BOILING CONDITIONS

As described in Section 3, three-phase applications in minerals processing have to be designed with utmost care to ensure that solids are suspended and to avoid flooding of the impeller. This situation gets even more severe if the slurries are processed close or at boiling conditions. This is often the case for atmospheric leach applications which are operated at highest possible temperatures to maximize the reaction rate [11, 12, 13, 14, 15]. At or close to boiling conditions the sparged gas will saturate with water vapor immediately. Due to this saturation with vapor the actual gas rate to be sparged is increased.

Figure 7 shows the increase of the volume of the sparged gas with increased temperature. Up to a temperature of approximately 75 °C the increase is quite moderate, but at 100°C the gas volume is increased by 85%. This of course cannot be neglected anymore and has to be considered during the agitator design [16].

In addition this increase of the actual gas flow changes the residence time of the gas, which will have implications on e.g. the mass transfer performance of the reactor. Besides that the oxygen partial pressure, meaning the driving gradient for mass transfer, is reduced.

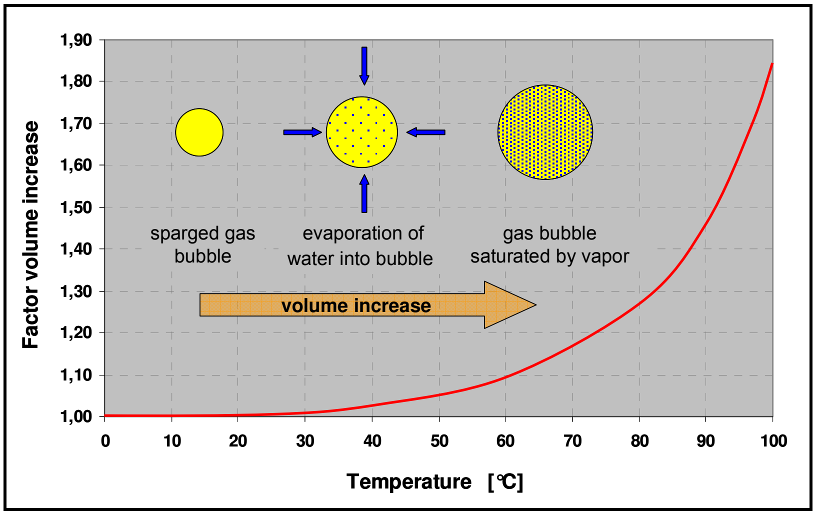


Figure 7: Increase of the actual gas flow rate with temperature, pressure at sparger 2.2 bara (atmospheric + hydrostatic pressure).

5. MECHANICAL DESIGN IMPLICATIONS

After having given special attention to the process design for gassed slurry applications, very important mechanical aspects have to be highlighted as well. The gas feed to an impeller does not only change its power number N_p but has implications on the radial force coefficient c_R as well. This dimensionless number is used to calculate the radial forces F_R acting on the shaft by which the bending moment M_b can be derived:

$$F_R = c_R \cdot \rho \cdot n^2 \cdot D^4$$

$$M_b = F_R \cdot l$$

where ρ is the density of the slurry and l the shaft length.

The bending moment as the torque have to be known to size the shaft of the agitator and the gear box.

Figure 8 shows the change of the radial force coefficient with increased gas feed rate. Depending on the ratio of the shaft speed n to the critical shaft speed n_c an increase of 1.5 to 2.5 times the ungassed radial force coefficient will occur. Under a specific set of operating conditions the increase in the radial forces could thus have a huge impact on the mechanical agitator design. Understanding the demands the process design thus will impose on the mechanical design of the agitator is thus essential.

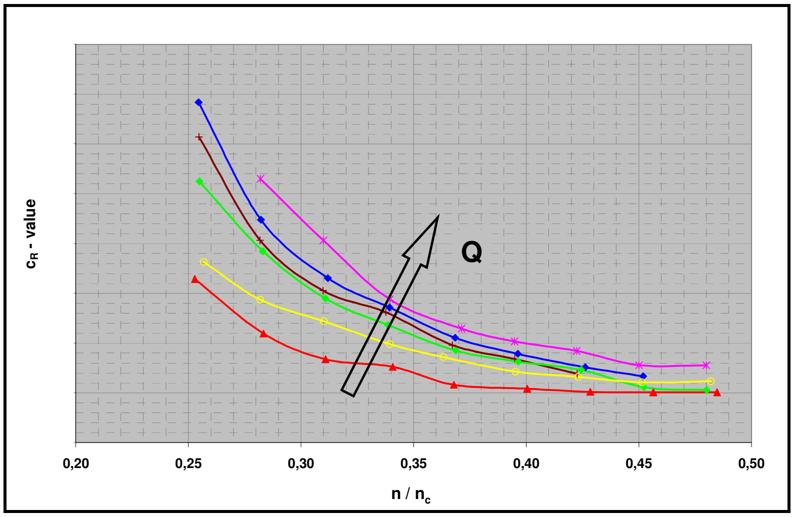


Figure 8: Increase of the radial force coefficient c_R with dimensionless gas feed rate Q.

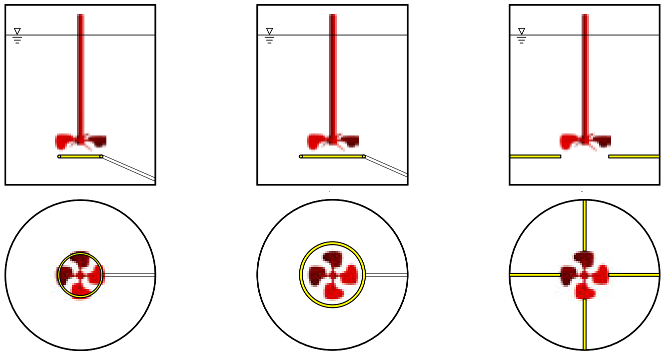
6. ADDITIONAL EQUIPMENT DESIGN AND OTHER PROCESS CONSIDERATIONS

Gas sparger design

The design of the gas sparger is often a point of discussion. It is quite common for the agitator supplier to provide recommendations regarding its design. A problem that may arise with gas spargers in processing minerals slurries is the blocking of the sparge ring holes by solids present in the slurry. Therefore quite often high gas outlet flow velocities are desired to limit blockages but which in turn leads to an increased pressure drop and wear of the sparge rings. An additional problem with some sparger designs is the backflow of slurry into the sparger, e.g., during a shut-down of the gas feed.

A variety of gas sparger designs exists. A standard design as shown in figure 9 a), not only applied in minerals processing, is a sparge ring with multiple holes. The diameter of this sparge ring typically is smaller than the impeller diameter. To avoid a direct loading of the impeller with gas, especially where the impellers are operated close to flooding, designs with sparge ring diameters bigger than the impeller diameter or multiple sparge pipes from the side are used – see figures 9 b) to d). Another commonly utilized design is direct sparging to the impeller through a hollow shaft – 9 e). This design is very unlikely to block but is mechanically more complex. Due to the addition of the gas in the low shear zone directly below the shaft the dispersion of the gas is typically not very effective. Not reflected in Figure 9 is the use of injection nozzles as applied in some oxidative leaching technologies with pure oxygen.

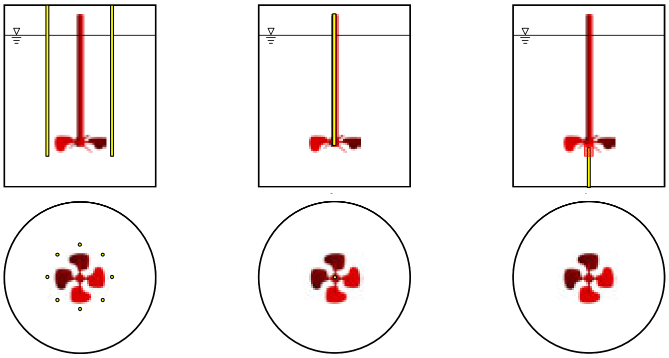
EKATO patented a technology where the gas is added to a rotating cylinder or distributer below the impeller – 9 f). One feed pipe extends into this distributer which is connected to the impeller blades via hollow beams. Here the gas is directly fed in the high shear zone of the impeller which is advantageous for the gas dispersion. Advantage of this design is that the single sparge pipe with the big diameter is very unlikely to block or wear. Cost wise the single pipe configuration will have benefits as well.



9a) standard sparge ring $D_R < D$

9b) sparge ring $D_R > D$

9c) sparge pipes



9d) sparge pipes

9e) down the shaft

9f) rotating sparger

Figure 9: Gas sparger options.

Viscosity

Data presented so far presumed turbulent flow conditions which will occur for most of the slurries processed involving a gas. Gas dispersion becomes very demanding at increased viscosities resulting in transient or laminar flow conditions or for slurries showing flow anomalies. Figure 10 shows a high viscous slurry at ungassed (left) and gassed (right) conditions. During testing it could be observed that gas was entrapped in the slurry and a foam of mousse-like consistency formed. The volume of slurry increased very fast to a steady state and then remained there. Pumping of the slurry at the impeller stopped due to a big gas cavity that formed around the impeller. Processing of the slurry at intended slurry viscosity was not possible, the slurry had to be diluted to obtain the intended process result.

Figure10: Gassing at increased viscosity (left ungassed slurry).

Feed points of liquid components

Figure 11 shows the impact of a gas feed on the mixing time. As can be seen already, at quite low gas feed rates the mixing time increases sharply for surface addition of any reagents or components. At a superficial gas velocity of bigger than 2 cm/s the mixing time increases by about 70% which may be critical for achieving the desired process performance. For such process conditions design aspects beyond only the impeller design need to be considered. The optimization of these process designs can only be achived by looking beyond the agitator per se.

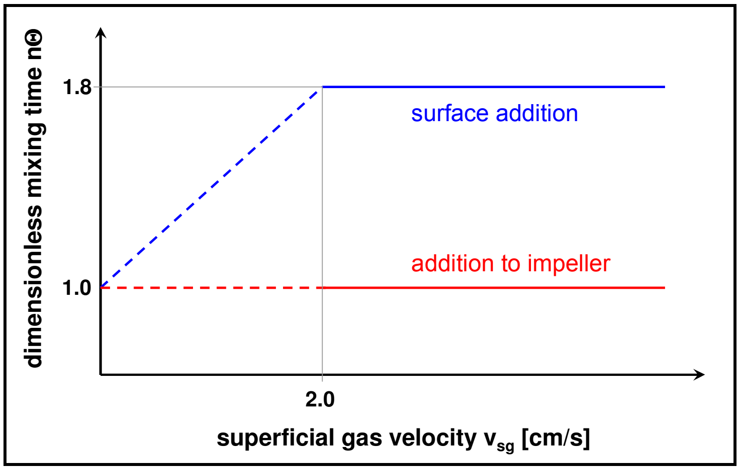


Figure 11: Effect of feed point on mixing time for gassed tanks.

7. SUMMARY AND CONCLUSIONS

The design demands for continuous stirred tank reactors can become quite challenging. For a simple suspending task without any other additional mixing requirement the agitator design is theoretically simple if all relevant process parameters are known.

More attention has to be paid to applications where an additional gas phase is involved; three phase mixtures. This additional gas phase alters the flow around impellers and therefore the hydrodynamics in the tank. If proper consideration of this additional phase is not given, or the impact of the gas on the agitation is unknown to the equipment supplier, the agitator might not operate as intended. Consequently the desired extraction rates are not attained. In addition a resulting accumulation of solids in continuous operated vessels with time will force the process to be shut down and the tanks cleaned. Besides the impact on the process an inadequate agitator design may lead to mechanical failures of the shaft or the gear box due to an increase in radial forces at gassed conditions.

A further consideration is that at boiling conditions actual gas flow rates in the tank increase due to the saturation of the process gas with vapor. This of course has an impact on the agitator design and has to be taken into account as well.

New impeller designs will not completely replace the hydrofoil and widefoil impellers but in certain cases they exhibit a superior performance for dispersing gases in slurries, even at the unfavorable boiling conditions. A careful selection of impellers based on the actual operation requirements will lead to optimal investment in capital costs as well as operating costs and to maximum reliability of the plant.

Pilot testing is still indispensable for reaching the optimum solution. With a wealth of knowledge in scaling down processes to a modeling size EKATO's technical center continue to investigate such complex process applications.

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BIOMINERAL PROCESSING OF AN APATITE RICH LOW-GRADE INDIAN URANIUM ORE

By

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CONTENTS

ABSTRACT

Enriched culture of a microbial isolate with mainly *Acidithiobacillus ferrooxidans* grown from source mine water was employed for bio-leaching of uranium from a low-grade apatite rich uranium ore of Narwapahar Mines, India while varying pH, pulp density (PD), particle size, etc. On varying pH at 35^{o}C using 20%(w/v) PD and <76µm size particles, 83.5% and 78% uranium bio-recovery were observed at 1.7 and 2.0 pH in 40 days as against maximum recovery of 46% and 41% metal in control experiments respectively. It was observed that the finer size (<45µm) of the ore exhibited higher uranium dissolution with a maximum bio-recovery of 96% in 40days at 10% (w/v) pulp density (PD), 1.7 pH and 35^{o}C. The bio-recovery of uranium fell from 96% to 82% on increasing the pulp density from 10% to 20% under the same condition. The higher uranium dissolution during bioleaching at 1.7pH with the fine size particles (<45µm) can be correlated with increase in redox potential from 598mV to 708mV in 40 days.

Key words: low grade ores, uranium, apatite, bioleaching, ferric ions, *A.ferrooxidans*

1. INTRODUCTION

The increasing use of uranium in nuclear power generation has put pressure on the existing high grade ore reserves, and therefore potential exploitation of low grade ores is becoming essential to treat and fulfill the energy expansion plans. In order to supply uranium for the planned and future power reactors, several low grade ores containing uraninite are being considered for treatment in India. Uranium recovery by conventional hydrometallurgical process is not very high and therefore other processing options are being explored (Tuovinen 1972, Guay 1977, Ehrlich & Brierley 1990, Rawlings & Silver 1995). Uranium leaching exemplifies the successful application of hydrometallurgical and biohydrometallurgical processes for metal recovery. Commercial applications of bioleaching of uranium from low grade ores have been practiced since 1960's. Best known are the in-situ leaching operations in the underground uranium mines in Elliot Lake district of Canada including the Stanrock, Milliken and Denison mines. Significant commercial developments are occurring in bio-hydrometallurgical processing particularly in recent years, parallel to the development of environmentally friendly other methods.

Uranium minerals such as uraninite or coffinite need initial oxidation before the metal can be solubilised (Mathur & Dwivedy et al. 1994, Dwivedy & Mathur 1995, Dwivedy et al. 2000, Abhilash et al., 2009). Uranium extraction by direct acidulation is not effective, and therefore oxidation of UO_2 to its hexavalent form is required which is expected in presence of Fe^{3+}. In bioleaching, Fe^{3+} can be bacterially generated from the iron bearing minerals such as pyrite, which can act as an ideal lixiviant for uranium minerals (Natarajan 1994, Ehrlich 2001, Hansford & Vargas 2001, Sand et al. 2001, Brierley and Brierley, 2001, Devasia & Natarajan 2004, Abhilash et al., 2009).

Uranium ore from the Narwapahar mines, UCIL, the subject of our study, is a type of vein deposit found in Singhbhum area of Jharkhand, India. The ore (0.047% U_3O_8), though of Singhbhum area, possesses exceptionally different mineralogy due to presence of some refractory minerals and richness in apatite (5%) resulting in a maximum 78% recovery in conventional processing practice at UCIL, with a very high consumption of sulfuric acid and pyrolusite, besides possible loss of uranium as uranium phosphate. To avoid usage of environmentally non-benign oxidants, remediation of influence of phosphates, and improve the overall process output of uranium, an alternate extraction technology using microbial leaching is worth exploring and the results are presented and discussed in the paper.

2. MATERIALS AND METHODS

Low grade uranium ore containing 0.047% U_3O_8 was collected in the form of lumps from Narwapahar mines, Jharkhand. The ore was crushed, ground and passed through a sieve of 150µm (-100 mesh) size. A representative sample was prepared by coning and quartering method for chemical analysis by fluorimetry for uranium and AAS for other metals (Table-1). The mineralogical analysis of ore showed Quartz: 52.5%, Chlorite: 36%, Magnetite: 3.8%, Apatite: 5.3%, Tourmaline: 0.8%, other transparent minerals: 0.3% and other opaques: 1.3%.

Table-1: Chemical Analysis of Narwapahar Ore

U_3O_8	SiO_2	Fe	Cu	Ni	Mo	S	P_2O_5	TiO_2	MnO	CaO	MgO	Al_2O_3
0.047	51.24	12.9	0.02	0.02	0.006	0.05	1.81	0.7	0.01	1.88	1.07	13.8

Mine water sample collected from Narwapahar uranium mines was the source of bacterium-*Acidithiobacillus ferrooxidans* (*A.ferrooxidans*) which was isolated in 9K media [$(NH_4)_2SO_4$: 3.0g/L, KCl: 0.1g/L, K_2HPO_4: 0.5g/L, $MgSO_4.7H_2O$: 0.5g/L, $Ca(NO_3)_2$: 0.005g/L, $FeSO_4.7H_2O$: 44.2g/L] at 2.0 pH. The oxidation of Fe^{2+} to Fe^{3+} by *A.ferrooxidans* was considered as an indication of its growth. Fe^{2+} concentration was analysed by titration against $K_2Cr_2O_7$. Cell count was performed in a Petroff-Hauser counter using Leica biological microscope. The wild strains of *A.ferrooxidans* isolated above were subjected to three times adaptation on 5% (w/v) ore and adapted isolate was used for bioleaching.

The bench scale leaching experiments were carried out in 500mL Erlenmeyer flasks in an incubator shaker. Flasks with 200mL of slurry with ore were inoculated with 10 %(v/v) of active liquid culture containing 7.4×10^8 cells/mL. Conditions like 35 ± 0.2^oC temperature, pH 2, PD 20 % (w/v), rpm 100 were maintained unless otherwise stated. A 0.5mL of the supernatant was withdrawn at 5 days interval for analysis of metals leached out. The ferrous ion concentration in the solution was determined by titrimetric method. All the inoculated sets had their corresponding sterile control sets prepared under the same conditions. The pH, redox potential and Fe^{2+} conc. of the leach solution was measured on alternate days. Redox potential (E) was measured against SCE. The pH was maintained with 10N H_2SO_4. Upon termination of the leaching experiments, the solid residues were dried and samples were taken for chemical analysis and XRD phase identification. The leaching results presented in the paper are from the average of duplicate experiments (with max. ±2% deviation) conducted under the same conditions.

3. RESULTS AND DISCUSSION

3.1. ISOLATION OF A.FERROOXIDANS AND MICROBIAL CELL COUNT

A.ferrooxidans from mine water samples was isolated in $9K^+$ media at pH 2.0 and 35^o C and the growth was measured in terms of cell count (Fig. 1). The grown culture in 12 days from the Narwapahar mine water had $6.8x10^7$cells/mL. Subsequent sub-culturing of the microbes showed the presence of 7.4×10^8 cells/mL in 7days. The variation of redox potential (E) during growth of *A.ferrooxidans* from mine water at pH 2.0 and 35^oC with time is also shown in Fig 1. There is a gradual increase in E values from 375-566mV during the growth of microbes in 7days from the mine water samples whereas no major change in E of control is observed. Thus, the growth of *A.ferrooxidans* is accompanied by increase in redox potential. There is a steady decrease in the concentration of Fe^{2+} and the bacteria (*A.ferrooxidans*) present in the system are responsible for this as they use Fe^{2+} as energy source to convert it to Fe^{3+}. A minute decrease is observed in control also because of oxidation of iron (II) by air. *The* most suitable pH for isolation of *Acidithiobacillus ferrooxidans* is 1.7-2.0 and hence pH of the growth medium ($9K^+$) was maintained at 2 by adjusting with 10 N H_2SO_4. After 5-6 days, the pH of inoculated sample remained close to 2 and very less H_2SO_4 was consumed for pH maintenance.

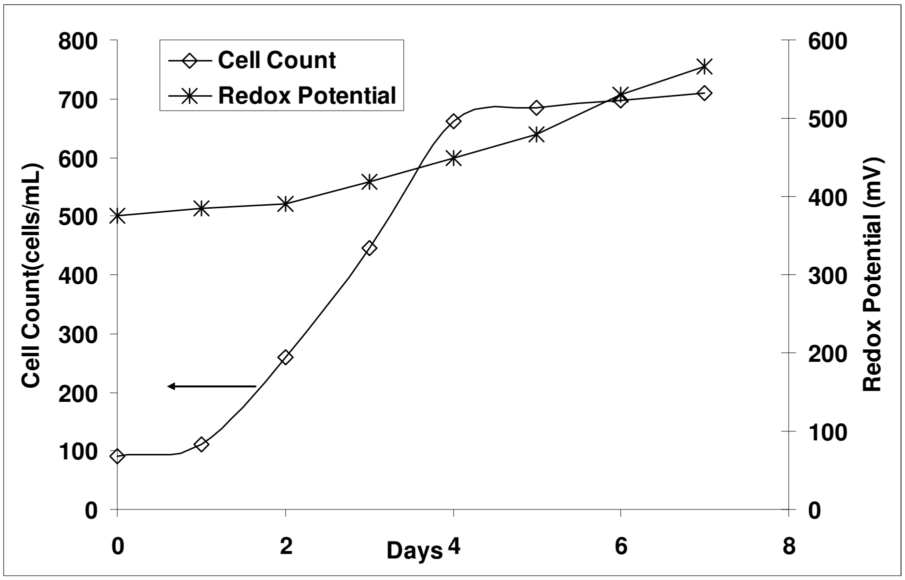

Fig.1: Variation of redox potential with rise in cell count during isolation of *A.ferrooxidans* from Narwapahar mine water in 9K media at 2.0pH and 35°C.

3.2. EFFECT OF PH

The effect of varying pH from 1.3 to 2.5 using 20% PD (w/v) with <76µm particle size while shaking at 100 rpm at 35°C temperature on bioleaching of uranium was examined. Uranium biorecovery of 83.5% and 78% were observed at 1.7 and 2.0 pH respectively in 40 days (Fig.2). An appreciable increase in bio-recovery of uranium to 83.5% at 1.7 pH with an increase in redox potential from 560mV to 690 mV in 40 days was noticed. At still lower pH, the metal recovery was low because of low oxidation potential of leaching system. Further rise in pH to 2.5 reduced the solubilisation of uranium which may be due to precipitation of Fe^{3+}. At pH 1.7, bio-recovery of uranium was very effective which may be attributed to the efficient conversion of U(IV) to soluble U(VI) by Fe (III) produced through bio-chemical action on the ore.

3.3. EFFECT OF PARTICLE SIZE ON BIO-LEACHING OF URANIUM

Effect of particle size on bio-dissolution of uranium is shown in Fig.3. It may be seen that fine particles have better uranium leachability. The recovery was 96% with the ore particles of size <45µm as compared to 78% uranium dissolution for 53-45µm size. Above this size, there was a steep decrease in recovery. Finer particles were thus increasingly exposed to oxidation to dissolve uranium from the silicate-apatite phase. The concentration of ferric ions (0.034 g/L) obtained by bacterial action on ferrous ions involved in chemically dissolving uranium was found to be much higher in case of leaching of finer size (<45µm) than that of (0.007g/L) coarser size particles (76-53µm).

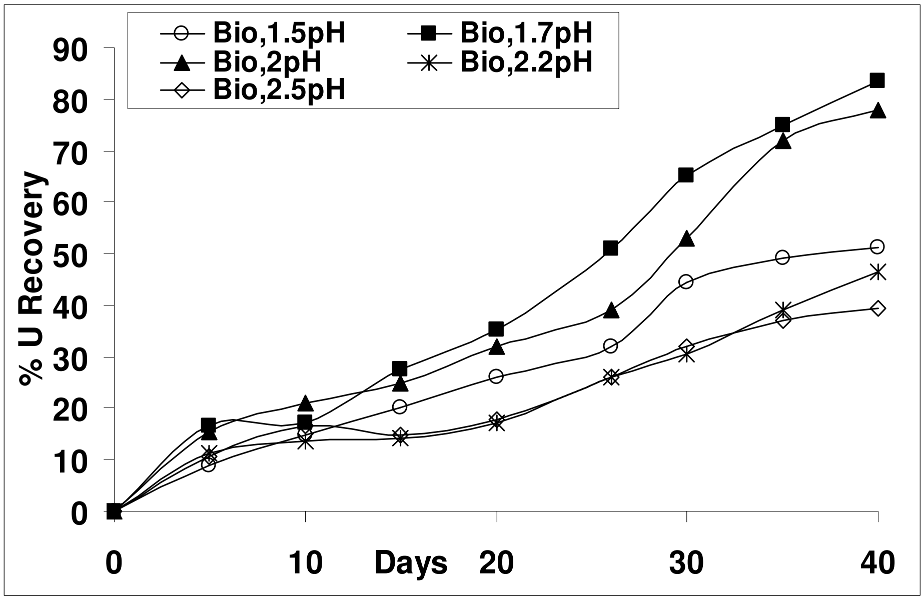

Fig.2: Uranium bio-recovery at varying pH using 20% PD(w/v) of <76µm particle size at 35°C temperature

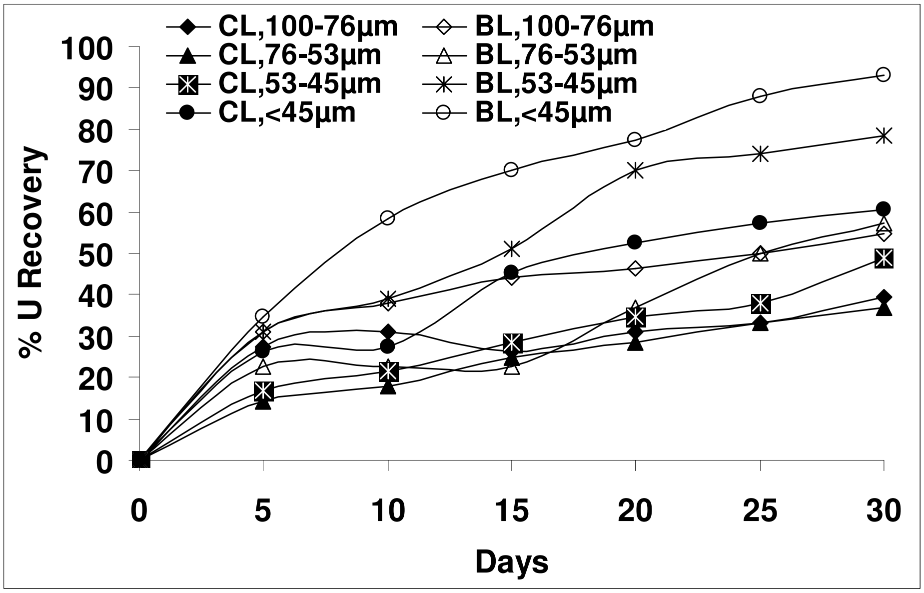

Fig.3: Uranium bio-recovery at varying particle sizes using 10% PD(w/v) at 1.7pH and 35°C temperature

3.4. EFFECT OF PULP DENSITY

Pulp density (PD), a parameter that determines the solid-liquid ratio in the bioleaching, was varied in the range 10-30% (w/v) with particles of <45µm size using 10% (v/v) adapted *A.ferrooxidans*, while shaking at 100 rpm, pH 1.7 and 35°C temperature. Data plotted in Fig.4 show that bio-recovery (96%) was maximum at 10% PD with a rise in E from 598 mV to 708 mV in 40 days. At a pulp density of 20%, the uranium recovery was 82% during this period. Under the above conditions, still higher pulp density (30% w/v) resulted in decrease in biorecovery to 25% (Fig.4) because of lower ratio of inoculum to substrate resulting in its inability to penetrate such high solid concentration.

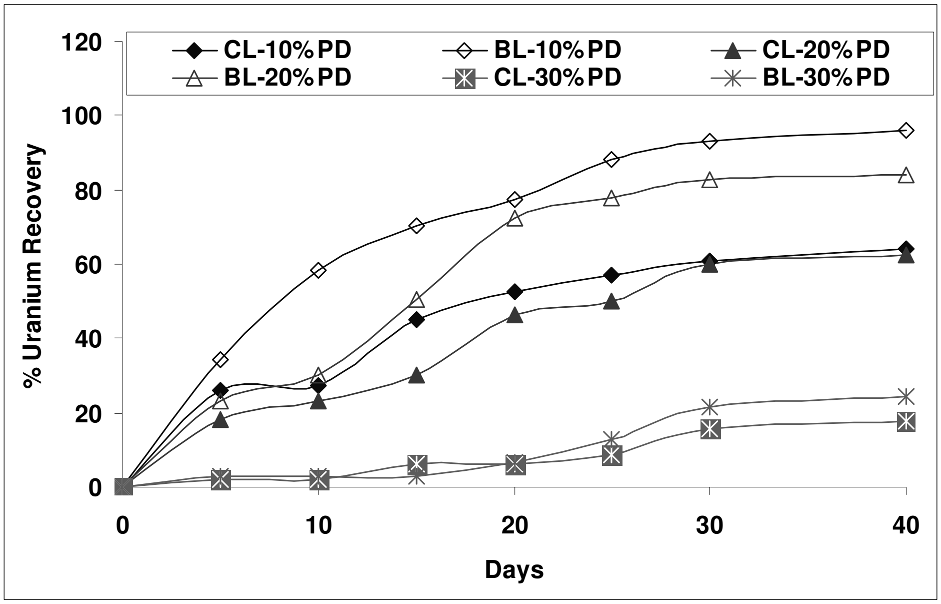

Fig.4: Uranium bio-recovery at varying pulp densities using <45µm particles at 1.7pH and 35°C temperature

The bioleaching of uranium by *A.ferrooxidans* follows *indirect mechanism* where the bacteria generate a lixiviant – Fe(III) by oxidizing the pyrite present in the ore.

$$FeS_2 + H_2SO_4 + \tfrac{1}{2}\,O_2 \xrightarrow{Bact} FeSO_4 + H_2O + 2S^o \qquad (1)$$
$$FeSO_4 + H_2SO_4 + O_2 \xrightarrow{Bact} Fe_2(SO_4)_3 + H_2O \qquad (2)$$

Enough iron(II) in the solution is available by the bacterial oxidation at ~ pH 2.0 which is oxidised to Fe(III) by *A.ferrooxidans.* In the pH range 1.5-2.5, bacterial oxidation of ferrous oxidation is about $10^5 – 10^6$ times faster than the chemical oxidation of ferrous iron (Muñoz et al. 1995). The sulphur obtained above may simultaneously be oxidized to sulphuric acid by *A.ferrooxidans*.

$$2S^o + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4 \qquad (3)$$

The role of *A.ferrooxidans* in indirect bioleaching of uranium from its ore involves oxidation of tetravalent uranium to the water-soluble hexavalent uranium:

$$UO_2 + Fe_2(SO_4)_3 \longrightarrow UO_2\,SO_4 + 2FeSO_4 \qquad (4)$$

Ferrous sulphate is reoxidised to ferric sulphate by bacteria. There is some report of *A.ferrooxidans* oxidizing U(IV) to U(VI) enzymatically (Eqn. 4) and using some of the energy of this reaction for the assimilation of CO_2 (Tuovinen 1972), but indirect mechanism is mostly accepted in the bio-recovery of uranium.

4. CONCLUSIONS

The *Acidithiobacillus ferrooxidans* from the uranium mine water samples were isolated in 9K media. In 10 days, the cell count was maximum at 6.8 x 10^7 cells/mL, which on sub-culturing attained 7.4 x 10^8 cell counts/mL. The bacteria adapted on the uranium ore when used for the bioleaching of the metal gave a maximum metal dissolution for the <45µm size particles at 1.7pH. The optimum uranium bio-recovery was found to be *96%* at 1.7pH with 10% PD at 35°C in 40 days. For the particles size of <45µm, recovery of uranium was explained with the help of redox potential (E) value monitored during the entire period. Bioleaching of uranium seems to follow the indirect mechanism of leaching with the help of Fe(III) generated by *A.ferrooxidans*.

5. ACKNOWLEDGEMENTS

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MINI PILOT PLANT CONFIRMATION OF A URANIUM ALKALINE LEACH FLOWSHEET

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CONTENTS

1. INTRODUCTION

Denison Mines Zambia Limited, a subsidiary of Denison Mines Corp (Denison), conducted a Definitive Feasibility Study (DFS) in 2008 to assess the technical and commercial viability of its Mutanga Project in Zambia.

SGS Lakefield Oretest Pty Ltd (SGS) was requested by Denison to construct and operate an integrated pilot plant to assess an alkaline leach process flowsheet option as part of the DFS.

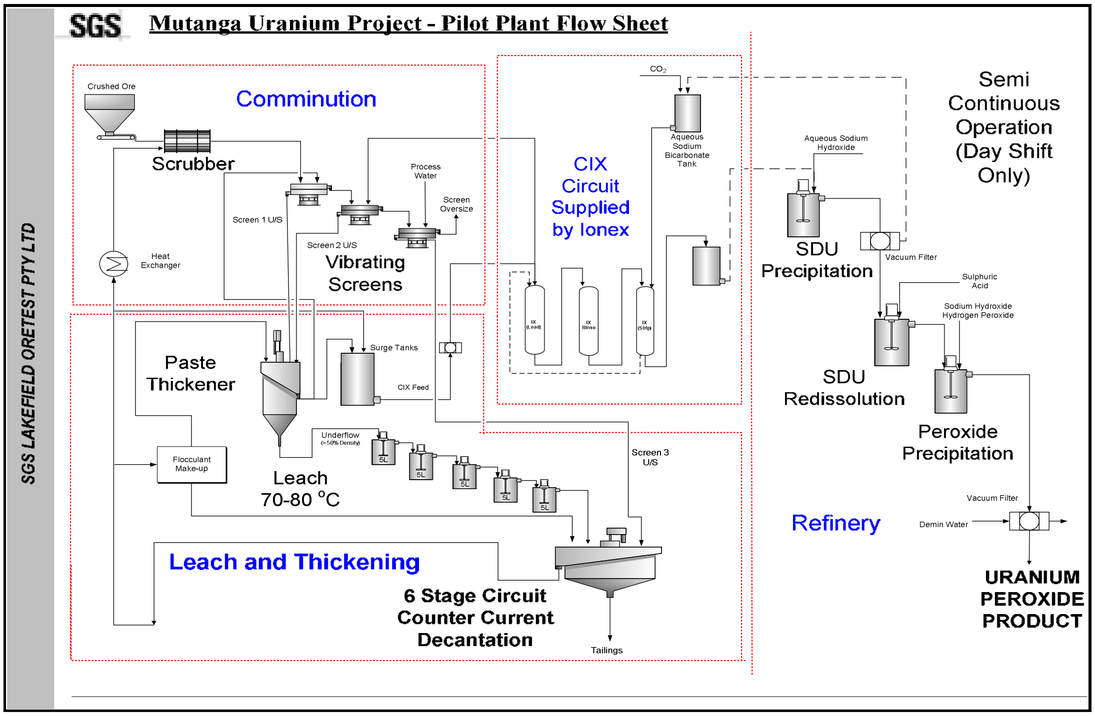
Mutanga consists of a single prospecting license covering 944 square kilometres. There are two main deposits, Mutanga and Dibwe, and a number of exploration areas. Both deposits are shallow and amenable to open pit mining

The Mutanga uranium deposit is a secondary uranium deposit with autunite (a hydrated calcium and uranium phosphate) being the primary mineral with an abundance of approximately 95 %. The autunite predominately occurs as discrete particles located along sandstone grain boundaries and is amenable to upgrading by scrubbing and screening techniques.

An intensive 47,000 metre reverse circulation and diamond drilling exploration program was conducted to characterise the mineralogy of the deposits and to provide samples for batch and pilot-plant metallurgical testwork.

The pilot plant consisted of continuous upstream leach, continuous ion exchange (CIX) and refinery circuits. The upstream circuit consisted of a rotary scrubber (also referred to as a bottle roll leach), reject screens (producing waste oversize/scats), paste thickener, leach and counter current decantation (CCD) unit operations. The CIX circuit consisted of absorption, scavenger and elution unit operations. The refinery circuit was operated on a semi-continuous basis and employed sodium di-uranate (SDU) precipitation, SDU re-dissolution, and peroxide precipitation to produce a final uranium peroxide product. The pilot plant process flowsheet is illustrated in Figure 1.

Figure 1: Mutanga Upstream and CIX Uranium Pilot Plant Overview



2. ORE SAMPLES TESTED

Denison supplied 7.8 tonnes of sample to SGS, predominantly as NQ and HQ drill core in a locked sea container. Core was designated as Mutanga Comminution, Mutanga Barren, Mutanga Core and Dibwe Core. Both Mutanga Comminution and Mutanga Barren contained less than 0.01 % U_3O_8. The masses of the core samples are given in Table 1.

Table 1: Core Samples Submitted by Denison

Ore Type	Ore Mass (kg)	Ore Mass Percentage (%)
Mutanga Barren	1262	16.2
Mutanga Comminution	738	9.5
Mutanga Core	3870	49.7
Dibwe Core	1924	24.7
Total	7793	100.0

Samples of Mutanga and Dibwe core were subjected to metallurgical testwork by SGS. Sample masses and the type of testwork conducted on them are summarised in Table 2 and Table 3, respectively.

Table 2: Mutanga Core Samples Used in Metallurgical Testwork

Testwork Performed	Ore Mass (kg)	Ore Mass Percentage (%)
Bulk Leach for Batch Ion Exchange	463	12.0
High Grade Scrub	79	2.0
Acid Leach Testwork	445	11.5
Continuous Pilot Plant Testwork	2883	74.5
Total	3870	100.0

Table 3: Dibwe Core Samples Used in Metallurgical Testwork

Testwork Performed	Ore Mass (kg)	Ore Mass Percentage (%)
Comminution	141	7.3
Acid Leach Testwork	447	23.3
Continuous Pilot Plant Testwork	1336	69.4
Total	1924	100.0

Ultimately, a total of 3.9 tonnes of dry ore was selected (taking into account free moisture and removal of feed sizing and assay samples) for the two, continuous mini pilot plant testwork with a total operating time of 744 hours. This equated to an average pilot plant feed rate of 5.2 kg/h of ore.

3. COMMINUTION BATCH TESTWORK PROGRAM

The feed ore mineralogy suggested that the ore may be amenable to beneficiation by means of scrubbing and screening and by rejecting a barren scats (oversize) fraction. A primary focus of the comminution program was to evaluate how the ore responded to scrubbing tests at different specific energy inputs. Scrubbed ore was screened into size fractions ranging from 125 mm to 0.038 mm and these products were subsequently weighed and assayed. Initial scrub tests were conducted on barren ore (provided for comminution testwork) to determine the effect of varying specific energy inputs. Once the optimum energy input was selected, a batch scrub was conducted on Mutanga core to determine the scatting rate and uranium upgrade at various screen sizes. Based on these results an initial screen size of 0.425 mm was selected for the mini pilot plant.

Unconfined compressive strength (UCS), SAG mill comminution (SMC), Bond abrasion index (BAi), Bond ball work index (BBMWi) and Bond rod mill work index (BRMWi) tests were also conducted.

4. HYDROMETALLURGY BATCH TESTWORK PROGRAM

A series of hydrometallurgical batch tests were conducted to provide critical mini pilot plant design criteria and included sighter atmospheric carbonate leach tests, flocculent screening tests on leach material and a bulk carbonate leach to generate liquor for ion exchange cycle tests.

Carbonate leach tests were conducted on both Mutanga and Dibwe material at temperatures ranging from 60°C to 90°C, at an initial Na_2CO_3 concentration of 35 g/L for duration of 8 to 12 hours. Leach extractions ranged from 84 to 87 % and 82 to 83 % for the Mutanga and Dibwe samples, respectively. Leach temperatures of 70°C gave the highest uranium extractions from both ore types. Aeration was not assessed because the deposit was a secondary uranium deposit containing oxidized uranium present as U^{6+}.

A batch leach was conducted on 400 kg of Mutanga core at a solids content of 40 % w/w, at 70 °C for 480 minutes with an initial Na_2CO_3 concentration of 35 g/L to generate liquor for the ion exchange cycle tests. Uranium in the leach liquor was concentrated by evaporating the filtered liquor by indirect steam heating to achieve a U_3O_8 concentration of 360 mg/L.

Six ion exchange cycle tests were conducted in three columns containing 250 mL of Amberjet 4400OH resin. These cycle tests were conducted to determine the maximum equilibrium loading of the resin, to identify a suitable elution treatment and to define an initial CIX flowsheet for the mini pilot plant testwork. The performance of a number of cycle tests enables the resin to equilibrate (uranium absorbed equals the uranium eluted) to levels equivalent to those achieved in the mini pilot plant and also allows the effectiveness of different intermediate stages to be trialled on equilibrated resin to optimise the eluant uranium and impurity concentrations.

Flocculent screening tests on leached material using carbonate solution as a diluent identified Magnafloc 800HP and Zetag 8140 as reagents suitable for use in the mini pilot plant paste thickener and CCD unit operations.

5. FEED PREPARATION

A challenge that had to be overcome was the the use of sodium carbonate as the scrub lixiviant prior to the removal (scatting) of oversize material by screening. It was also impractical to continuously scrub the material because of the low feed rate and because the mini pilot plant scrubber (bottle roll leach) feed chute could not accommodate the relatively large feed particle size. The challenge of re-crushing and recycling coarse material (up to 125 mm) at such low flowrates resulted in the abandonment of this processing scheme. Batch scrubbing the material in sodium carbonate solution was also abandoned due to aging of scrubbed material and excess leaching of uranium caused by exposure to sodium carbonate solution prior to being fed into the mini pilot plant.

It was subsequently decided that the material would be batch scrubbed in 50 kg lots in deionised (DI) water (as was done in the batch comminution testwork program), screened at 10 mm and 2 mm and dried at 50°C in a gas fired oven. The dried +10 mm material was stage crushed to less than 10 mm and the dried -2 mm (which contained agglomerated fines) was gently dis-agglomerated by hand to prevent the generation of further -2 mm material.

Products from each Mutanga mining year and Dibwe were blended separately and were then rotary split into 8.7 kg batches for analysis by a Scantech gamma analyser.

6. PLANT PARAMETERS

6.1. PRELIMINARY PROCESS MODELLING

Elemental Engineering (EE) used batch testwork results and scoping study information to model the proposed process flowhseet and produced a detailed mass balance of the proposed mini pilot plant. This information was used by SGS to design the mini pilot plant.

The EE model was recalibrated throughout the pilot plant campaign using actual pilot plant data.

6.2. PLANT EQUIPMENT AND PILOT PLANT SETUP

The EE mass balance was used by SGS to design and fabricate the equipment for the mini pilot plant. Ionex Pty Ltd (CIX consultants) provided the CIX unit.

Because sodium carbonate solution is non corrosive, a wide range of construction materials were suitable for fabricating pilot plant equipment items.

SGS selected a belt feeder to control the feed rate to the scrubbing circuit (bottle roll leach). The feeder was equipped with a suitable drive and belt speed control mechanism supplied by Electrical Systems Engineering Pty Ltd. Initial commisioning of the belt feeder established it could maintain consistent feed rates.

A challenge for the piloting team was the design of a mini rotary scrubber (bottle roll leach) that could accept dry feed ore as well as allowing the discrete addition of warm uranium bearing carbonate solution to produce a 60 % w/w slurry and providing 3 minutes retention time with no leaks from the feed pipe. The requisite diameter of the mini scrubber was calculated to be 70 mm. Initial tests proved unsuccessful due to difficulties encountered transferring the scrubber discharge slurry onto the primary scats reject screen and leaks from the feed pipe. A trommel was added to the scrubber discharge to promote the effective transfer of the discharge slurry onto the Kason screen. Further materials handling ehancements were realised by inclining the scrubber on a slight angle from the feed end to the discharge end.

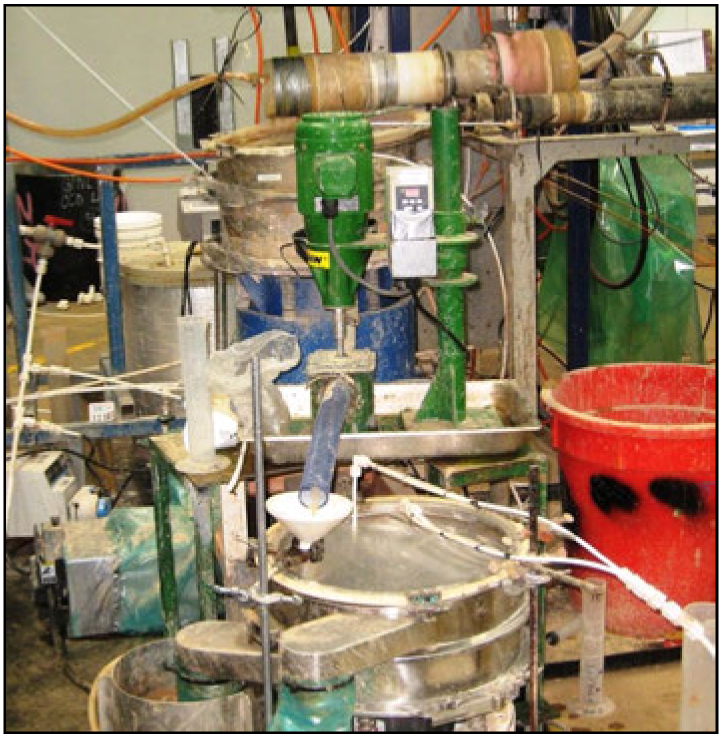
The run 1 scrubber configuration is illustrated in Figure 2.

Figure 2: Run 1 Scrubber and Kason Screen 1 Configuration

Efficient washing of pregnant leach solutions from the primary screen oversize particles in the secondary and tertiary batch screening operations was difficult because of the very low wash solution volumes dicated by the tight solution balance. After trialling various options the most effective method proved to be frequent manual spraying of the oversize using a 1 L pressure spray bottle filled with the requisite amount of wash solution.

During the second mini pilot plant trial, an attritioner was added to the Kason Screen unit operation. The successful operation of this unit was dependant on a controlled flow of material through the attritioner, correct blade orientation and wash solution addition. The attritioner is illustrated in Figure 3.

Figure 3: Pilot Plant Attritioner



The stainless steel and glass tanks used in the CIX and leach circuits were heated to pre-determined temperatures using hotplates equipped with thermocouples linked to controllers. Owing to the non corrosive nature of the slurry and liquors, stainless steel was a suitable material of construction.

The leach circuit is illustrated in Figure 4.

Figure 4: Pilot Plant Leach Circuit

A six stage counter current decantation (CCD) wash circuit was used to separate pregnant leach solution from the leach residue solids. Dilute flocculent was added to the pre-mix tank ahead of each thickener which then discharged by graviy into the thickener feed well. A portion of the thickener overflow stream (supernatant) from each thickener was pumped into the pre-mix tank of the preceeding thickener to dilute the thickener underflow solids to promote effective flocculation. Gravity was used where ever possible to reduce the number of pumps required. A challenge for the piloting team was operating this circuit with no fresh water additions for wash water or flocculent dilution/makeup whilst maintaining steady state operation and achieving the target wash ratio.

The CCD circuit is illustrated in Figure 5.

Figure 5: Pilot Plant CCD Circuit

Digital and analogue controlled peristaltic hose pumps were used throughout the mini plant because of their ability to accurately deliver low flowrates. Digital pumps were excellent for solution transfers because, once calibrated, they reliably and accurately maintained the desired process solution flowrates. Flowrate adjustments were easy to establish due to the linear nature of the pump calibrations.

7. PLANT PARAMETER MEASUREMENTS

Material transferred throughout the pilot plant was typically measured using electronic balances. The duty and standby surge tanks between each unit operation were placed on electronic balances so that material flowing into and out of each unit was measured accurately. All plant balances were connected to a data logger that recorded load cell readings every minute. Information for all units was also manually captured on logsheets on a routine basis.

By the the end of the piloting campaign there were approximately 100 feed, recycle and reagent streams throughout the mini pilot plant. Whilst the flowrates of major input and output streams from each unit operation were recorded by the data logged balances, stream data was also determined by performing manual measurements. Typically the volumetric flows were measured using a calibrated measuring cylinder and a stopwatch. These measurements were conducted every two hours.

Other manually recorded data included pH, Eh and slurry specific gravity measurements. Slurry specific gravity measurements were converted to a solids content using previously determined solid and liquor specific gravity results that were tabulated to facilitate conversion by the operators. These measurements provided immediate feedback for individual unit operations particularly the CCD and paste thickener circuits where underflow and feed solids contents were critical to stable operations.

8. PILOT PLANT ASSAY SAMPLE SIZES

A large proporton of the mini pilot plant liquor inventory was continuously recirculated between individual unit operations or across different circuits. Approximately 1 L/h of process liquor was entering or exiting the pilot plant at any one time; consequently the sample aliquots and sampling frequencies had to be minimised to maintain the plant liquor inventory. This enabled plant data to be collected whilst not compromising steady state operation. Mass balance and profile samples were collected at discrete locations and timed to minimise circuit inventory depletion.

9. PILOT PLANT ANALYTICAL TECHNIQUES

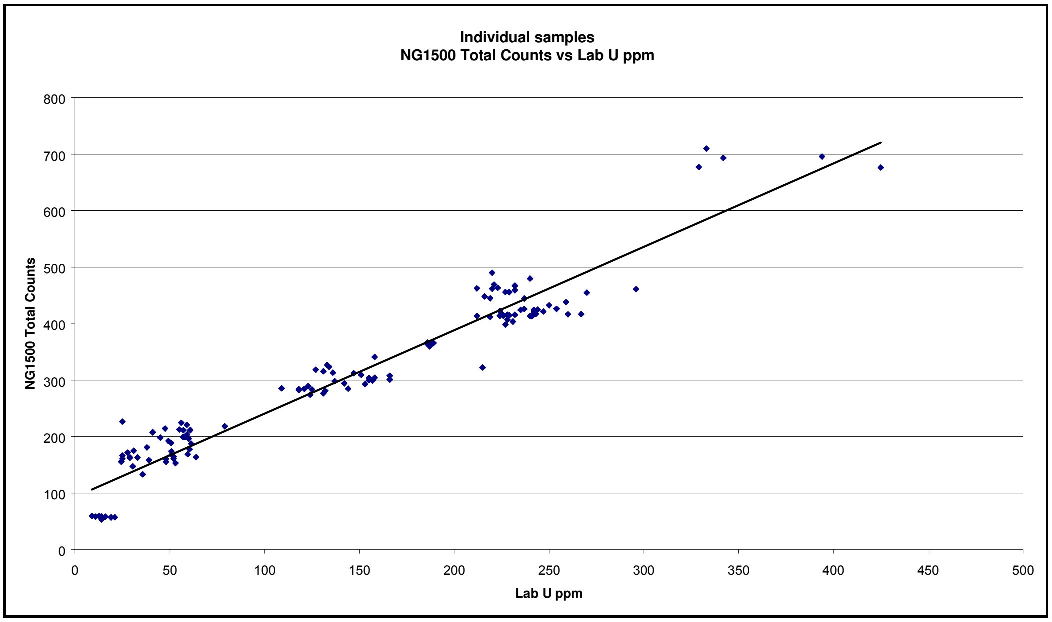
The SGS in-house sample preparation and analytical laboratory achieved fast turn around times and produced accurate assay results (liquor and solid turnaround times of 2 and 6 hours respectively) for process control and mass balancing purposes. The instruments used for the analysis of solids and liquors were Perkin Elmer ICP MS and ICP OES analysers. The ICP MS was used for accurately assaying for uranium, thorium and molybdenum. Conventional titration methods were used to determine chloride and total alkalinity. These methods were further optimised to obtain accurate results using reduced aliquot volumes. The accuracy of these modified methods was confirmed prior to piloting.

An Outotec Courier XRF onstream solution analyser was installed on the mini pilot plant to assess it’s suitability for a continuous onstream analysis duty in a full scale plant. The onstream XRF unit also provided a non destructive analytical technique that was useful for profiling the CIX unit.

10. ANALYTICAL TECHNIQUE AND SGS QUALITY CONTROL COMPARISONS

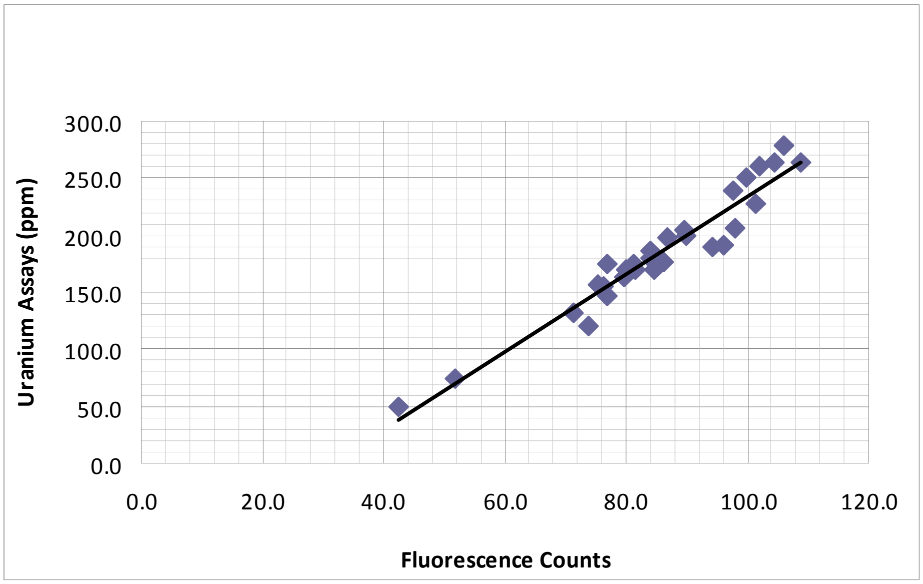
Before and after piloting, a number of the 8.7 kg feed and scat (reject solids) samples were analysed using a lab scale Scantech Analyser to determine its suitability for use in uranium ore feed grade monitoring. The analyser consisted of a sample bucket which held 6 L of sample and a gamma ray detector which was surrounded by the sample during analysis. The analyser was contained within a lead shield to remove any background radiation effects. The natural gamma radiation from each sample was determined over a 30 minutes period. The natural gamma reading results provided a correlation of 0.99 against uranium assays and is presented graphically in Figure 6.

Figure 6: Scantech Gamma Ray and Uranium Assay Comparison



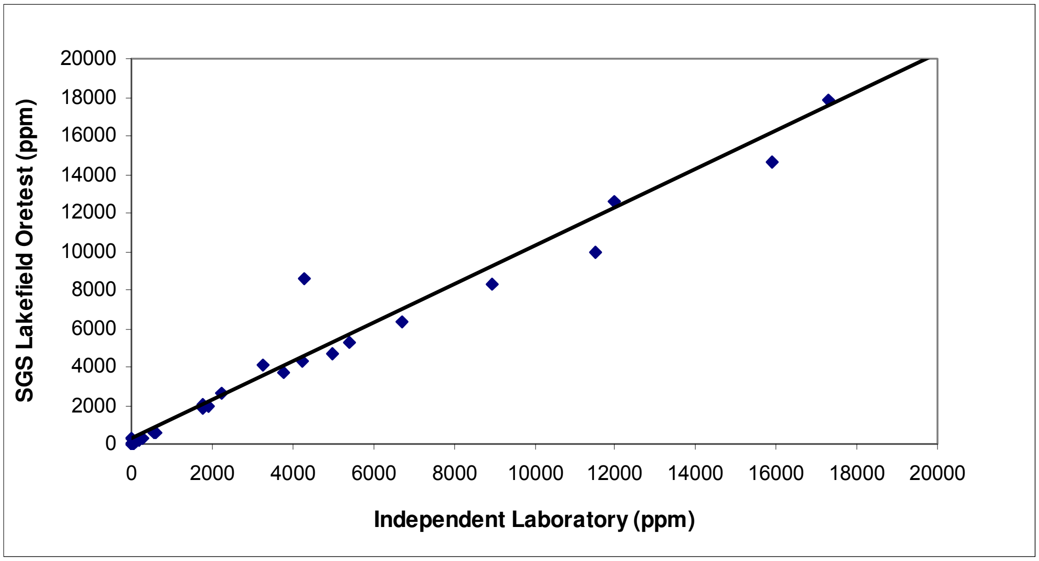
Solution samples destined for XRF analysis were split into two fractions, one for ICP and the other for XRF analysis. This ensured that the same solution was being analysed by both instruments. Uranium assays determined by ICP are compared to fluorescence counts from the Courier XRF in Figure 7.

Figure 7: Outotec Courier XRF Fluorescence Counts versus Laboratory Uranium Assays



Qulity control check assays were conducted on profile and mass balance solid and liquor samples. This allowed the in-house analyses to be confirmed and analytical techniques to be refined to minimise measurement uncertainty. A uranium liquor correlation of 0.99 was achieved and is presented in Figure 8.

Figure 8: Liquor Uranium Analytical Quality Control Comparison



11. LIQUOR BALANCE CHALLENGES AND EVAPORATION

As previosuly mentioned, approximately 1 L/h of process liquor entered and exited the pilot plant at any one time with the majority re-circulating throughout and between the individual unit operations. This presented SGS with the challenge of maintaining a large circuit liquor inventory and ensuring that the CIX circuit had sufficient liquor to maintain a continuous operation.

This balance was achieved by using designated surge and reagent monitoring and rigourous flow control. Two full inventory evaluations were performed on a daily basis to determine the liquor losses for every 12 hour period. The shift metallurgist was responsible for maintaining this balance as well as ensuring reagent stocks were prepared (these were dissolved and diluted with plant liquor).

SGS, used its proprietary metallurgical accounting data base system to capture all liquor inputs and outputs including outputs from sampling/assaying. This allowed the piloting team to monitor and control liquor losses. Areas within the flowsheet identified as sources of liquor losses were the Kason screens where relatively high volumes of pregnant plant liquor were used to wash uranium bearing clay particles off the oversize (waste/scats) material. Screen covers were subsequently installed to minimise mist losses.

Evaporation losses were also identified as a source of liquor loss and DI water additions were strategically added to maintain the overall circuit tenor concentrations. Pre-piloting, evaporation tests were conducted on heated sections of the pilot plant to enable DI water additions to be calculated. During the piloting campaign DI water additions were further refined by tracking sodium tenor increases and decreases throughout individual unit operations on a day to day basis.

12. MINIMISING SODIUM LOSSES THROUGHOUT THE PILOT PLANT

Sodium and, to a lesser extent, uranium losses occuring as a consequence of operator measurements, handling of pilot plant material or maintenance of pilot plant equipment were evident early in the mini pilot plant campaign. The majority of liquor streams contained high levels of sodium based reagents which is a major cost in running a uranium alkaline leach system.

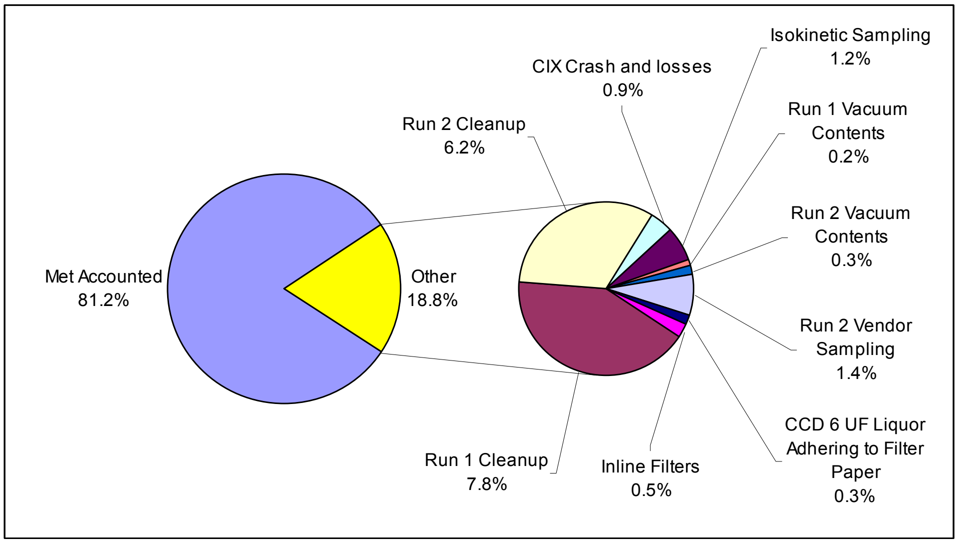
Owing to the small scale of the operation this was identified as a significant issue prior to piloting and to ensure complete containment of the circuit HDPE bunds were placed under each unit operation. The overall pilot plant area was also encompassed by a concrete bund with spoon drains which were linked to a central collection sump.

An overall sodium and uranium balance capturing the pilot plant input and output streams was developed during the first piloting run to effectively track these losses. This was monitored on a daily basis together with the solution balance. A more detailed mass balance was also conducted on specific unit operations to determine where sodium losses were most prevalent.

Actions taken during the piloting campaign to minimise sodium and uranium losses included washing of operator gloves prior to disposal and collection of all washings into bulki boxes. This also enabled washings from specific mass balance periods to be separated and accurately measured. Reduction of screen sizes from 0.425 mm to 0.212 mm in the Kason screen unit operation reduced the sand fraction thereby reducing downstream pump hose wear, thickener blockages and pilot plant materials handling issues. The addition of screen covers also significantly reduced process mist liquor losses in the screening area.

At the conclusion of each run, pilot plant equipment and bunds were carefully cleaned and all washings were captured and assayed. Overall, for the campaign, 96.5% of the sodium and 102.2% of the uranium were accounted for. Sodium deportment at the completion of the pilot plant campaign is illustrated in Figure 9.

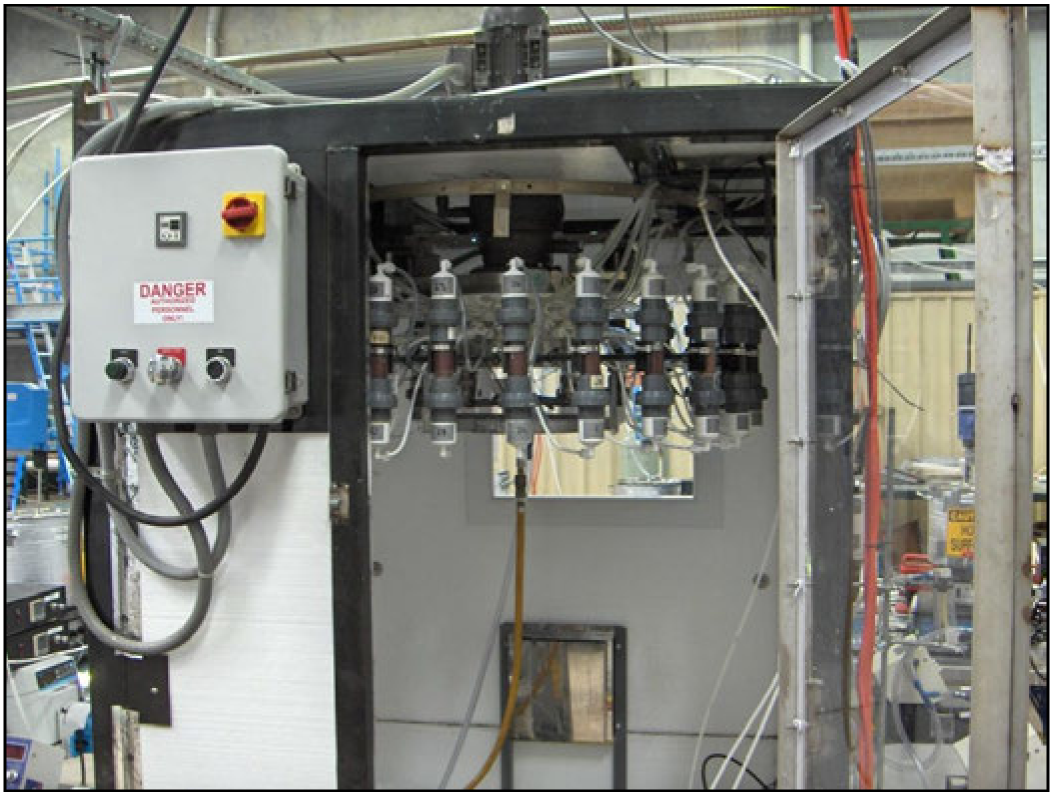
Figure 9: Sodium Deportment throughout Piloting Campaign



13. URANIUM REFINING VIA CIX

A CIX pilot unit was used to produce an eluant suitable for downstream uranium precipitation. The pilot plant consisted of 24 identical ion-exchange columns attached to a rotating carousel. The columns were connected, both inlet and outlet, to a rotating valve that sequenced them through 24 steps. Each column was filled with Amberjet 4400OH resin that had been conditioned with sodium carbonate solution prior to piloting. The circuit consisted primarily of absorption and elution zones with various intermediate conditioning and rinse zones. SGS supervised the overall operation of the ion exchange plant. Consultants provided advice and assitance with specific operational issues and assisted with optimising the CIX circuit performance. The setup of the columns in the CIX unit is illustrated in Figure 10.

Figure 10: CIX Piloting Unit



The CIX piloting unit was situated in a heated enclosure with operator access achieved by means of door. Windows allowed the process to be monitored externally. The CIX unit enclosure was maintained at approximately 50^{o}C.

Sodium bicarbonate was selected as the eluant and a final uranium concentration of 8.5 g/L was targeted. This was generally exceeded during steady state operation of the CIX unit. Through various circuit configuration changes during the piloting campaign a final eluant elemental analysis achieved when processing of the Dibwe ore is provided in Table 4.

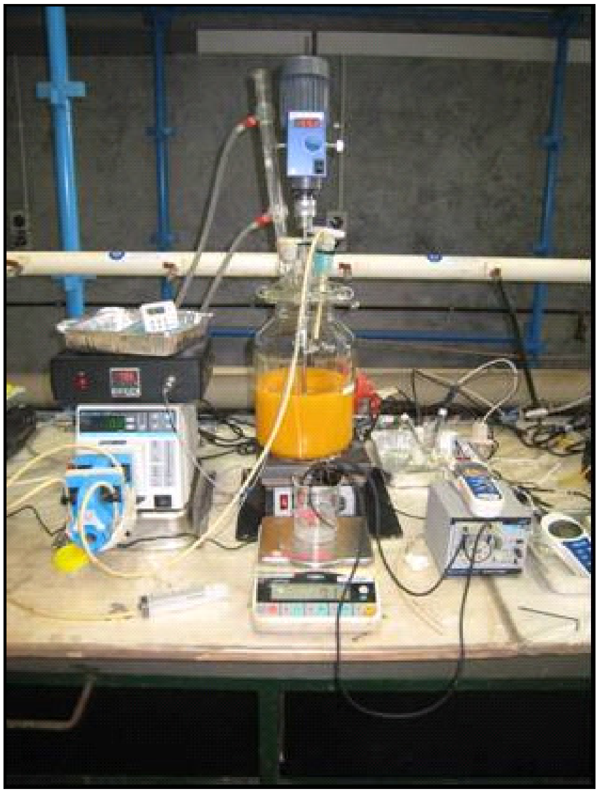
Table 4: Mass Balance 16 Final Eluant Concentrations, mg/L

U	Na	Mg	Al	Ca	P	V	Mo	Si	Th	S(t)	Cl-
13500	49690	1.24	1.00	0.10	57.1	1.5	5.18	19.6	0.005	1082	232

14. URANIUM PRECIPITATION CIRCUITS

Sodium Diuranate ($Na_2U_2O_7{\cdot}7H_2O$) was precipitated from the eluate solution at 80ºC in a 5 L agitated vessel equipped with a condenser. Seed recycle was used to promote precipitate growth. Initial stoichiometric amounts of sodium hydroxide (NaOH), barren solution and seed were mixed and heated. Once at temperature, NaOH and concentrated eluate were introduced over the required reaction period. The SDU precipitation circuit is illustrated in Figure 11.

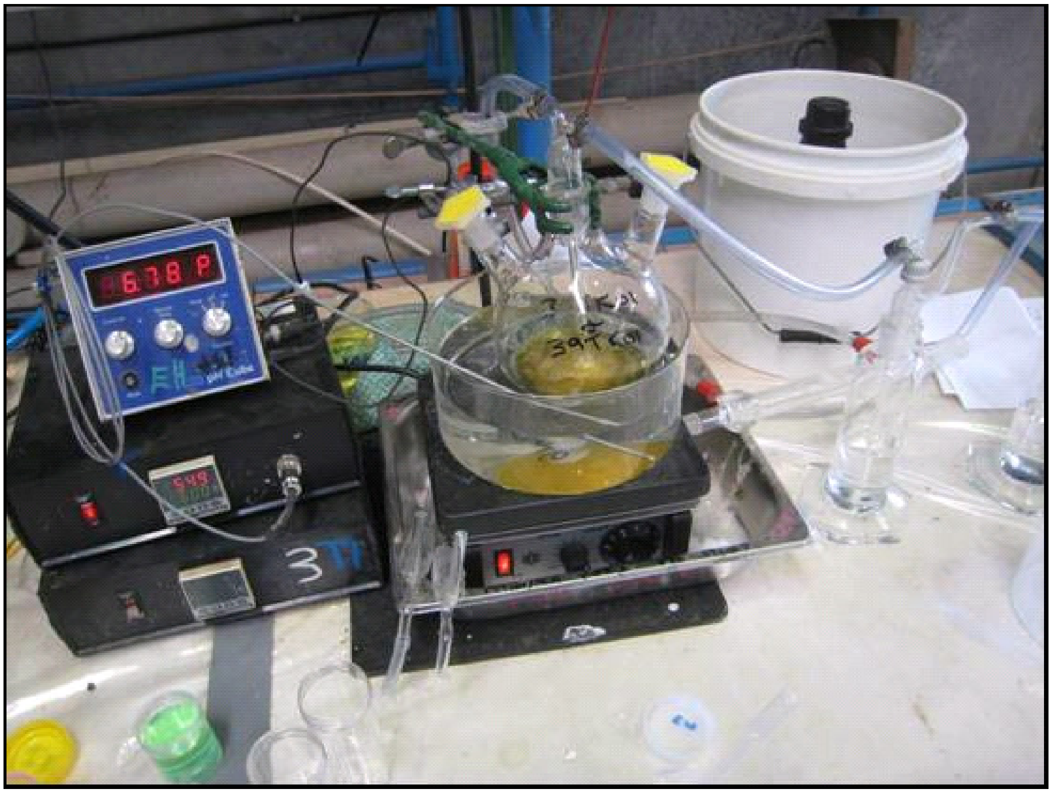
Figure 11: SDU Precipitation Circuit



SDU redissolution and peroxide precipitation to produce a final UO_4 product was conducted in an appropriately sized round-bottom flask agitated by a magnetic stirrer. The SDU redissolution circuit was also equipped with a nitrogen sparger and 2 Dreschel bottles acting as carbon dioxide scrubbers. The slurry was maintained at temperature and acidified with sulfuric acid. The system was sparged with nitrogen which acted as a carrier gas to transport evolved carbon dioxide through the two scrubber vessels. The resulting solution containing uranyl sulfate was then advanced to the peroxide precipitation stage.

The SDU re-dissolution circuit is illustrated in Figure 12.

Figure 12: SDU Redissolution Circuit



The carrier gas and carbon dioxide scrubbers were removed and substituted with pH and Eh probes prior to performing peroxide precipitation. The final uranium pentoxide (UO_4) product was then precipitated by the additions of sodium hydroxide and hydrogen peroxide to maintain a target pH range. UO_4 precipitation is illustrated in Figure 13.

Figure 13: UO4 precipitation with ORP and pH probes in the reaction vessel

The typical SDU and UO_4 product analyses are detailed in Table 5.

Table 5: Typical SDU and UO_4 Solids Composition Data, %

Product	U	Na	P	V	Si	Th	S(t)	Cl	C(t)
SDU	67.1	7.74	0.072	0.080	0.237	0.0001	0.01	0.01	0.28
UO_4	67.9	0.056	0.010	0.087	0.010	0.0000	0.09	0.03	0.01

15. PERSONNEL SAFETY CONSIDERATIONS

Before continuous testwork commenced a design review and Formal Risk Assessment (RA) was conducted with relevant recommendation implemented for the continuous testwork programme. Although the RA concluded that radiation exposure levels would be low during the piloting, SGS mandated the wearing of thermoluminescent device (TLD) badges for all operators, sample preparation and laboratory staff as a precautionary measure in accordance with world's best practice. Daily radiation readings were also conducted throughout each area of the plant with most areas giving readings only slightly above background levels. The refinery area exhibited the highest radiation readings; however, based on exposure times and measured dose rates, the refinery operator received a radiation dose well below the maximum stipulated by the Western Australian Radiological Council. This area was restricted to the refinery operator and, occassionally, the client and SGS management. Owing to the use of concentrated caustic solution, the refinery operator as well as any visitors to the area were oblidged to wear extra PPE.

Extraction hoods were installed above the leach and bottle roll leach circuits primarily to remove any steam generated by heating the slurries throughout the pilot plant and to provide extra ventilation.

External consultants were engaged to sample ambient air using personal and fixed samplers, to test for uranium levels. Exposure levels were found to be well under those designated harmful by the Western Australian Radiological Council.

16. ACKNOWLEDGMENTS

The assistance provided by Denison and its consultants during the testwork campaign is gratefully acknowledged.

Grenvil Dunn of Hydromet Pty Ltd was the Denison client representative assisted by John Vagenas of Elemental Engineering. Denison employed Ionex Pty Ltd representative Gordon Rossiter to assist with operation and optimisation of the CIX process along with Warwick Dainton from Outotec to optimise XRF operation and conduct required maintenance. Mike Adams of Mutis Liber Pty Ltd and John Turner of SGS formed part of the SGS team and assisted in the metallurgical and operational aspects of the project.

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Study on the solid liquid separation equipment in Uranium processing

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ABSTRACT

Uranium circuits have a variety of hydrometallurgical concentration processes all containing solid liquid separation processes. Some of the successful operations can be reviewed to understand which technologies are most effective.

In Uranium processing solid liquid separation represents a large portion of the CAPEX involved. The majority of research and process design focuses on metal recovery. Solid liquid separation performance, like metal recovery is defined by the process conditions and the optimum conditions are often vastly different.

In the never ending pursuit of reducing CAPEX the logical point to study is the larger cost areas. Where solid liquid separation costs are high optimising process conditions may provide benefits. To help separation in most proposed flow sheets it is worth looking at the logic behind the selection of equipment and possible new technologies that may offer improved solutions.

Keywords: Pressure filtration, Vacuum Filtration, Cake filtration, Dewatering, Solid liquid separation,

Background

Uranium processing is considerably different to most mineral processing industries. In some ways it can be considered to be a relatively recent mineral processing field with the first plants being developed in the 40,s and little development after the 80,s. To date there has been enormous variation in the types of flow sheets developed utilising either acidic leaching or Alkaline leaching techniques.

While essentially a leach process Uranium processing is often associated with multiple solid liquid separations in part due to the requirement to minimise Uranium in waste streams. Whenever agitated leach processes are involved these equate to large volumes and sometimes difficult separations. As varied as the processes themselves the technologies utilised in solid liquid separation are sometimes vastly different.

Solid liquid separation principals.

Whether it is thickening or filtration the fundamentals of equipment sizing are based on the slurry characteristics principally particle size and liquid viscosity. For filtration a simple form of the Darcy equation (1) shows the interdependence of pressure, viscosity and cake resistance. Cake resistance is a function of the cake thickness and the resistance to flow through the pores in the cake, which are determined by the particle size and shape. For thickening (2) the driving force is gravity, viscosity has the same relationship and particle diameter determines the rate

$$Q = \frac{A\Delta p}{\mu\ (R_m + R_c)} \qquad (1) \qquad Q = \frac{KAd^2(\rho_s - \rho_l)g}{\mu} \qquad (2)$$

In the primary separation of pregnant leach solution from gangue or leach residues mineralogy determines the particle size or filterability. The principal process drivers are particle size and shape with the major effect coming from the finest 20% of the solids to be separated from the solution. This effect is most pronounced where there is a wide distribution of particle sizes or where clays are present. Hence the grind size required for liberation, the technology employed to achieve size reduction and solids attrition during leaching define the slurry filterability or rate of thickening. Solids attrition can be significant with a 2 to 5 fold increase in the sub 20µm fraction not uncommon when comparing pre-leach and post leach particle size analysis's.

When there is a wide distribution of particle sizes the finer fraction can migrate through the filter cake forming a layer of the finest material at the separation interface. The behaviour of the whole separation is then defined by the most difficult portion of the slurry. When slurries demonstrating these behaviours are encountered coagulants and flocculants can be beneficial in preventing fines migration often showing significant improvements filterability.

The relative difference between separation technologies is that Filtration has a significantly higher sensitivity to fines than gravity separation technologies. This tends to dictate that high levels of fine fractions favour CCD circuits, and this is enhanced by the better flocculation possibilities of thickening.

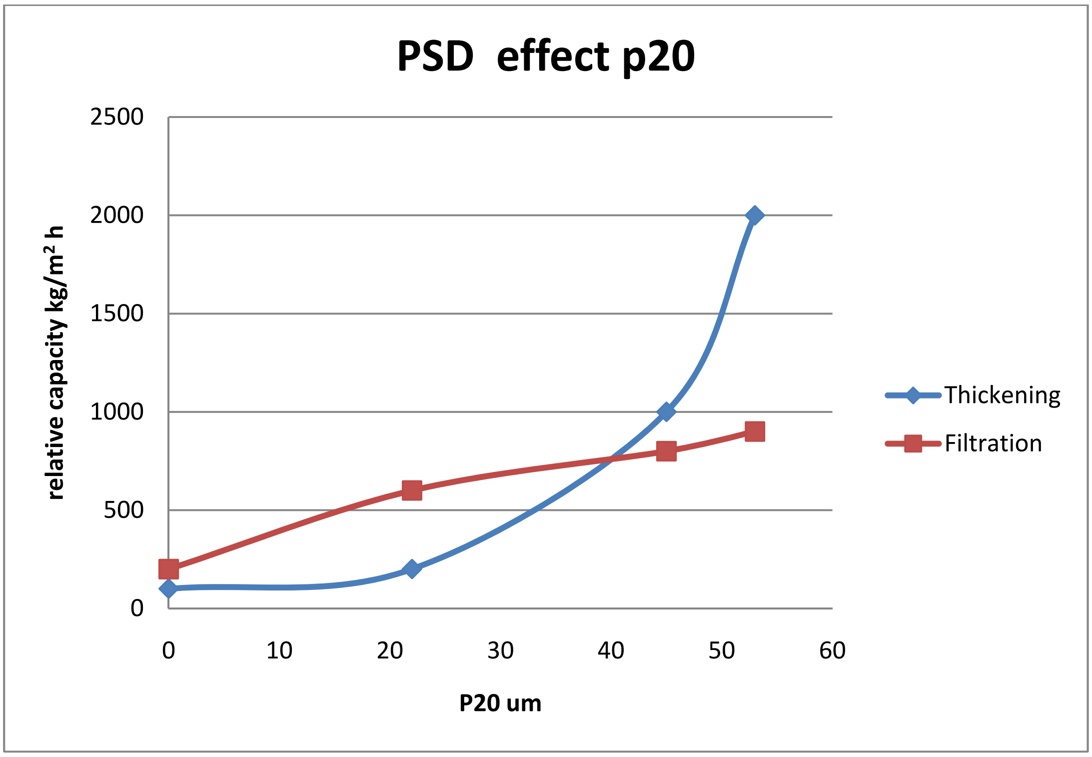
Filtration technologies are best suited to tighter size distributions and slurries with a lower fraction of sub 20 µm material. This low sensitivity can be best understood by looking at the separation that takes place during filtration. To achieve good washing results or dry cakes it is necessary not only to form a cake but also to displace the liquid from the pores in the cake by using gas flow displacement. At small diameters the liquid in the pores is affected by surface tension at the gas liquid interface and a certain pressure is required to overcome the capillary forces.

When considering gas flow displacement then the relative permeability models of Lloyd and Dobbs [1972] can be applied. This model can be used to predict the threshold pressure required for airflow.

$$P_b = \frac{4.6\ (1-\varepsilon)\ \sigma}{\varepsilon\ x}$$

Putting this relationship into context for vacuum filters to be effective for dewatering of leach residues with a typical void fraction of 50% and differential pressure of 0.8 Bar, vacuum filter possibilities should extend to a mean particle size in the range of 25µm to 30µm.

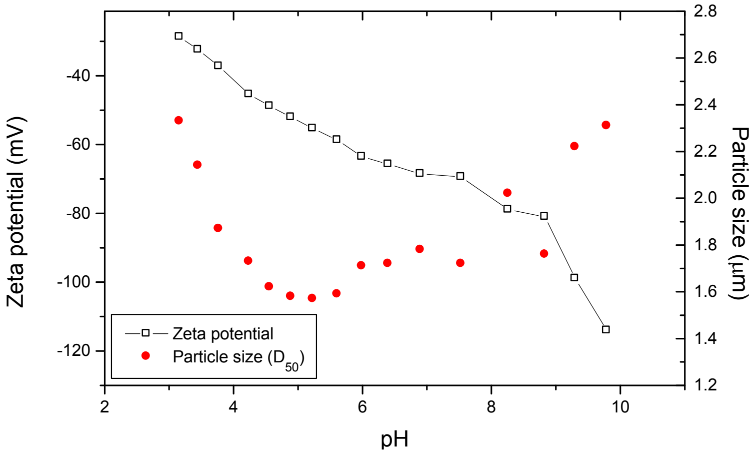
Pressure filters remain a possibility for dewatering difficult slurries and here with a similar void fraction of 50% and differential pressure of 10 Bar, pressure filter possibilities should extend to a mean particle size in the range of 2.5µm.



Operationally coagulants and flocculants can significantly reduce the equipment CAPEX by significantly reducing the separation equipment size, all be it at the expense of an slight increase in OPEX from the cost of reagents.

Flocculation effectiveness can vary with changes in ore type or with process upsets and under these conditions the separation equipment sized for the increased separation rates may be inadequate and emergency storage should be considered. Reagent dosing control systems can considerably improve performance and are much less prone to process upsets than manually controlled systems.

Clays are present in many of the ores hosting uranium and they can present more difficulties than just their fine size. Shape and surface chemistry have a large influence on how the particles pack in the filter cake and the apparent filtration resistance can be significantly worse than that predicted from size alone. (Graph 2 Si zeta potential) In Alkaline leach circuits the zeta potential of clays can be highly negative causing poor filterability without coagulants. In Acidic circuits the zeta potential is closer to zero improving filterability but there is a high risk for Alumino-Silicate based clay minerals to form gels. Under high intensity acid leaching the formation of these gels and amorphous Al-Si precipitates will blind filter media making filtration an unacceptable option and dictating CCD washing as the best process option. Even with CCD circuits colloidal silicate gels will report to the solution overflow and may create upsets in downstream SX circuits. Pre leach separation of clays or split processing routes should be investigated in ores containing high clay levels.



Currently trends are to treat the leach residue as a single stream to simplify the process route, however many of the earlier plants utilised de-slimeing and sand removal circuits to great success.

The following process solutions have been used

North American sandstone hosted ores with alkaline leach used 2 or 3 stage filtration with CC repulping and washing, drum filters were the principal technology.

Southern African installations often utilise HVB filters with multiple CC washing stages

Acid leach processes such as Olympic dam operate CCD circuits with variations from 4 to 8 stages reported.

Water balance

As with most leach processes solid liquid separation alone fails to achieve a complete separation between solids and the liquid, where the solution contains the product this leads to product losses and washing is required. When considering washing technologies it is necessary to establish a balance between product recovery, wash water consumption and solution concentration. Selecting the best technology to optimise the water consumption or maximise the PLS concentration has no hard and fast rules. Following are some simple guidelines.

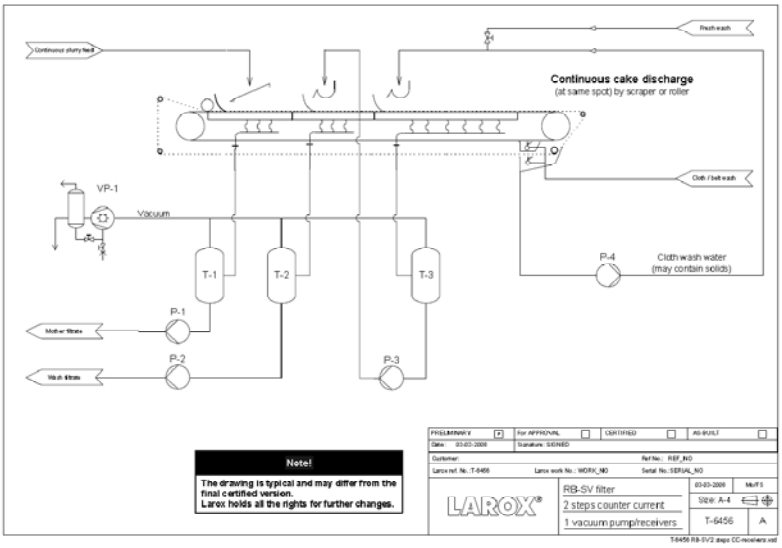
Filtration with inter-stage repulped CC washing

For very easily dewatered slurries where cake moistures below 10% can be achieved repulp washing begins to be the technology that requires the lowest water consumption. Theoretically 2 stage CC washing requires 10 x the cake liquid content which reduces to 4 x the cake liquid content with 3 stages CC.

In practise for slurries this easy to dewater they may contain a large fraction of particles with a size over 500µm and sanding can becomes a problem, this requires either a sand removal circuit or filtration with horizontal surfaces and HVBF or top feed drum filters are the best choice. Drum filters are something of a forgotten technology whereas HVB filters have developed significantly is size and reliability and with the added benefit of belt washing would be the preferable technology today.

Filtration with integrated washing

Filtration systems with Counter current washing can deliver lower wash water consumption and higher PLS concentrations than Co current washing systems however larger equipment will be required to achieve similar wash efficiencies. On relatively easily dewatering ores and HVB filters wash ratios of 0.5 to 0.8 m^3/t can achieve 99% pregnant solution recovery. Stage efficiencies are typically 75 to 95% and 2 to 3 stage CC is the normal practise.



Cake washing is not a pure displacement wash as there is some mixing and bypassing within the cake. Typical washing results from the lab indicate that washing can be modelled with a dispersion wash model. Dispersion numbers in the range of 1 to 5 are typical.

While washing is effective the most effective component of filtration washing is gas displacement of the remaining liquid from the cake. Where pore sizes are large up to 80% of the remaining liquid can be removed. Once there is a substantial portion of sub 10µm material present gas can no longer enter the cake under vacuum filtration conditions and washing results can be poor.

When the leach residue is desilmed with a low portion of sub 40µm material and low cake moistures can be achieved and filtration capacities in the range of 1000kg/m^3 h to 5000 kg/m^2 h are achievable.

Where there is a large portion of clays or the particle size is small the filterability decreases rapidly and thickening becomes a more attractive technology. Under these conditions the filtration rate may fall to below 100 kg/m^2 h

CCD thickener washing

As particle size and filterability decreases CCD circuits become more attractive as the solid liquid separation solution. CCD circuits have the added benefit of low maintenance and operations involvement and recent developments in control have simplified their operation. Where good separation between solids and liquids is achievable on whole ore leach residues and underflow densities of 60% or above are achievable then 99% wash efficiencies can be achieved with wash ratios of 1.2 m^3/t in seven stages. In practise wash ratios of 1 to 2.5 m^3/t have been reported.

Washing with barren liquor or electrolyte may be necessary to prevent uranium precipitation or adsorption to clays. Overflow clarity can vary and depending upon the downstream process option clarification may be necessary.

In cases with ultra fine solids or high clay loadings the achievable separation can be reduced to 40% w/w underflow densities and wash ratios may increase to over 3m^3/t.

In process with a coarse or sandy slurry screening or de sanding cyclones may be required to prevent blockages in the CCD circuit.

Settling rates of thickeners are less affected by changes in particle size than filters ad capacities may vary in the range of 0.2 t/m^2 h to 1.0 t/m^2 h.

Testing and process modelling

To date there have not been any process models that allow accurate modelling of solid liquid separation without testing as the primary input. Process modelling is however quite useful for analysing and interpretation of test data.

Whenever planning a testing campaign for solid liquid separation flocculant screening and classification should be optimised before separation testing.

S/L separation testing from a manufacturer’s perspective

Larox undertakes hundreds of testing campaigns every year, many of which relate to known process where the objective is just to establish the required equipment sizing and confirm process performance, some like the washing of leach residue are complex and can easily be given too narrow a focus and may not always determine the optimum solution and tend to just quantify the presumed technical solution. Whenever practical it can be advantageous to take a step back and review the options in light of the consequences to the overall process.

- What is the purpose of solid liquid separation in this process?
    - To produce dry solids?, To recover valuable liquid?, To remove contaminants?
- What are the upstream and downstream operations?
- How does filter performance affect the overall process?
- Acceptable range of filter performance?
    - Filter cake moisture? Cake washing efficiency? Filtrate clarity?

- Whenever possible the slurry and process requirements should be well defined and the sample representative of the entire reserves.
- Solids composition
- Particle size distribution and Particle shape are difficult to define, screen sizing does not characterise the sub 40µm faction which has the greatest influence on S/L separation.
- Grade / size sensitivity, what happens when everything is not running perfectly? When solid liquid separation is applied to the entire process stream not just a concentrated product temporary storage may not be an option and process flexibility may have to be designed into the proposed solution.
- Feed slurry solids concentration can substantially effect flocculant effectiveness
- Feed slurry temperature, Liquid viscosity – effects of temperature and composition can have significant effects to S/L separation equipment performance
- Corrosion potential – suitable materials
- Health, safety and environmental
-

The amount of material required to conduct a filtration test campaign depends on the equipment size and the number of tests conducted. The smallest equipment size commonly used today requires a minimum of 2 kg of material for a vacuum filtration test. At this scale, the filtration rate and cake properties can be established with reasonable accuracy. Vacuum filter tests are generally accurate, as a larger area can be used for the same cake weight. Vacuum filter tests are generally conducted using a Buchner funnel with an area of 0.01 m^2 to simulate horizontal belt filters, or a dip test disc with an area of 0.01 m^2 to simulate disc or drum filters.

Data Collection

Data collection techniques are quite mature, and test scale equipment has generally better measurement systems than some full scale process equipment.

Slurry properties

Solids density, liquid density, viscosity, temperature, specific surface area and particle size are parameters that affect filtration performance and can all be accurately defined ***prior*** to filtration testing.

Cake properties

Weight, density, void fraction, moisture and thickness are required to quantify filtration performance and can all be accurately determined ***after*** filtration tests.

Time dependent variables

While physical properties can be easily measured, some parameters such as filtrate volume, for example, vary with time during filtration testing. Improved analysis and reduced testing can be achieved when these parameters are measured and recorded electronically. Time dependent variables include filtrate volume, cake thickness, drying air flow, vacuum (thinned air) flow, wash water, filtrate concentration and pressure

Equipment design

While health and safety are an important consideration whenever designing equipment the Uranium industry adds an additional layer of complexity to delivering the best solution. Technologies that minimise the need for maintenance or contain the process solutions to limit exposure have added benefits.

Solution polishing prior to extraction

Extraction processes requiring clear solutions have utilised several technologies with varying degrees of success. Some of the reported equipment include

Depth filters including Sand, multimedia and activated carbon filters

Pre-coat filters including pressure leaf, rotary or tubular with DE, perlite or cellulose as a pre-coat

Pin bed clarifiers and fabric media depth filtration are recent developments that may provide reliable polishing of PLS streams.

The performance of CCD circuits and filters vary and it is possible to improve the performance of both but it can be expected that the solution prior to polishing will contain 150 to 300 ppm of solids. In addition process upsets or filter cloth failure can results in spikes of poor solution clarity 10x that level. In solution polishing the solids capture with filtration does not provide a major challenge as filtrate clarities of 20ppm are readily achievable. Systems should be designed to handle the occasional high solids loading. Systems with 3 or more units will allow 1 unit to be offline for cleaning/backwash without the need of large storage and is normally the preferred solution.

The biggest challenge for solution purification equipment is media blinding. In acid leach systems high levels of Calcium and Iron tend to form precipitates that blind the cloth, metal hydroxides are often slimy and are difficult to clean. Al/Si gels where present are extremely difficult to manage and high solids loading require efficient and sometimes vigorous cleaning strategies.

PLS ponds provide some benefits by buffering peak solids loading but also provide an additional source of contaminate to remove from the solution. Where precipitation blinding is the dominant cause of media blinding seed recycle or other measures to promote precipitation in the pond should be considered. PLS solutions also cool in ponds and should be re heated prior to filtration.

Where blinding or slimy precipitates are an issue pre-coat filters can be easier to operate as the blinding tends to occur on the pre-coat and is discharge with the cleaning cycle. With all polishing filters media selection is important to achieve the best results and any process where blinding is anticipated should have a CIP circuit and cleaning chemical strategy in place.

Product precipitate dewatering.

Uranate, hydroxide or oxide the form of the final product is as varied as the process routes. Hydroxides and ADU are difficult to dewater. The solids can tend to be fine and slimy, on vacuum filters they have a tendency to shrink after cake formation and cracks develop inhibiting further drying by gas displacement. Pressure filters can achieve better results but still struggle to provide cake moisture of around 30% achievable, they can offer good cake washing. There are good results reported with horizontal centrifuges with cake moistures down to 25% w/w, they can suffer from poor centrate quality and require a solids recycle to prevent product losses.

Better performance in dewatering can be effected by improvements in precipitation and thickening. Seed recycle and multi stage precipitation tends to produce larger precipitate sizes that are easier to filter and a 2 stage CCD washing/thickening prior to dewatering reduces viscosity and removes slimes.

SDU precipitates by comparison are relatively easy to dewater and on larger scale processes excellent results have been achieved with pressure filtration. Cake moistures down to 10% w/w with high wash efficiencies are achievable.

On projects with design capacities of 2000 t/a the product moisture is of relatively low consequence but as the scale of operation increases drying costs increase and can be considerable.

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“REAGENTS, A KEY DRIVER IN YOUR URANIUM BUSINESS”

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CONTENTS

1. INTRODUCTION

Uranium in recent years has emerged from the doldrums of more than 25 years of depression in which the industry has found itself since the 1980's. Currently there are about 430 nuclear reactors in operation and 56 new reactors under construction. Many more are planned in the next two decades, especially in China and India. Concerns that primary production of Uranium will not keep up with the increasing demand has resulted in Uranium Oxide prices increasing fivefold during the last 8 years.

This market development has resulted in an increased activity for Uranium exploration and new mines. Globally, a number of projects are in various stages of feasibility and development.

Uranium, pending its valence condition, can be extracted either in high or low pH regimes. Most of the existing Uranium mines use Sulphuric Acid to leach the Uranium bearing ore. There are however, well-established operations that use alkaline leaching technology. In 2007, Paladin Energy commissioned Langer Heinrich Uranium in Namibia.

In this paper, the Namibian Uranium mining industry including its current developments is presented as reference cases. However many of the issues will be relevant to other Uranium production operations elsewhere.

2. ACID LEACH OPERATIONS

As an example, the existing and developing acid leach operations in Namibia are typically looking at acid consumptions of 15kg/t to 25kg/t, depending on the carbonate content of the ores. Uranium grades for these operations range from 200ppm to 500ppm, with an overall uranium recovery of about 85% average. From the table below, it can be seen that unit costs of sulphuric acid per pound of uranium range anywhere between USD$2.36/lb and USD$ 9.85/lb, depending grade and consumption rates. These costs are based on a landed cost of acid on site for USD$150-00/t

The table below provides Acid Cost in USD/lb U_3O_8 for various Uranium grades and Acid Consumption scenarios

Table 1: Acid Costs expressed as USD$/lb U_3O_8

		ROM Ore Grade (ppm U3O8)					
		100	**200**	**300**	**400**	**500**	**600**
Acid Cons. Kg/t	**10**	7.88	3.94	2.63	1.97	1.58	1.31
	15	11.81	5.91	3.94	2.95	2.36	1.97
	20	15.75	7.88	5.25	3.94	3.15	2.63
	25	19.69	9.85	6.56	4.92	3.94	3.28
	30	23.63	11.81	7.88	5.91	4.73	3.94
	35	27.57	13.78	9.19	6.89	5.51	4.59

The key drivers for total acid consumption:

- **Acid consuming minerals in the Ore** – The largest contributors in this area are carbonate minerals. However, there are a number of other minerals that could react with the acid (e.g. base metals)

- **Grind Size** – There is normally a strong correlation between the acid consumption and final grind size before the leach process. The finer the grind, the higher the acid consumption. This however differs from ore to ore and must be established during the initial metallurgical test work as to optimize the process design.

- **Leach Retention Time** – The longer the acid is in contact with the ore, the more acid will be consumed. As a result there is a trade-off in leach retention time, acid consumption and uranium recovery. In many occasions, it is found that towards the end of the leach, acid consumption cost out strip the value of diminishing Uranium recovery. Leach retention must therefore be designed to optimize both acid consumption and Uranium recovery.

- **Free Acid losses** - After the leach and liquid/solid separation process, there is still a free acid value of about 2 g/l in the tailings stream. This acid is typically lost to the tailings. Sometimes the waste is neutralized before going to the dump. It is important that plant design is optimized to reduce the amount of acid that is loss in this manner.

2.1 IMPORTING OF ACID

There are only two options for obtaining the required acid for the leaching process. Either the company buys acid from 3rd parties or it invests in an acid plant to produce its own acid. In many cases, no acid producer is found close-by the uranium operations. The same applies to Namibia where a number of new operations are developing. Importing acid in bulk tankers via a port is the only means of getting acid into the country, unless an investment is made to build an on-site acid plant. Should the importation of acid be decided on, the following matters require attention.

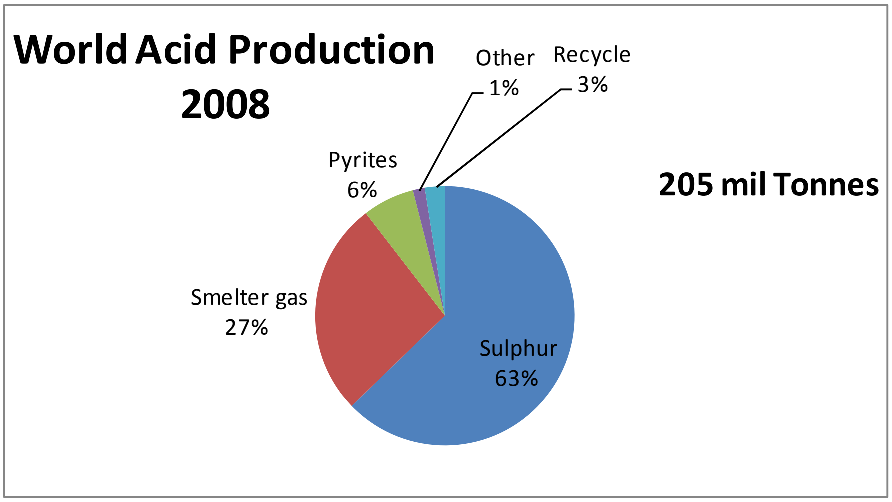
2.1.1 Acid Market

In 2008, the total global acid production was 205 mil tonnes. The breakdown of this production is illustrated with the pie-chart below. The long-haul acid trade graph further down indicates that only 1.7% (3.5t mil) of the world’s acid is traded across the oceans. The rest is either produced at site, or used within close proximity. This includes both voluntary and in-voluntary producers. The fact that there is so little acid trade between continents makes this market very price sensitive and volatile.

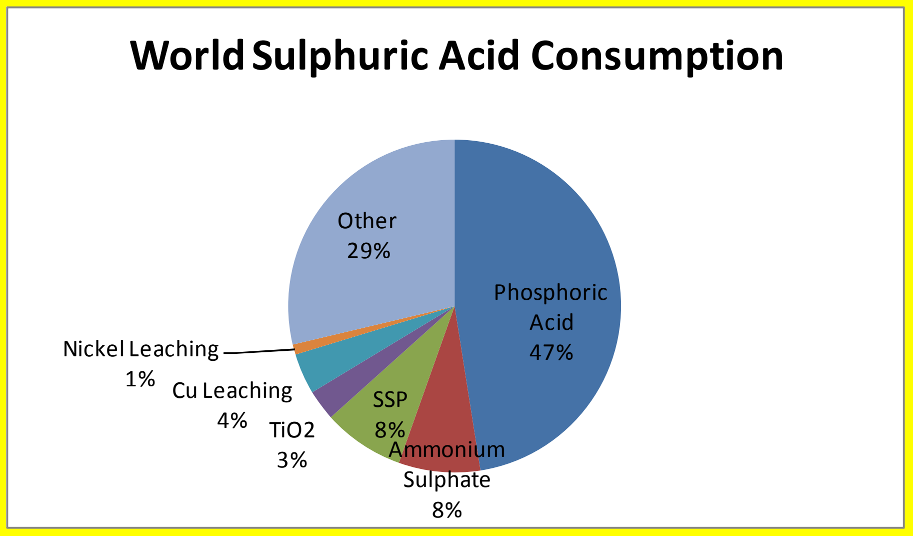
In-voluntary producers supply most of the acid traded across the oceans. Typically the in-voluntary producers have limited storage capacities and therefore must “move” acid to continue running their smelter operations. During periods of low demand for acid, storage capacities fill up quickly around the globe and the price can drop drastically. In recent months severe oversupply resulted even into negative FOB prices. Under this situation, producers would pay customers to take acid off them. This type of Acid is sometimes referred to as “Lethal Acid” and is normally produced from smelter off-gases.

Normally, under conditions of high demand for acid globally, the shortfall from the voluntary producers is sourced from the smelter off-gas producer market. Just a small increase of in global demand often results in substantial demand for these sellers. This process can drive prices up drastically. Often copper leaching and uranium leaching operations around the world are caught short of the market and end up paying 2 to 3 payoff their average purchase price for acid.

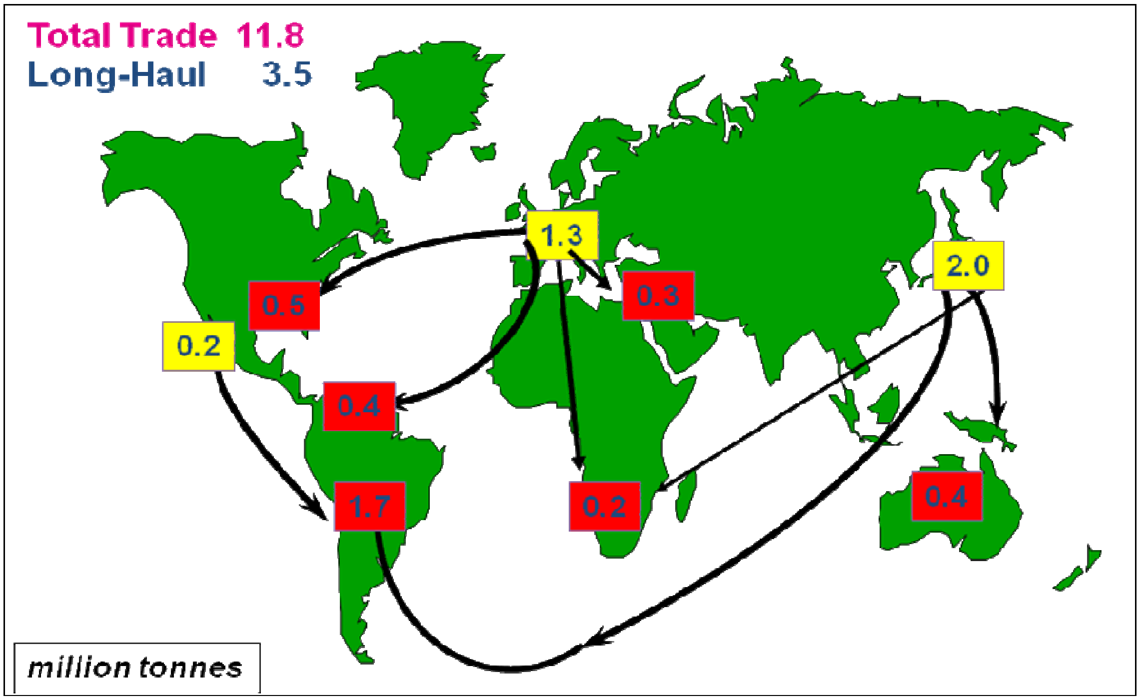
Graph 1



Graph 2



Graph 3 - Long-Haul Ocean Trade



2.1.2 Important Commercial Considerations

A large uranium operation like Rossing Uranium would use 300 000t to 400 000t of acid per year. This is roughly a large shipment of 30 000t every month. In the light of the above market volatility, a contracting strategy is very difficult. No market player is willing to lock in price for periods longer than 3-6 months. As a result acid buyers frequently need to go back to market and negotiate new contracts. For uranium mines in Namibia, this means negotiations with Asian and European Smelters. Further to this, negotiating and arranging for shipping of the commodity often turns out to be just as challenging.

2.1.3 Capital Investments for Importing Acid

All of the current and emerging uranium mines in Namibia are located within 100km distance from the port of Walvisbay. In order to import acid via Walvisbay, companies need to secure land and erect acid storage tanks to take on and handle the acid shipments. Typical shipment sizes ranges from 15 000t to 30 000t. Larger shipments are preferred as shipping cost per ton is reduced substantially. This however means that a minimum of 40 000t storage capacity must be provided for at the port. Spare capacity is required if two shipments are arriving close to each other. At least four 10 000t storage tanks have to be installed. For safety these tanks are normally installed in a contained area that could hold at least 50% of the total capacity, should an uncontrolled leak occur. Cathodic protection systems prevent corrosion of the tanks. Regulations like bi-annual safety inspections apply. Pumping systems and pipelines from ships are pressure tested for leaks every time before vessels are offloaded. Further, this tank farm must then be equipped with a rail-tanker loading station, with the capacity to load 20 rail-tankers simultaneously.

From experience at Rossing Uranium, it is known that the cycle of loading, travel to site, off-loading and travel to back to port takes 24 hours for a 1000t acid train. One train every day of the year must be loaded, railed to site and off-loaded to ensure acid supply to this uranium operation.

Any new operation would require a rail connection to site, as road transport proved to be impractical and high risk. Experience in Namibia has shown that the uranium mines need to invest in their own rolling stock of tankers. The National Rail carrier is un-willing to invest in such specialized equipment.

On site, provision must be made for a 20-station rail-tanker off-loading facility, from where the acid would be pumped into site acid storage tanks. Again, on this side, about 40 000t of storage capacity (30 days of strategic stock) is required. Logistics dictate that when the next shipment arrives in the port, tanks at the port need to be empty and tanks on site should be nearly full.

2.1.4 Risk associated with importing Acid

- Acid prices are extremely volatile, this makes budgeting, and financial planning extremely difficult.
- Because of the relative small market volumes that are traded across the oceans, availability cannot always be guaranteed.
- The nature of shipping brings risks associated with that industry. These include delays at loading ports, bad weather and highjacking by pirates. Such events could result in weeks of stock-outs of acid if stock levels were low.
- Acid consumption and acid procurement plans are extremely difficult to align. Acid shipments are confirmed 3 to 4 months in advance. Any major event during this period resulting in more or less acid usage, could result in a stock-out or full tanks by the time that the next ship arrive at the port. Full tanks will result in roughly USD$50 000 a day in demurrage cost if the ship is delayed as a result.
- Pumping, railing and handling of large tonnage of acid poses the risk of injury or environmental incidents. These risks are not only applicable to the work force but for the public at large, since acid would move through public areas. As a result, extreme control must be exercised over procedures. Further, full emergency response systems have to be set up to deal with worst-case incidents on a 24 hrs per day basis.

2.1.5 Costs to import acid

The table below provides a low, medium and high price scenario to import Acid based on historic prices.

Table 2: Acid Supply Chain Costs

Supply Chain Costs	US$/t	Low	Medium	High
FOB	US$/t	0.00	30.00	60.00
Shipping Cost (CFR)	US$/t	50.00	70.00	90.00
Namport Port Landing Charge	US$/t	20.00	20.00	20.00
Clearing Agent Charges	US$/t	1.00	1.00	1.00
Railing to mine site	US$/t	10.00	10.00	10.00
Storage and Handling Cost	US$/t	5.00	7.00	10.00
Acid Agent Fee	US$/t	3.00	6.00	9.00
Total Landed Cost to Site	**US$/t**	**89.00**	**144.00**	**200.00**

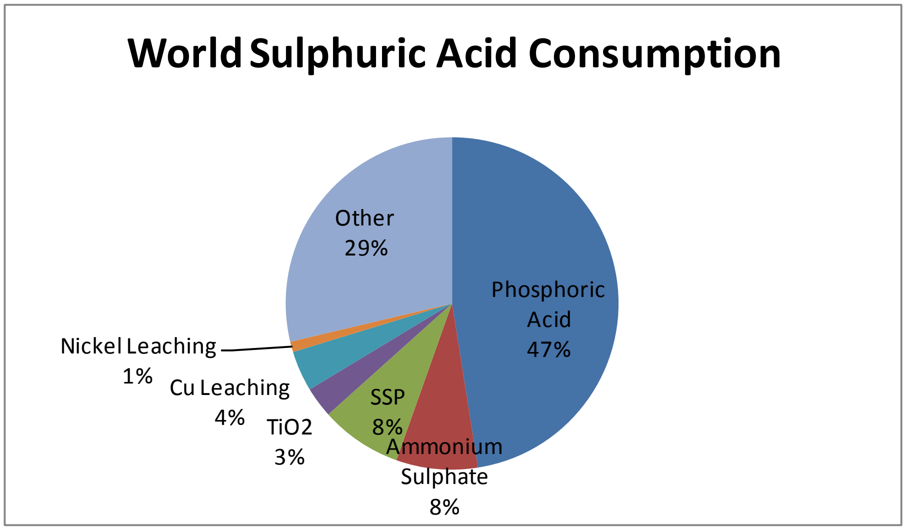
2.2 ACID PRODUCTION FROM SULPHUR

An alternative to the importation of acid would be to import sulphur and then produce acid at the uranium mine site. This requires substantial capital investment in an acid plant.

2.2.1 Market Considerations

Sulphur is a waste or by-product form the oil and gas refining industries. Its major use is to produce Sulphuric acid, which is use in many industries, but mainly for the fertilizer production.

Graph 5

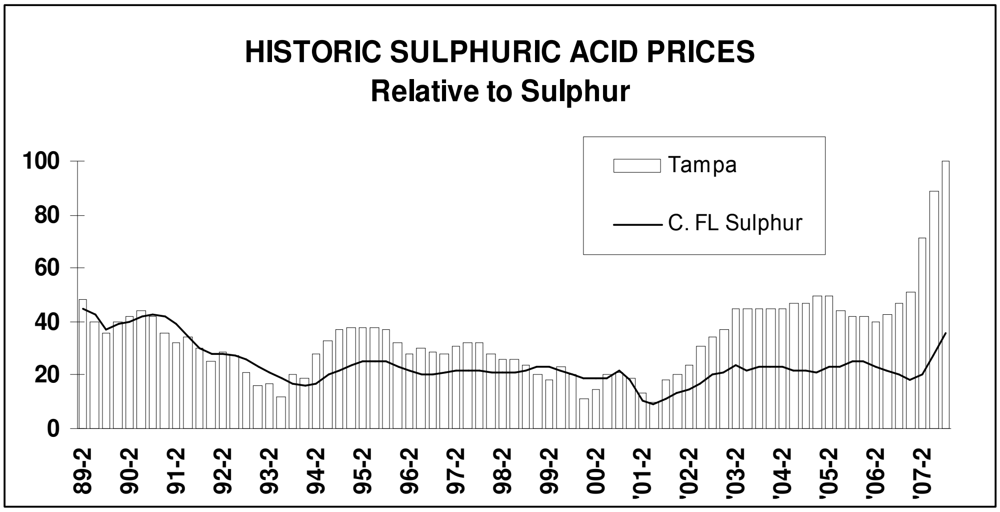


The sulphur market, although volatile, tends to be less volatile than the Acid market. This is because sulphur can be stored more easily in open stockpiles during periods of lower consumption. Sulphur storage is common practice in North America. If price drop too low in terms of FOB Vancouver, then Canadian sulphur producers would just stockpile sulphur until prices recover before railing is resumed to the port. This way they can ensure to recover at least the railing cost to Vancouver, thereby creating a floor price for sulphur globally. However seasonal volatilities occur driven by two factors. Firstly, during extreme winter conditions, railing in Canada and the Black Sea areas can be disrupted for a few months. This results in shortages of available sulphur on the markets. Secondly, the fertilizer markets are seasonally too and therefore do experience periods of higher and lower demands. These demands could ripple back into the sulphur markets, causing volatility.

Link between Sulphur and Acid Prices

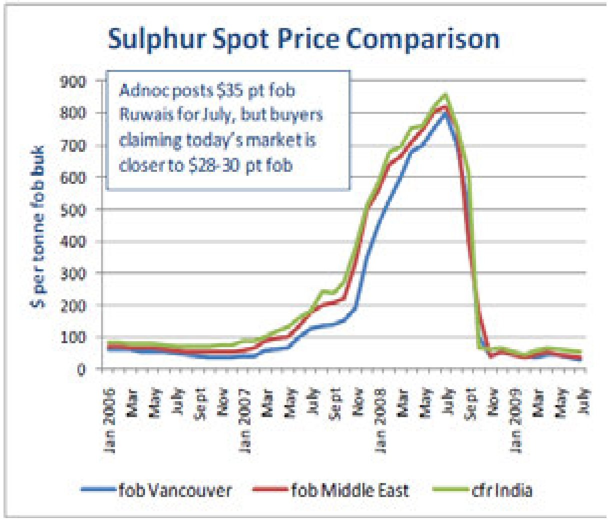
From the graph below, it is clear that there is a price correlation between Acid and Sulphur prices. What is further evident is that in recent years, Acid has become more expensive relative to sulphur. This development has made the case stronger for Acid production rather than buying or importing Acid. In practical terms acid importers were paying a premium for the sulphur content in the merchandize, measured against the global sulphur price.

Graph 6


HISTORIC SULPHURIC ACID PRICES
Relative to Sulphur

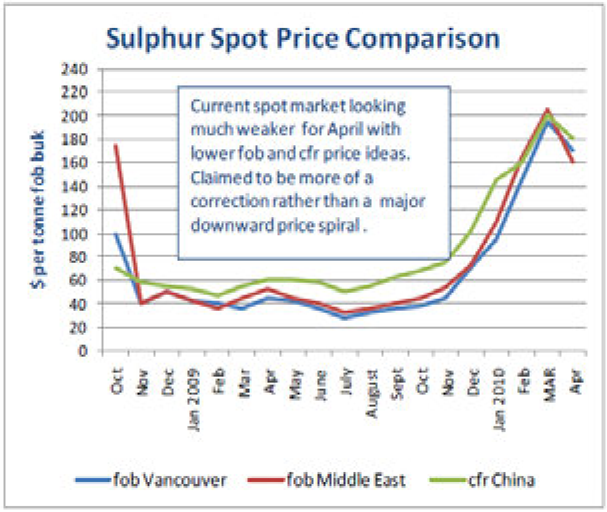
Graph 7 below clearly show the sulphur price "bubble" experienced 2008, when sulphur prices went through the roof and back within a period of 12 months. This is again just a reminder that companies entering this industry should be monitoring this market as closely as the Uranium market.

Graph 7


Sulphur Spot Price Comparison

Adnoc posts $35 pt fob Ruwais for July, but buyers claiming today's market is closer to $28-30 pt fob

Graph 8


Sulphur Spot Price Comparison

Current spot market looking much weaker for April with lower fob and cfr price ideas. Claimed to be more of a correction rather than a major downward price spiral.

Graph 8 shows the sulphur price subsequent to the "bubble". Of note is that again prices have changed fivefold during the last 18 months, indicating the volatility of the industry.

2.2.2 Capital Investment Required for a Sulphur Burning Acid Plant

In the case that the nearby port is equipped to handle bulk sulphur cargos, then most likely the uranium producers will have to invest capital to set up such facilities. Port regulations globally are getting stricter by the day, and therefore facilities have to be compliant to the highest environmental standards. Investment in ship off-loaders, conveyor belt systems, under roof storage with fire and dust control systems are required. Other requirements are rail loading and truck loading systems.

A key decision is to either employ rail or road trucks for transporting sulphur from the harbour to the acid plant.

On site, capital will have to be spent on sulphur storage facilities, the sulphur burning acid plant with a turbo generator as well as acid storage tanks.

Below is an estimate of what such an investment would be for roughly a 1200t/d plant, producing about 400 000t/a of Sulphuric Acid. These costs are based on a number of recent studies done in Namibia. They do not represent a specific project, but give a good indication of what would be needed for a typical project of this size.

Table 3 : Capital Estimate +/- 30% accuracy

Acid Plant (1200t/d)	**USD$ '000**
Port Facilities for Sulphur	**18 250**
Rail Infrastructure (30km)	**20 000**
Bottom discharge rail-wagons (12)	**4 000**
Site Sulphur Storage System	**4 500**
Demin Water Plant	**1 000**
Acid Plant Equipment & Engineering	**60 000**
Bulk Materials and Construction	**30 000**
Utilities and Storage Facilities	**25 000**
Total Installed Cost	**162 750**

2.2.3 Costs to import Sulphur

The table below provides a breakdown of cost to import sulphur for a sulphur burning acid plant. For demonstration purposes, it is assumed that the FOB price of sulphur is USD$ 55-00

Table 4: Sulphur Supply Chain Costs

SULPHUR at Site	**Unit**	**USD$/t**
FOB (Long-term ave)	USD/t	55.00
Shipping	USD/t	25.00
CIF	**USD/t**	**80.00**
Namport Port Charge	USD/t	15.50
Stevedoring & Storage Charges	USD/t	14.00
Railing to Site	USD/t	10.00
SULPHUR Agent Fee 5%	USD/t	2.75
Total Landed cost at Acid Plant	**USD/t**	**122.25**

2.2.4 Costs to produce Acid

The table below provides the annual operating cost and unit cost to produce acid on site. The following major assumptions were made;

- Sulphur input cost was based on the above calculated USD$ 122.25
- Maintenance cost was estimated at 5% of installed capital cost
- Cost of capital (Opportunity Cost) is assumed to be 10%/a
- There will be a net export of electricity generated at current market prices

Table 5 Acid Production Costs

Acid Production	**USD$/a**	**USD$/t Acid**
Sulphur Cost	16 137 000	40.34
Labour Cost	1 950 000	4.88
Maintenance Cost	8 137 500	20.34
Water Cost	4 400 000	11.00
Other Reagents & Consumables	1 000 000	2.50
Admin Overheads	500 000	1.25
Cost of Capital (10%/a)	16 275 000	40.69
Energy Credits	-4 646 400	-11.62
Total Operating Cost	**43 753 100**	**109.38**

2.3 OTHER IMPORTANT REAGENTS FOR ACID URANIUM LEACH

2.3.1 Ferric Iron

In order to effectively leach primary Uranium minerals, ferric iron (Fe3+) must be present in the acidic leach solution. The Fe3+ is used to convert U4+ to U6+, thereby reducing to Fe2+. Some of the Fe3+ is consumed by other ore minerals. Some of the Fe2+ is lost to the tailings. These losses are made up partly by iron bearing minerals contained with the ore. Nevertheless, additional ferric iron must be added continuously to the process in order to maintain the required levels. For a large acid leach operation in Namibia, this Fe makeup could be as much as 100t/d of Hematite or Magnetite ore. For practical and cost reasons, it is important to obtain a high purity Iron ore for this process.

Exploration in view of mining a suitable iron ore deposit as well as beneficiation and conditioning of the iron should be considered during the feasibility and design phase of a project to cater for the above.

2.3.2 Oxidant

As described above the ferric iron is converted in the leach process to Fe^{2+}. Large quantities of Fe^{2+} are recycled in the process back to the leach and have to be converted back to Fe^{3+} again. There are a number of options to oxidize the Fe^{2+} to $Fe^{3+.}$ These discussed briefly in the following.

- **MnO_4:** This oxidant can be used effectively to convert Fe^{2+} to Fe^{3+} in the leach process, by simply adding fine grinded, high purity MnO_4 ore to the leach under controlled conditions. For a large acid leach operation in Namibia, up to 25 000t/a of MnO_4 ore are needed for this process. Logistic implications include the following:

    - A close-by suitable MnO_4 ore source.
    - Off-loading and bulk storage facilities of the ore. (2-4 weeks of requirements)
    - A small ball mill circuit in close-loop with thicker and agitated storage tanks.

- **SO_2 Gas**: Oxidation of the Fe^{2+} can also be achieved by using SO_2 gas in a compressed injection into the leach. Using the SO_2 from a sulphuric acid plant constitutes an option but bears a number of technical challenges. Effective mixing of the gas/slurry and control the addition in such manner that free SO_2 does not escape the process are considered problematic.

- **Hydrogen Peroxide (H_2O_2):** This oxidant converts Fe^{2+} to Fe^{3+}effectively. By means of an inline mixer the H_2O_2 is injected into a Fe^{2+} containing solution. Mixtures of H_2SO_4 and H_2O_2 added to the leach have proven to provide the oxidation requirements. However, due to the unstable nature of H_2O_2, high losses will occur if the conditions are not controlled tightly. Much of the H_2O_2 will simply decompose or escape and the required oxidation will not take place. When using H_2O_2 special logistics and storage requirements for H_2O_2 need to be implemented. H_2O_2 poses a high risk of fire and explosion. Strict design and management has to be exercised over these installations. Due to its high price H_2O_2 does not normally provide the most cost effective option.

3. ALKALINE LEACH OPERATIONS

Ore from deposits of secondary uranium mineralization containing carbonates is economically leached by an alkaline leach process. Chemicals used in this application are **soda ash** (Na_2CO_3), **sodium bi-carbonate** ($NaHCO_3$) and **caustic soda** (NaOH). Heated tank leach or a heap-leach constitute the most commonly used options. Once the Uranium is in solution, it is then loaded on resin in an ion exchange process. In this process, bi-carbonate is used in large quantities to strip off the Uranium from the resin to produce a concentrated uranium solution. From the concentrated solution, the Uranium is precipitated with caustic soda. The precipitated sodium di-uranate is then washed and re-dissolved with sulphuric acid (H_2SO_4) before it is finally precipitated with H_2O_2 as UO_4.

Each of the above chemicals will be discussed in more detail below.

3.1 SODA ASH

3.1.1 Soda Ash Market

Soda ash is produced from natural soda ash deposits known as trona, with the USA (Green River Basin/Wyoming) being the largest producing region and a number of operating companies. In Africa, BotAsh (Botswana) and Lake Magadi (Kenya) are the only natural Soda Ash deposits in operation. In the rest of Europe and Asia, soda ash is produced with the synthetic process known as the Solvay process. In this process, NaCl is converted to $NaHCO_3$ in the presence of CO_2 and NH_4. NH_4 is recycled by boiling it off with CaO. $CaCl_2$ is produced as a by-product. The $NaHCO_3$ is calcined in kilns and converted to Na_2CO_3. This product can be shipped in bulk or bags globally.

More than 40% of the worlds Soda Ash production is used in the glass making industry. The rest is consumed in a number of different industries, mainly the detergents as well as the paper and pulp industries.

World prices for soda ash are driven mainly by energy cost (coal, gas and electricity) and shipping rates. Prices are relatively stable but have increased over the last 3 years in relation to the input costs.

Graph 9

WORLD SODA ASH PRICES HISTORIC AND FORECAST

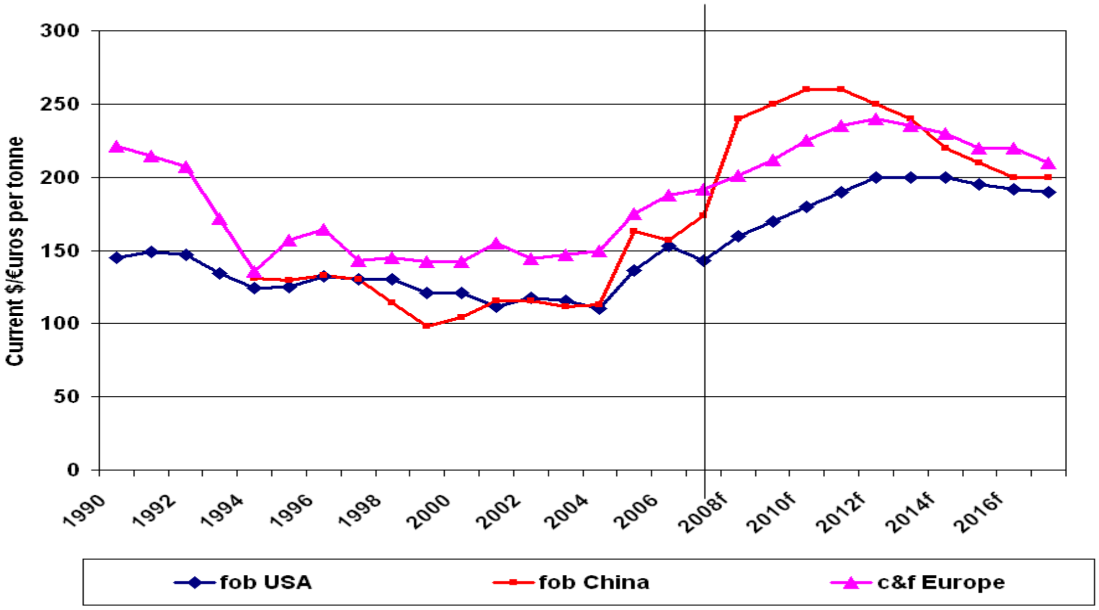


Table 6: Supply chain cost for Soda Ash

Soda Ash to Site	**Unit**	**Low**	**Medium**	**High**
FOB	USD/t	210.00	236.00	275.00
Shipping	USD/t	40.00	80.00	110.00
CIF	**USD/t**	**250.00**	**316.00**	**385.00**
Namport Port Charge	USD/t	15.50	15.50	15.50
Stevedoring & Storage Charges	USD/t	5.00	5.00	5.00
Transport to Site	USD/t	25.00	25.00	25.00
Agent Fee	USD/t	25.00	25.00	25.00
Total Landed cost at Mine	**USD/t**	**320.50**	**386.50**	**455.50**

3.1.2 Soda Ash in Uranium Leaching

The leach solution is commonly maintained at concentrations of 30g/l to 40g/l soda ash for both heap and tank leach operations. Very little of the Soda Ash is consumed by the ore and most of the losses of soda ash in the process is via entrainment in the tailings after uranium has been recovered. There are however, some minerals like gypsum ($CaSO_4$) that will react with the Na_2CO_3 to form $CaCO_3$ and $NaSO_4$. The former and latter constitute the total soda ash consumption in the process. With low gypsum in the ore, the soda ash consumption calculates as a function of total tones treated. Further, all of the bi-carbonate that is added downstream in the process is converted with the addition of caustic soda into soda ash. Subsequently the soda ash liquor is returned to the leach process. This stream normally constitutes a large contribution of soda ash to the leach process. Normally only a few kg/t of fresh soda ash is added to maintain leach conditions. This "top-up" of Soda Ash to the leach will differ between tank leach and heap leach operations.

3.1.3 Impact of Soda Ash on U_3O_8 Production cost

Alkaline leach uranium mines have no alternative but to buy from soda ash producers. Supply contracts and logistic chains need to be efficient and reliable. In the Namibian example, this, for now, means importing form China, Europe and USA via shipping either bagged product or bulk product. In Port of Walvisbay facilities were erected to offload and store 5000 to 10 000 tonnes per shipment. The cost of Soda Ash for a tank leach operation could range between USD$1.00/lb U_3O_8 to USD$3.00/lb U_3O_8, depending on the ore uranium grade and wash efficiencies.

3.2 BI-CARBONATE OF SODA

3.2.1 Bi-Carbonate Market

The soda ash producers also supply industrial-grade bi-carbonate. In bi-carbonate production soda ash is dissolved in water and then carbonated with CO_2 to form refined bi-carbonate. The product is then filtered, dried and bagged. The price of bi-carbonate closely trends with the soda ash market, but is generally higher than that of soda ash.

Table 7: Supply chain cost for Bi-carbonate

Bi-Carbonate to Site	**Unit**	**Low**	**Medium**	**High**
FOB	USD/t	245.00	310.00	350.00
Shipping	USD/t	85.00	100.00	115.00
CIF	**USD/t**	**330.00**	**410.00**	**465.00**
Namport Port Charge	USD/t	15.50	15.50	15.50
Stevedoring & Storage Charges	USD/t	5.00	5.00	5.00
Transport to Site	USD/t	25.00	25.00	25.00
Agent Fee	USD/t	25.00	25.00	25.00
Total Landed cost at Mine Site	**USD/t**	**400.50**	**480.50**	**535.50**

3.2.2 Uranium stripping from resin with Bi-Carbonate

The largest application of bi-carbonate is to strip the uranium from the ion exchange resin. The key consumption driver in this process is the ultimate concentration of uranium in the strip solution. Most operations would achieve between 7.5g/l and 15g/l of U_3O_8 in the strip solution. A bi-carbonate solution of about 80g/l is commonly used regardless of the uranium concentration. A 7.5g/l uranium concentration uses double the amount of bi-carbonate compared to 15g/l U_3O_8. This is expressed as the bi-carbonate consumption per kg of U_3O_8 produced.

3.2.3 Impact of Bi-Carbonate on U_3O_8 Production cost

Depending on the elution technology employed, bi-carbonate consumptions could range from 15kg/kg U_3O_8 to 25kg/kg U_3O_8 produced. Using a bi-carbonate prices ranging from USD$400 to USD$535 and the above consumption range, the unit cost of bi-carbonate to the process ranges between USD$2.72/lb U_3O_8 and USD$6.70/lb U_3O_8

3.3 CAUSTIC SODA

3.3.1 Caustic Market

Caustic is produced globally as a waste/by-product of the chlorine industry, where NaCl is converted through a process of electrolysis into NaOH and Cl2 gas. The Cl gas is used in many applications, but largely in the PVC industry.

Caustic on the other hand is used in the aluminium, paper and pulp and detergent industries. Normally if the PVC market is booming, then there is plenty of NaOH available and prices would be low. However, if there is low demand in the PVC market, then caustic prices can increase drastically due to shortness of supply. Most of the caustic is traded in 50% concentrated lye, which can be railed or shipped anywhere. Some companies dry the lye and then bag the resulting dry flakes or pearls into 25kg bags for smaller consumers. This procedure however makes the product substantially more expensive.

If there are facilities available to receive caustic lye in large shipments, product can be bought in this format from a number of producers globally. Storage tanks and pumps at the harbour with rail or truck loading facility. However, notice must be taken that 50% of the product will be water, and shipping and transport cost will play a major role if long distances needs to be covered. Alternatively, dried product that is more expensive can be bought, and transported more economically. This however requires a caustic lye make-up plant on site, since ultimately a 30% caustic lye solution is used in the process.

The graph below gives an indication of what Caustic lye prices did over a 3-year period.

Graph 10 – Asian Caustic Prices

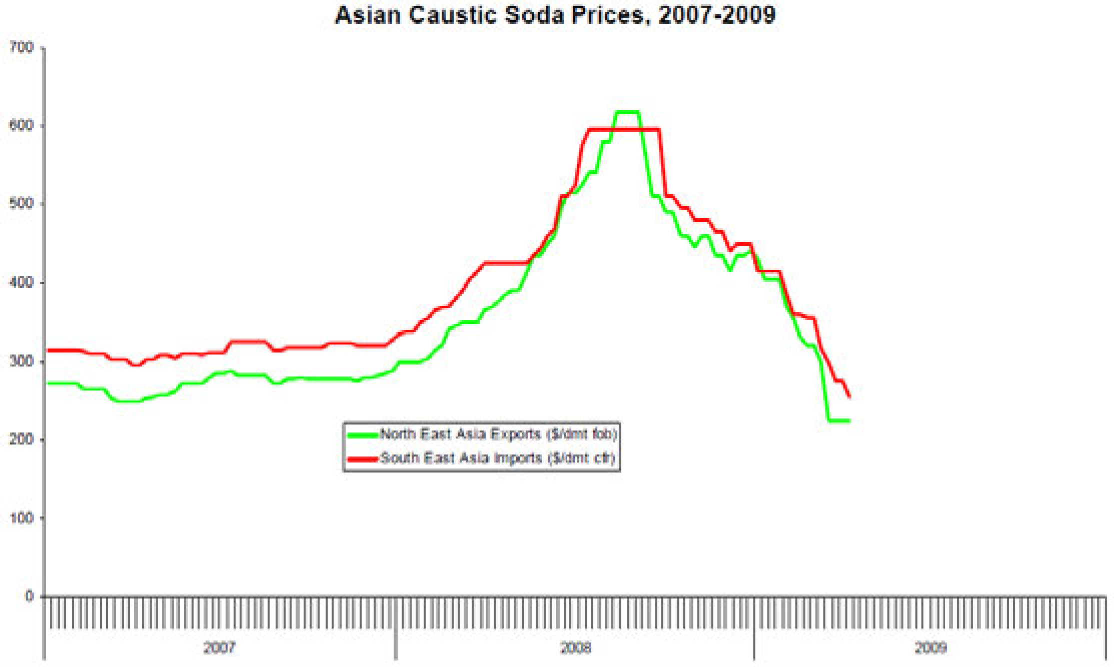


Table 8: Supply chain cost for Caustic Soda

Caustic Flakes To Site	Unit	Low	Medium	High
FOB	USD/t	450.00	550.00	750.00
Shipping	USD/t	85.00	85.00	85.00
CIF	**USD/t**	**535.00**	**635.00**	**835.00**
Namport Port Charge	USD/t	20.00	20.00	20.00
Stevedoring & Storage Charges	USD/t	5.00	5.00	5.00
Transport to Site	USD/t	25.00	25.00	25.00
Agent Fee	USD/t	35.00	35.00	35.00
Total Landed cost at Acid Plant	**USD/t**	**620.00**	**720.00**	**920.00**

Note: The above prices are for caustic flakes and hence about USD$100/t more expensive than caustic lye

3.3.2 Uranium Precipitation with Caustic Soda

The concentrated strip solution resulting from the above is contacted with a NaOH solution in the next step of the process to precipitate the uranium as sodium di-uranate ($Na_2U_2O_7{\cdot}6H_2O$). This process requires up to 10g/l of free NaOH for the precipitation to take place. Caustic is added in the form of a 30% concentrated solution of caustic lye.

3.2.3 Impact of Caustic Soda on U_3O_8 Production cost.

In the sodium di-uranate precipitation process the caustic consumption could range from 7kg/kg U_3O_8 to 12kg/kg U_3O_8 produced. Using a caustic soda prices ranging from USD$620 to USD$920 and the above consumption range, the unit cost of caustic soda to the process could range USD$2.00/lb U_3O_8 to USD$5.05/lb U_3O_8

3.4 OTHER IMPORTANT REAGENTS FOR ALKALINE URANIUM LEACH

In the final precipitation step, sulphuric acid and hydrogen peroxide is used to produce uranium oxide (UO_4). Although small quantities are used in this process, provision must still be made on site to procure and store these chemicals. Like sulphuric acid also hydrogen peroxide requires specialized installations and risk management during operation.

4. CONCLUSION

It is evident that whether acid leach or alkaline leach is applied, the reagents used in these processes could have a substantial impact on the cash production cost of uranium. These costs could range from about USD$5.00/lb U_3O_8 to USD$15.00/lb U_3O_8. Most new uranium operations are trying to keep their cash production cost below USD$30.00/lb U_3O_8 setting the margin in today's uranium market of about USD$60.00/lb U_3O_8. Your reagents could constitute as much as 50% of your total operating costs.

To ensure a reliably source and storage of the reagents, large amounts of capital must be invested. Planning and setting up reliable supply chains for these reagents will take considerable managerial efforts to ensure a low risk system. Spending this time will pay good dividends in the long-term. Finally yet importantly, Uranium miners must make efforts to better understand the markets of these reagents, as these could have substantial impact on the operators' bottom line!

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ION EXCHANGE FORUM

URANIUM RECOVERY BY CONTINUOUS ION EXCHANGE OF ALKALINE LEACHATE

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CONTENTS

ABSTRACT

One of the challenges of the alkaline leach process is to deliver a high concentration eluate of purity to the refinery. Ion exchange often plays a role in this process. This paper describes a sequence of flowsheet improvements to an ion exchange circuit to achieve this objective.

Some testwork data is provided to describe the journey taken in improving the CIX circuit to deliver the required eluate composition. The linkages between the refinery and the ion exchange circuit are described as well as the typical stream purities and composition of final oxide product.

Modelling of a continuous ion exchange process allows the behaviour of the process to be investigated, and the process to be quantified. An example is included to demonstrate some of the key factors that should be included when modelling ion exchange processes.

1. INTRODUCTION

Australia has the largest known recoverable uranium resources in the world. With recent increase in the demand of uranium, there is a growing interest in the processing of more challenging secondary uranium ore such as surficial calcrete deposits. A significant amount of Australia's uranium deposit (4.9%) is surficial (calcrete) uranium deposit (McKay, A.D. and Miezitis Y., 2001), such deposits are commonly extracted via the alkaline leach method.

Surficial uranium deposits usually have secondary cementing minerals such as calcite, gypsum, dolomite, ferric oxide and halite (McKay, A.D. and Miezitis Y., 2001). However, uranium deposits in calcrete are the largest of the surficial deposits. The calcrete deposits are interbedded with tertiary sand and clay, which are usually cemented by calcium and magnesium carbonates (McKay, A.D. and Miezitis Y., 2001).

Yeelirrie Mine in Western Australia is the world's largest surficial deposit with 52,500t of U_3O_8 in resources at an average grade of 0.15% U_3O_8 (McKay, A.D. and Miezitis Y., 2001). Other significant surficial deposits in Western Australia include Lake Way, Centipede, Thatcher Soak and Lake Maitland (McKay, A.D. and Miezitis Y., 2001).

2. TYPICAL ALKALINE URANIUM LEACH FLOWSHEET

There are a number of different methods of leaching uranium depending on the ore type, type and contribution of gangue minerals and impurities. Acid and alkaline uranium leaching are the most common employed today for the recovery of uranium. Generally, the acid leach process has faster kinetics with higher recovery and can be done at lower temperature compared to the alkaline leach processes.

However, with ore bodies containing significant acid consuming gangue materials, in particular calcite, alkaline leach process can be a more cost effective option in this scenario. A general guide has been that if the ore contains more than 12% of carbonates, then alkaline leaching often is more economical than acid leach (Yan D. and Connelly D., 2008). Although, other considerations such as efficiency of uranium extraction, reagents cost, water and energy consumption, product quality and environmental impact must also be considered (Uranium Extraction Technology,1993).

The alkali leach is generally more selective than acid leach and often reduces the impurity load that has to be removed in the downstream processes. However, the alkali leach has slower kinetics, which requires the process to be carried out at elevated temperature of 75-120°C and at around a pH 10-11. Sodium carbonate solution (30g/L) with small quantity of sodium bicarbonate is generally employed in the alkali leach process.

A typical alkaline uranium leach flowsheet for calcrete hosted uranium is as shown in Figure 1. The uranium in the ore body can be concentrated in the clay. Crushed ore is scrubbed in re-circulated CCD overflow sodium carbonate solution (30g/L Na_2CO_3) to remove the clay from any sand and some uranium is leached in the scrubber. The scrubber product is then screened, or cycloned, in the stage desliming process and the oversize fraction (scats) is finally washed with clean water before rejected as a barren. The screen underflow, or cyclone overflow, is thickened and the overflow then reports to the continuous ion exchange (CIX) circuit. The concentration of uranium in the overflow solution in parts per million is nominally similar to the uranium concentration in the ore in grams per tonne.

The thickener underflow is leached at approximately 85°C. Heat recovery from the leach discharge is introduced into the advancing leach slurry. Uranium occurs in nature in either hexavalent or tetravalence form (Uranium Extraction Technology,1993). Secondary uranium ores generally contain oxidised uranium, and the alkaline leach reaction is as described in Equation 2.1.

$$K_2(UO_2)_2V_2O_8 \bullet 3(H_2O) + 2Na_2CO_3 + 4NaHCO_3 \longrightarrow 2Na_4UO_2(CO_3)_3 + 2KVO_3 + 5H_2O \tag{2.1}$$

The leached slurry enters a washing stage using a series of counter current decantation (CCD) thickeners to recover the leached uranium. The washing efficiency of uranium can be improved by recovering uranium from a bleed stream from a CCD thickener overflow and recovering the uranium in the ion exchange circuit before returning it as wash liquor lower down in the CCD train.

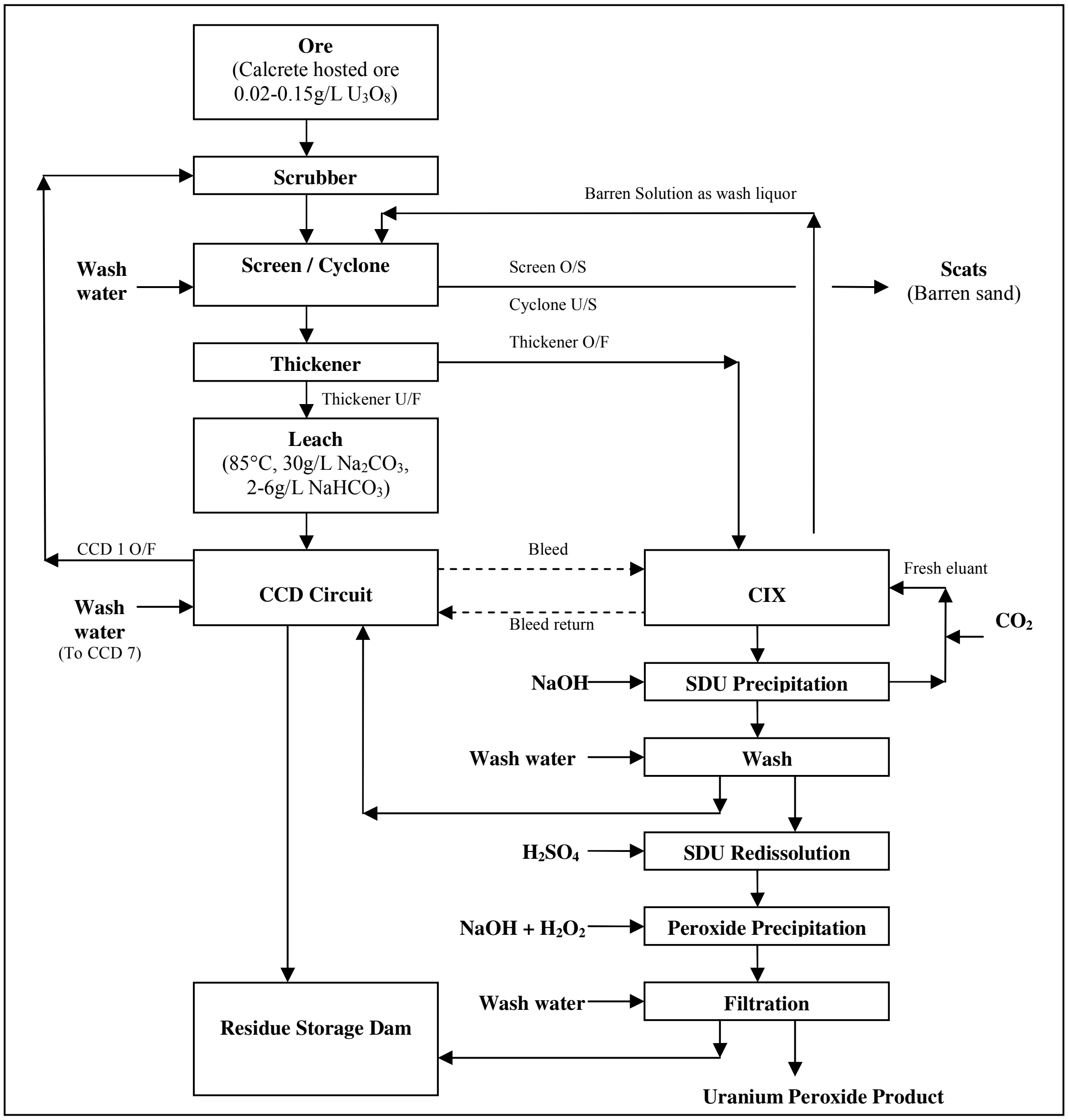

Figure 1: Typical alkaline uranium leach flowsheet

Uranium is loaded on the ion exchange resin and barren liquor is produced containing as little as 2mg/L U. Certain anionic impurities e.g. vanadium, phosphate, sulphate, chloride can also be extracted along with uranium. Some of these impurities on the resin can be scrubbed prior to elution.

Sodium bicarbonate is often the reagent of choice in the elution step.

$$R_4UO_2(CO_3)_3 + 4NaHCO_3 \longrightarrow 4R(HCO_3) + Na_4(UO)_2(CO_3)_3 \qquad (2.2)$$

The refining process for uranium normally employs a sodium diuranate precipitation step followed by a sulfation resolution in sulphuric acid, and finally the precipitation of an oxide from the product with sodium hydroxide and hydrogen peroxide.

Sodium hydroxide is used to precipitate the dissolved uranium to form sodium diuranate ($Na_2U_2O_7.xH_2O$), as shown in Equation 2.3 below. The sodium hydroxide initially reacts with the bicarbonate ion in the alkaline leach solution. Then, with the presence of excess sodium hydroxide, uranium will hydrolyse and precipitate at pH12 and above (Merritt, R.C., 1971).

$$2Na_4UO_2(CO_3)_3 + 6NaOH \longrightarrow Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O \qquad (2.3)$$

To increase the purity of the final product, the sodium diuranate is re-dissolved with sulphuric acid as shown in equation 2.4 and then re-precipitated with hydrogen peroxide solution in equation 2.5 as hydrogen peroxide is highly selective in the precipitation of uranium.

$$Na_2U_2O_7 + 2H_2SO_4 \longrightarrow 2UO_2SO_4 + 2NaOH + H_2O \qquad (2.4)$$

$$UO_2SO_4 + H_2O_2 + 2H_2O \longrightarrow UO_4 \bullet 2H_2O + H_2SO_4 \qquad (2.5)$$

3. ION EXCHANGE

Solvent extraction or ion exchange is normally employed to concentrate and purify the uranium leachate and remove impurities. Solvent extraction and ion exchange both involve the interchange of ions between the aqueous solution and either a liquid organic solution or a solid resin.

As the pregnant liquor solution (PLS) in carbonate leaching normally has a relatively low concentration of uranium (approx 150 to 1000ppm U), an upgrading step is normally required prior to oxide recovery. In most cases, ion exchange is ideal in this duty.

3.1 URANIUM ION EXCHANGE CHEMISTRY

In uranium ion exchange, strong base anion resins are normally used. The strong base anionic resin for uranium ion exchange contains quaternary ammonium functional group. The degree and type of cross linking varies between different manufacturers. This influences the chemical and mechanical characteristics of the resin (Merritt, R.C., 1971).

The uranium adsorption reaction that occurs in the resin can be described by the equation 3.1 below:

$$4RX + [UO_2(CO_3)_3]^{-4} \longrightarrow R_4UO_2(CO_3)_3 + 4X^- \qquad (3.1)$$

The adsorbed uranium can be released in the elution stage by using a strong sodium bicarbonate solution. The reaction can be described in Equation 3.2 below

$$R_4UO_2(CO_3)_3 + 4NaHCO_3 \longrightarrow 4R(HCO_3) + Na_4UO_2(CO_3)_3 \qquad (3.2)$$

3.2 FIXED BED ION EXCHANGE VERSUS CONTINUOUS ION EXCHANGE (CIX)

Traditionally, fixed bed ion exchange is used in industry. Conventional fixed bed ion exchange typically employs a few large columns with for example, 2 or 3 columns in loading phase, 1 column in scrubbing, and another in the elution phase. As the loading, scrubbing and elution cycle times are different, there is frequently a column idling for a period of time in fixed bed arrangements.

The continuous Ion Exchange (CIX) process utilises a larger number of smaller ion exchange columns (frequently more than 20 columns) which operates in a continuous manner via counter-current contacting of liquid with resin. Although having a larger number of smaller columns adds a degree of complexity in the circuit, it also introduces a flexibility that is not available in a fixed bed ion exchange circuit.

Some of the benefits of continuous ion exchange over conventional fixed bed arrangements are as follows (Rossiter, G.J., 2009):

1. Reduced Resin Charge (50-80%) reduces the capital cost of resin inventory in column and equipment size.
2. Higher concentration eluate product (by a factor of 3-4) which translates into lower volumetric flow of concentrated eluate to the refinery and oxide recovery circuits and hence lower capital cost. Having a higher purity product also helps to maintain higher recovery in the precipitation step.
3. Higher first pass uranium recovery.
4. Reduced reagents consumption (eluants), reducing plant operating cost.
5. Reduced water consumption (40-60%).
6. Maximises new water addition to the CCD washing circuit.
7. Permits the use of a pre-elution stage and /or a post adsorption scrubbing stage to remove co-loaded impurities and produce a purified eluate, which allows simplification in the downstream product recovery process.

In CIX, having a larger number of smaller columns (e.g. 5 to 10 columns in series) in the loading step allows the ion exchange resin in the leading column to be loaded to near saturation without compromising on the overall recovery. To illustrate this, an example from ion exchange batch testwork with 3 columns in series is shown in Figure 2. As demonstrated, uranium was able to be loaded to saturation in column 1, whereby the concentration of uranium into and out of the column were approximately the same. There was a significant amount of breakthrough uranium in column 2. By having an additional column 3, there is negligible uranium breakthrough when the first column is at or near saturation.

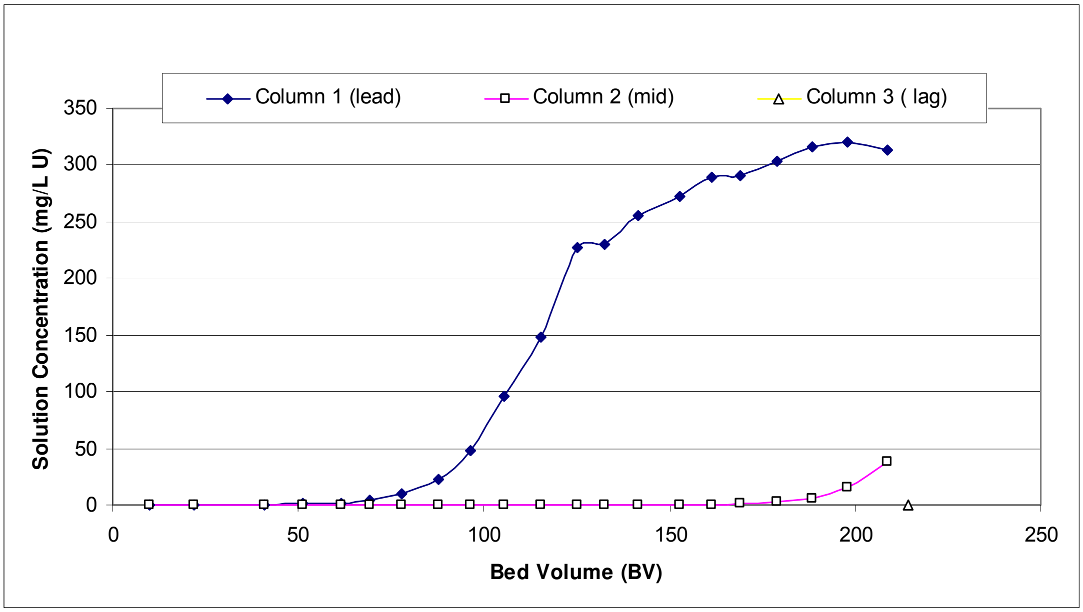

Figure 2: Typical breakthrough curve for uranium ion exchange

3.3 CONTINUOUS ION EXCHANGE CIRCUIT

Due to the flexibility of the CIX circuit, intermediate steps such as feed displacement, pre-elution and conditioning stages are able to be introduced to remove impurities and improve on the grade of the eluate. Figure 3 shows the configuration of a CIX pilot plant.

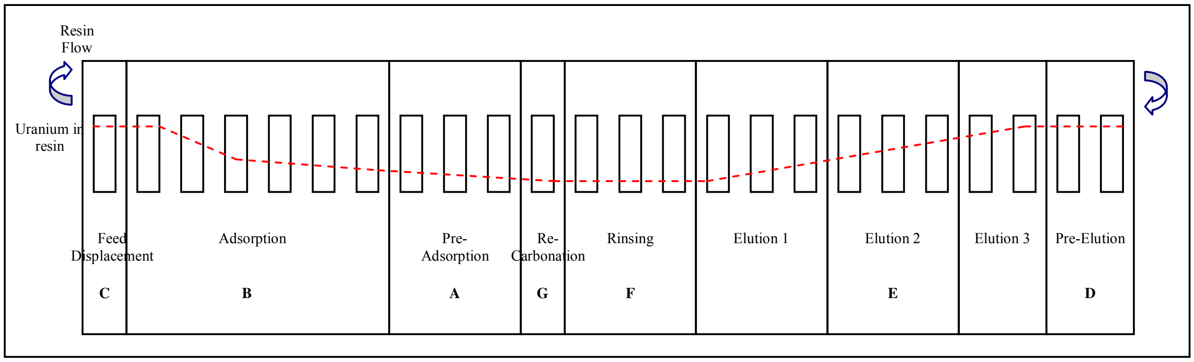

Figure 3 Continuous Ion Exchange circuit configuration

The CIX circuit configuration for alkaline uranium can for example consist of:

A. **Pre-Adsorption Zone:** Bleed solution from the CCD circuit overflow is contacted with the freshly regenerated and rinsed resin. The uranium fed to this zone is about 10 to 15% of the total uranium feed to the CIX.
B. **Adsorption Zone:** Solution from thickener overflow (PLS solution) is fed counter current to the resin to optimize on the resin loading.
C. **Feed Displacement Zone:** Resin leaving the adsorption zone passes through the feed displacement zone whereby the entrained liquor is displaced from the columns with rinse solution and returned to the adsorption zone.
D. **Pre-Elution Zone:** In the pre-elution zone, concentrated eluate is sacrificed to displace the low concentration and purity interstitial fluid in the column. The displaced solution is returned to the PLS feed tank.
E. **The Elution Zone:** The fresh eluant flows in counter current direction to the ion exchange resin in this zone to strip the uranium from the resin. Warm sodium bicarbonate solution is used in this process. The elution zone can be divided into 3 stages.
F. **Eluant Displacement Zone:** The column is rinsed with CIX barren solution from the adsorption stage to displace the eluant and any stripped uranium in the resin.
G. **Re-Carbonation Zone:** The column is recirculated with barren solution to condition the column and displaces bicarbonate from the resin.

4. DEVELOPMENT OF THE CIX CIRCUIT

The findings from some batch and continuous testing will be presented showing the optimisation developments in producing uranium high grade eluate.

4.1 BATCH TESTWORK

Early batch testwork was conducted using three ion exchange columns connected in series. Strong base anion resin (Amberjet^{TM} 4400HCO$_3$) was tested and used in the ion exchange columns. These columns were loaded with uranium PLS solution and then subjected to the subsequent steps of washing, scrubbing, elution and conditioning. The results from the batch testwork are shown in Figure 4. The typical PLS solution composition in batch testwork is as shown in Table 1.

Components	Typical Concentration (g/L)
U	0.2-0.4
P_2O_5	0.2-0.3
SO_4^{2-}	0.8-1.2
Cl^-	0.1-0.3
Mo	0.001-0.005
Si	0.005-0.03
V_2O_5	0.001-0.003

Table 1: Typical Uranium alkaline leach PLS solution

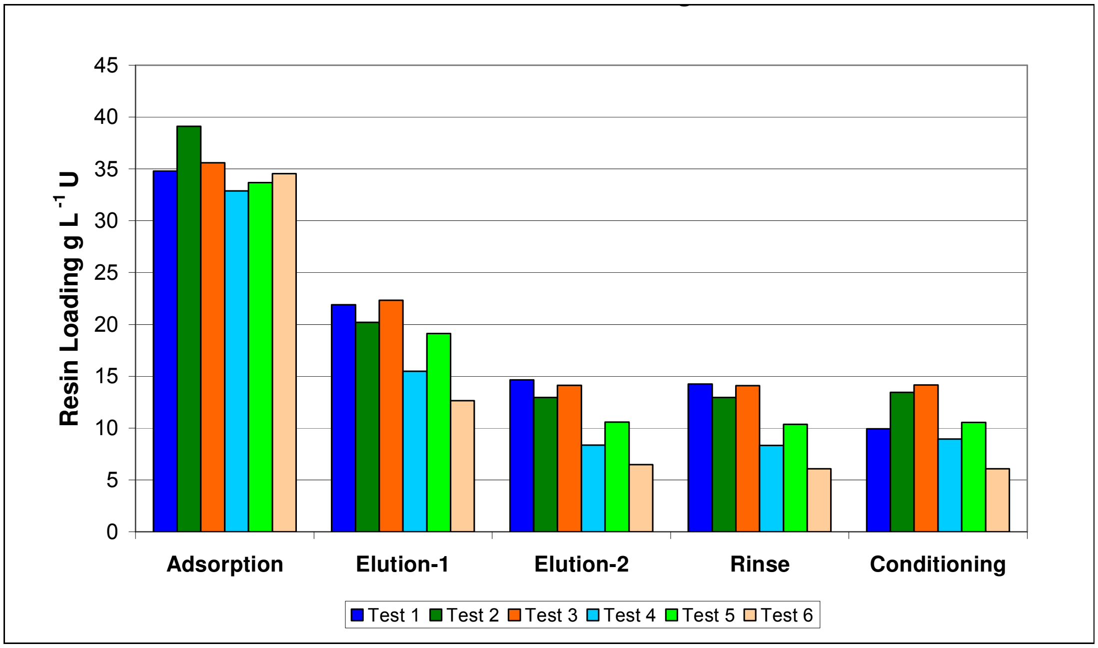

Figure 4: Batch testwork results of uranium loading and stripping

The uranium loading on the resin after adsorption was approximately 35g/L U. The early testwork showed that the uranium was not fully eluted with the stripped resin uranium concentration of 8-14g/L U. As a result of incomplete stripping, the net uranium loading capacity of the resin was between 21 to 27 g/L U.

The eluant concentration was 1 Molar sodium bicarbonate. It is customary to employ elevated temperatures (typically 40-60°C) in the elution of ion exchange resins employed in uranium duty as this was the case in this work. The earlier tests (Test 1 to 3) reflect data from a low temperature elution and the latter tests (Test 4 to 5) are for an elution performed at 40-50°C. This temperature elevation improved the uranium elution somewhat (reducing the uranium on resin by approximately 5g/L U).

4.2 PILOT TESTWORK SETUP

An IONEX (Ionex Separations, USA) multiport pilot valve of the type shown in Figure 5 was employed in the continuous testwork. The optimised batch testwork outcomes provided the foundation for the continuous circuit flowsheet. A three stage split elution circuit operated at elevated temperature of 40-60°C was employed. The eluant comprised of a blend of 1 Molar sodium bicarbonate with 0.15 Molar of sodium carbonate. Carbon dioxide was gassed through the eluant and the interstage eluates to convert eluted carbonate to bicarbonate.

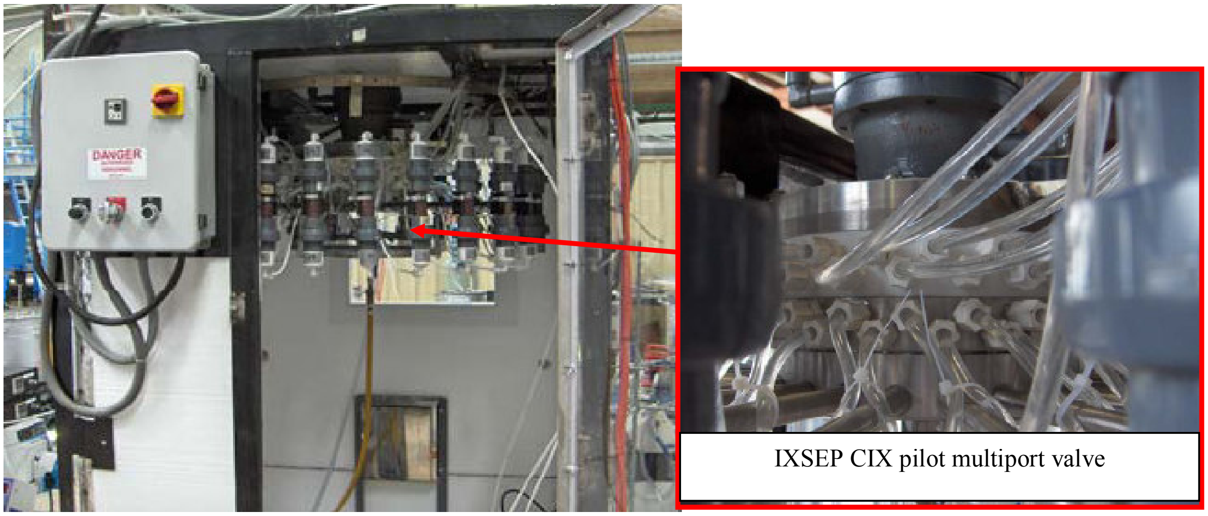

Figure 5: Pilot plant setup for the Continuous Ion Exchange (CIX) unit housing the ion exchange columns and valve head

4.2.1 Enhancing Overall Uranium Recovery – CCD Intervention

In an alkaline leach circuit, two efficiency issues present themselves to the process engineer tasked with the design of the circuit. These are:

- Uranium recovery from the leachate, and
- Minimisation of reagent loss from the leach residue solid-liquid separation step.

These have to be balanced with the bleed of unwanted solute rich in vanadate, sulphide, chloride and other impurities. Supporting the optimisation of these objectives is the minimisation of the introduction of extraneous water to the circuit other than in the residue washing stage.

A further enhancement that was explored was the introduction of a CCD uranium wash. This incorporated CCD #2 thickener overflow uranium PLS that was contacted with freshly conditioned resin and the barren from which was then returned to CCD #6. This flowsheet is shown in Figure 6. This served to improve the overall circuit uranium recovery.

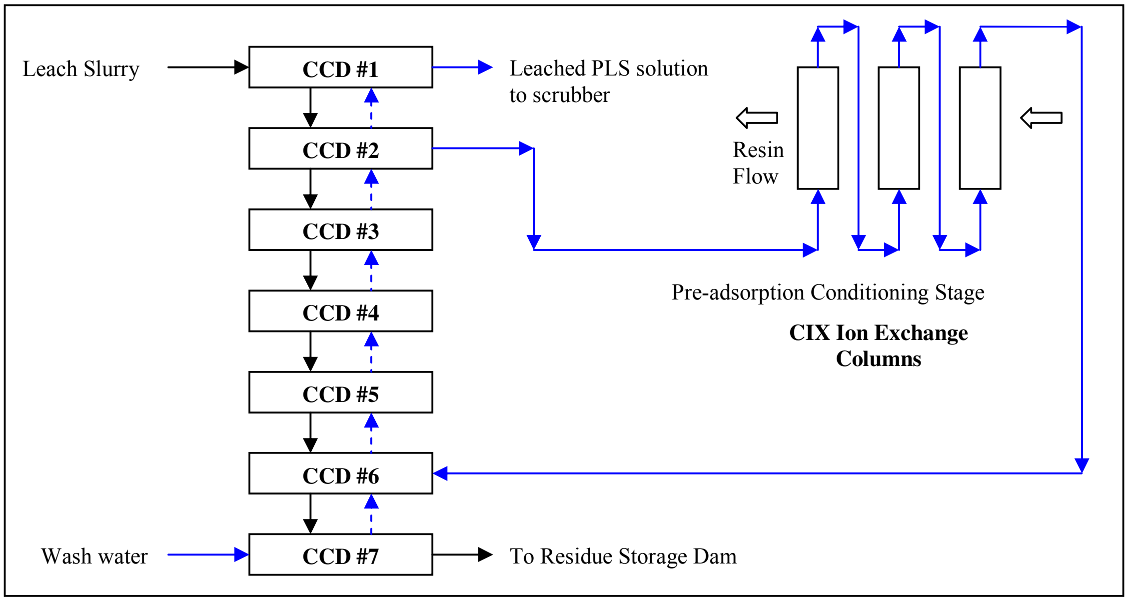

Figure 6: CCD#2 PLS solution to Ion Exchange

4.2.2 Enhancing Overall Uranium Recovery – Concentrated Eluate

In both acid and alkaline leach circuits that front up to direct precipitation of uranium from the eluate, higher concentrations of uranium in the eluate favour both first pass and overall uranium recovery. The pre and post elution components of the flowsheet in Figure 7 support this objective. The initial attempt at achieving higher uranium tenors and recoveries in the elution circuit adopted an eluant entrainment rejection step termed “rinsing” in Figure 7. The rinsate was then employed in leach PLS entrainment step termed “pre-elution” in Figure 7. The eluant (shown in equation 4.1) comprised 1 molar sodium bicarbonate solution. Interstage carbon dioxide gassing was employed to convert eluted carbonate to bicarbonate thereby restoring the interstage elution efficacy in the ensuing split elution stage.

$$R_4UO_2(CO_3)_3 + 4NaHCO_3 \longrightarrow 4R(HCO_3) + Na_4UO_2(CO_3)_3 \qquad (4.1)$$

$$R_2CO_3 + 2NaHCO_3 \longrightarrow 2R(HCO_3) + Na_2CO_3 \qquad (4.2)$$

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3 \qquad (4.3)$$

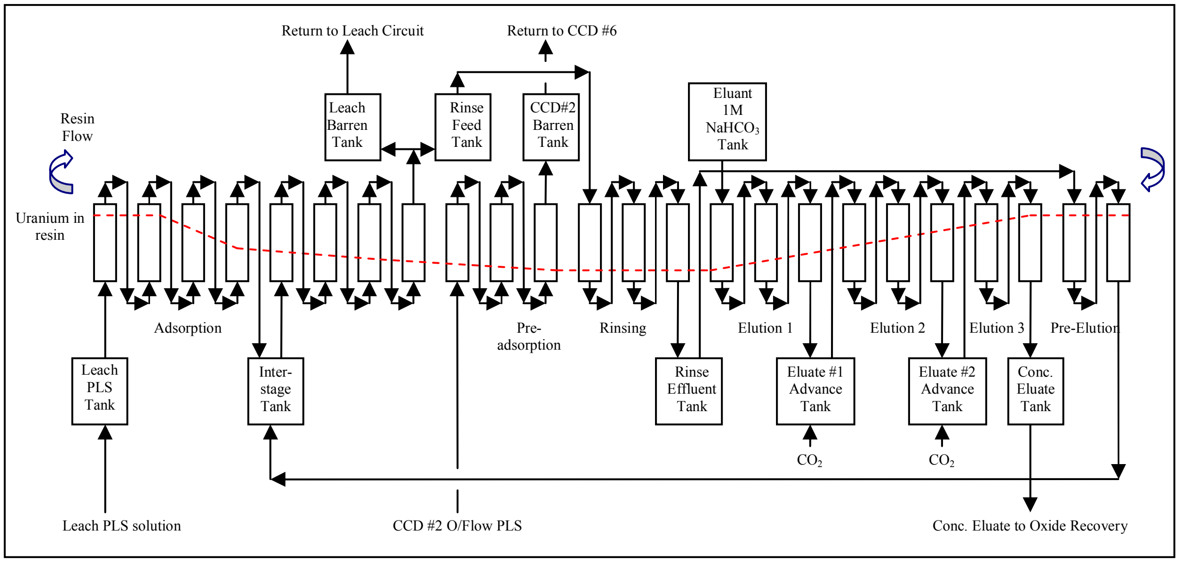

Figure 7: Initial Flowsheet

The enhancements from this initial phase of leaching are provided in Table 2 feature of which were:

1. The overall uranium recovery was low at approximately 94% from the leach PLS and approximately 90% from the CCD #2 overflow PLS
2. Net resin loading of 22g/L uranium was achieved and often exceeded.
3. Final concentrated eluate of 8.5g/L U was considerably lower than the target of 15g/L U.

Solution Assays – g/L								
Assay	**U**	**Na**	**P**	**Mo**	**Si**	**SO_4**	**Cl**	**pH**
Leach PLS	0.234	13.020	0.082	0.000	0.018	1.593	0.027	10.5
CCD #2 PLS	0.095	11.510	0.095	0.000	0.012	1.419	0.020	10.3
Eluant	0.028	22.460	0.072	0.001	0.027	1.494	0.017	9.2
Rinse Feed	0.011	15.560	0.116	0.001	0.014	1.877	0.027	10.6
PLS Barren	0.014	13.330	0.084	0.000	0.017	1.575	0.024	10.6
CCD #2 Barren	0.011	12.120	0.098	0.000	0.012	1.135	0.071	10.1
Eluate 1	2.990	28.790	0.026	0.001	0.007	0.551	0.131	8.7
Eluate 2	13.940	28.170	0.007	0.005	0.001	2.275	0.040	8.7
Concentrated Eluate	8.370	26.420	0.058	0.000	0.004	3.392	0.131	9.4

Table 2: Typical solution assays achieved from the initial flowsheet

4.2.3 Enhancing Eluate Concentration

The rapid turnaround of profile solution assay across the continuously operated pilot plant permitted changes to the flowsheet. Several variations were considered, however, the final circuit that was derived from this cycle of testing was that shown in Figure 8.

This flowsheet incorporated:

- Leach PLS entrainment displacement after extraction employing the eluant entrainment displacement barren.
- A pre-elution step in which some concentrated eluate was employed to displace the interstitial fluid in the loaded resin column before advancing into the elution step. The barren fluid from this pre-elution step contained a small quantity of sacrificed eluate that was released to the leach PLS tank.
- An eluant concentration increased to 1.3 Molar sodium bicarbonate.
- The split interstage eluate carbon dioxide gassing was retained to convert eluted carbonate to bicarbonate, and
- A bicarbonate elution step prior to the pre-adsorption step.

The removal of several adsorption stages was required to incorporate the above changes.

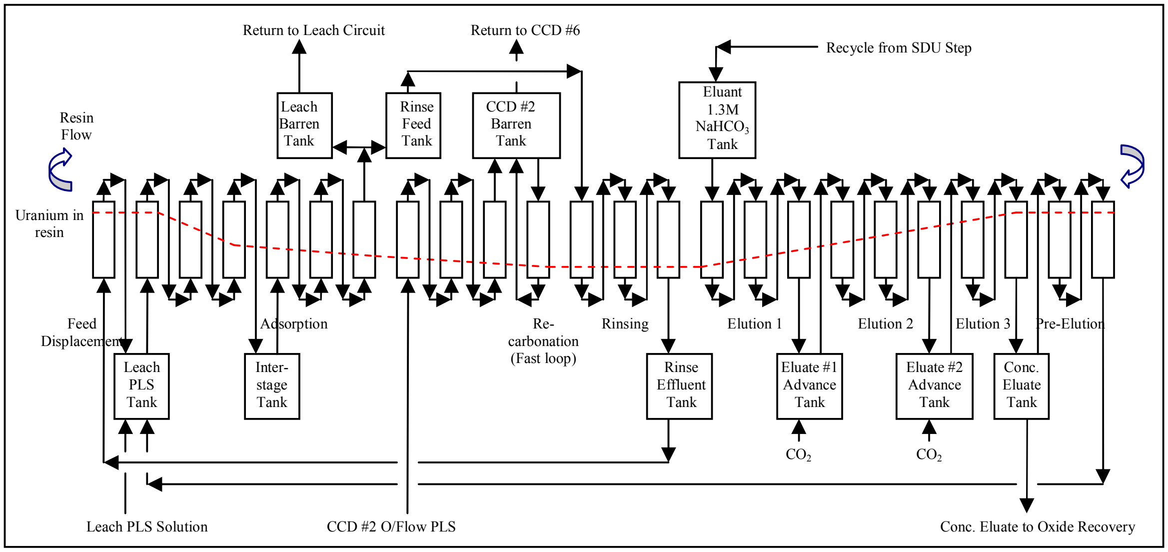

Figure 8: Final CIX Pilot Circuit Configuration

The final stages of the pilot plant yielded the results shown in Table 3. Of importance here was,

- The leach PLS uranium recovery increased a further 4% and that from the CCD#2 PLS by 7-8%.
- Concentrated eluate to oxide production had a uranium tenor of 13.8g/L U (still lower than the target of 15g/L U) but commensurate with the low PLS tenor into adsorption.
- The leach barren liquor uranium levels were reduced below 5mg/L U.

Solution Assays - g/L								
Assay	**U**	**Na**	**P**	**Mo**	**Si**	**SO_4**	**Cl**	**pH**
Leach PLS	0.233	13.320	0.068	0.001	0.013	1.677	0.047	10.3
CCD #2	0.071	12.170	0.065	0.001	0.006	1.401	0.081	10.3
Eluant	0.238	39.900	0.000	0.015	0.000	2.524	0.145	8.7
Rinse Feed	0.002	11.430	0.076	0.001	0.015	1.287	0.061	10.3
PLS Barren	0.002	13.580	0.069	0.001	0.013	1.706	0.084	10.3
CCD #2 Barren	0.002	12.520	0.067	0.001	0.008	1.156	0.088	10.2
Eluate 1	4.281	39.030	0.050	0.006	0.017	2.371	0.229	8.7
Eluate 2	14.490	39.230	0.049	0.013	0.017	2.299	0.229	8.6
Concentrated Eluate	13.770	42.940	0.061	0.015	0.013	4.790	0.229	9.1

Table 3: Typical solution assays achieved from the final flowsheet

5. URANIUM OXIDE PRODUCT

The flowsheet that was employed in the production of the final oxide is shown in Figure 9.

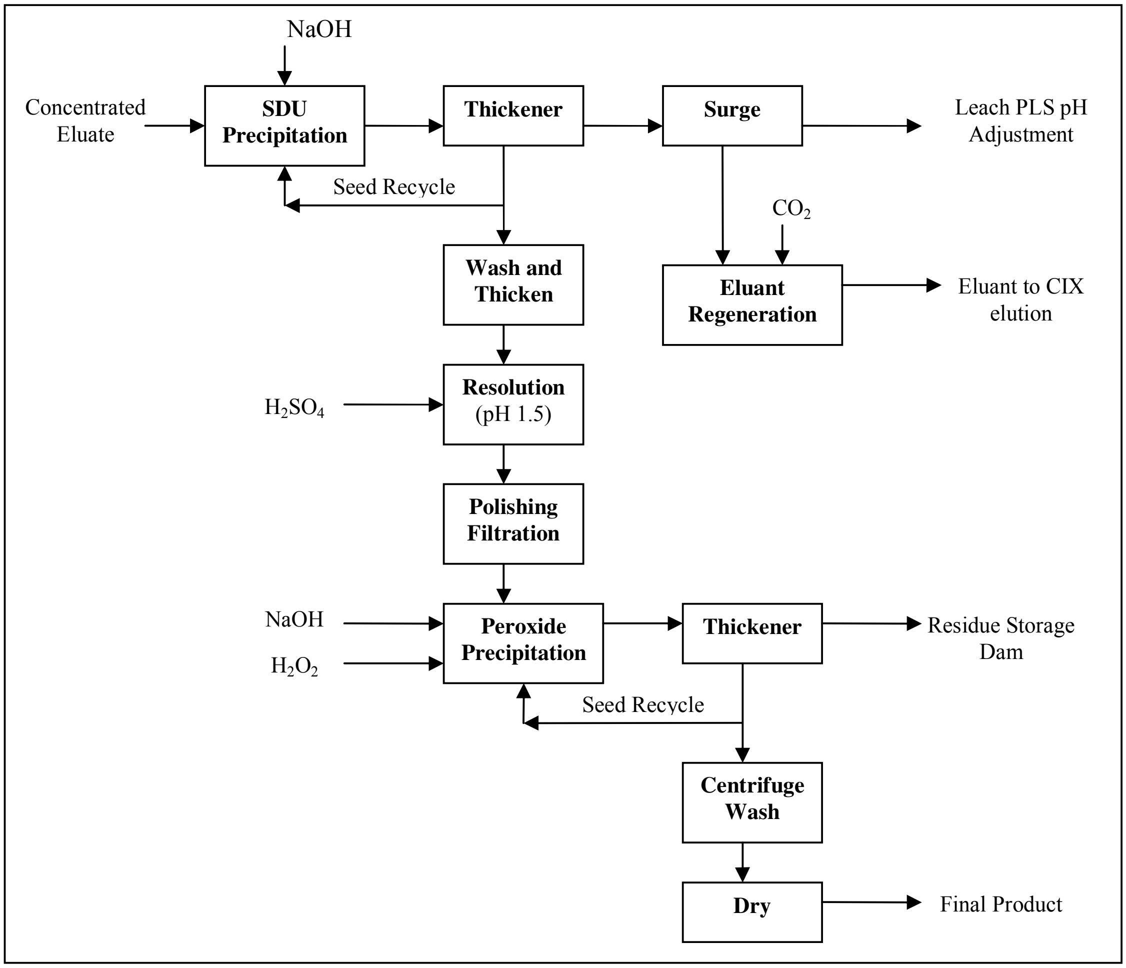

Figure 9: Uranium Peroxide Production Flowsheet

The concentrated eluate from the CIX circuit was converted to acceptable purity uranium peroxide. A sodium diuranate intermediate was produced in order to recover a barren that could readily be converted in part to the eluant for use in the CIX circuit. A bleed of SDU barren was always maintained to the leach PLS to adjust the pH prior to ion exchange. This pH adjusted step is particularly important when carnotite ores are processed and also assists in improving the selectivity of the resin for uranium over vanadium. The final product purity is as shown in Table 4.

Solid Assays - %										
Assay	U	Na	Ca	P	V	Mo	Si	SO_4	Cl	CO_3
SDU Precipitate	62-68	6-8	0.001	0.01-0.3	0.07-0.1	<0.001	0.2-0.8	0.03-0.15	0.001-0.03	0.5-3
UO4 Precipitate	62-68	0.001-0.1	0.001	0.001-0.1	0.07-0.1	<0.001	0.01	0.03-0.4	0.001-0.03	0.05

Table 4: Typical solid assays for alkaline uranium leach

6. STEADY STATE MODELLING OF CIX SYSTEMS

Modelling of ion exchange circuit at steady state requires consideration of the batch nature the process. The modelling aspect is broken down into two sections,

1. Chemical
2. Physical

The chemical aspects cover the interactions of the resin with the solutions present in the circuit. Based on the solution concentration, flowrate and column configuration, the key variables that need to be determined are

- Resin Bed Volume Requirements
- Resin Chemical Properties
- Resin Chemistry

Physical aspects address the entrainment and impurity deportment issues that relate to the mechanical design of the unit. The key variables that need to be determined are,

- Resin Physical Properties (size & packing characteristics)
- Resin Inventory
- Column & pipe work Properties

Pilot plant data is used to calibrate the resin behaviour. Relationships can be developed to generate a predictive model of the resin for the PLS solution matrix. In order to gain a greater insight, samples of liquor can be taken from individual columns at any stage through the process. This allows the actual data to be cross checked against testwork data.

When the CIX unit is scaled up to production size, the physical change in the unit, and changes to piping volume can be modified to identify the change in interstitial solution hold up, and the change in mechanical impurity entrainment.

There are two separate ion exchange models. The first is the plug flow, the second is the flow dependent mixing option.

6.1 OPTION 1: PLUG FLOW

Plug flow is a simplified view of flow through the column. The interstitial liquor in the column does not mix with the incoming liquor. The displacement is volume based therefore a solution density can cause mass changes in the column when changing positions.

For high column flow scenarios, typically greater than 2 bed volumes, and low flow scenarios less than 0.4 bed volumes, are accurately represented by the plug flow column.

Shown in Figure 10 is an example of a 3 column displacement wash cycle. The assumption has been made that the station time (the time each column spends in a given position) is long enough to cause complete mixing of the two liquors. Alternatively if the step time was short, the two liquors can be left in their respective positions without mixing. The new flow of 1 BV is introduced to column 3, to displace entrained uranium in stream P105 and prevent it from reporting to stream P108.

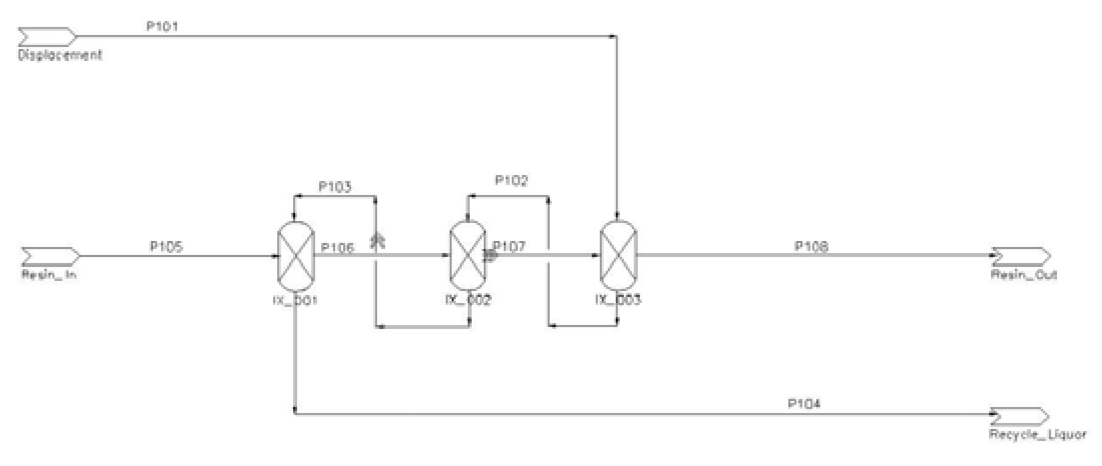

Figure 10: Three Column Displacement Wash Cycle Flowsheet

Stream Number		P101	P102	P103	P104	P105	P106	P107	P108
Stream Name		**New Liquor**	**Column 3 Discharge Liquor**	**Column 2 Discharge Liquor**	**Displaced Liquor**	**Resin In**	**Resin Transfer C1 to C2**	**Resin Transfer C2 to C3**	**Resin Out**
Total mass	kg/h	89	89	89	88	175	176	176	176
Solids	kg/h	-	-	-	-	100	100	100	100
Liquids	kg/h	89	89	89	88	75	76	76	76
Total flow	L/h	88.5	88.5	88.5	88.5	163.7	163.7	163.7	163.7
Solids	L/h	-	-	-	-	88.5	88.5	88.5	88.5
Liquids	L/h	88.5	88.5	88.5	88.5	75.2	75.2	75.2	75.2
Liquids Mg	kg/h	0.180	0.178	0.174	0.026	-	0.148	0.151	0.153
Liquids U_3O_8	kg/h	-	0.001	0.002	0.050	0.050	0.002	0.001	-
Liquids Mg	g/L	2.034	2.007	1.963	0.294	-	1.963	2.003	2.034
Liquids U_3O_8	g/L	-	0.009	0.023	0.568	0.664	0.023	0.010	-

Table 5: Example Mass Balance

As demonstrated in the example, all soluble uranium is displaced and prevented from reporting to the next stage.

6.2 OPTION 2: FLOW DEPENDENT MIXING

Flow dependent mixing is based on the flow characteristic of solution through an ion exchange column. The interstitial liquor is no longer directly replaced by incoming liquor. Depending of the number of bed volumes of new liquor introduced to the column, the amount of interstitial liquor that is ejected is a function of the resin hold up. This makes allowances for liquor that is held up in the resin and not subjected to the bulk flow through the column.

A typical curve of this system is show in Figure 11.

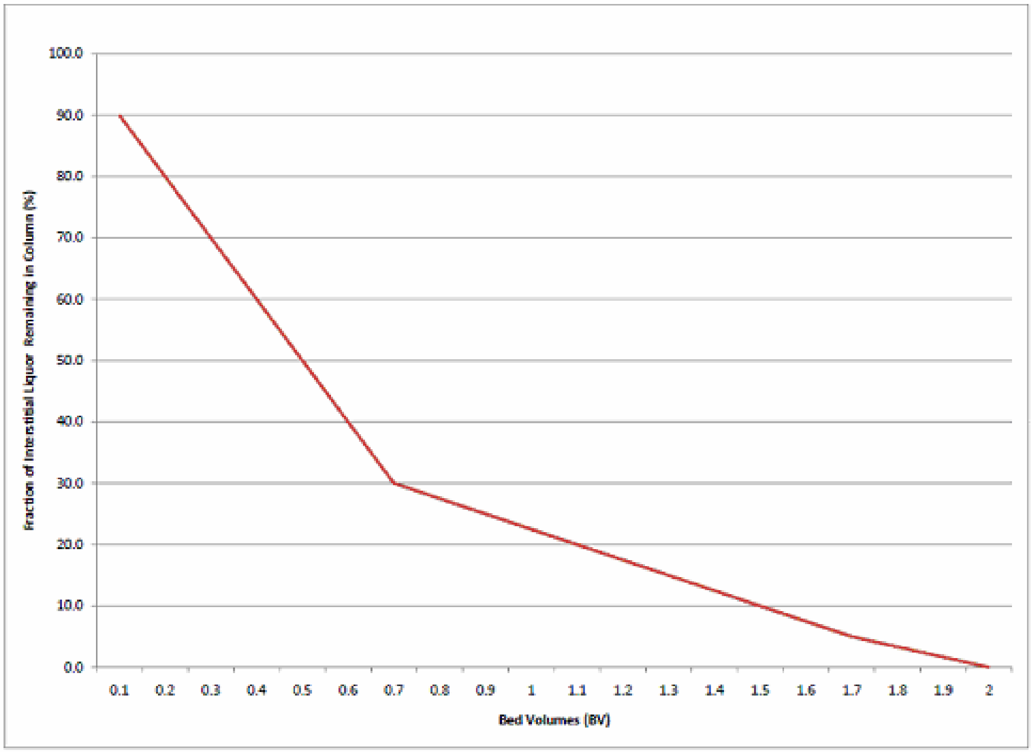

Figure 11: Interstitial Liquor in Column Vs Bed Volumes of New Liquor

7. CONCLUSION

The process to achieve both high first pass and high overall recoveries for uranium coupled with acceptable purity from the alkaline leach liquor has been described. The following steps played an important part in achieving these objectives

- The use of multicolumn ion exchange columns supported by an efficient rotary distribution valve of the type produced by Ionex Separations;
- Incorporating column interstitial liquor entrainment removal intervention;
- High concentration eluant with interstage carbon dioxide conversion of eluted carbonate to bicarbonate;
- Eluted resin reconditioning prior to adsorption;
- Incorporating the CCD#2 overflow into the ion exchange circuit to enhance uranium wash recovery, and
- Three stage split elution circuit.

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TOWARDS A FUNCTIONAL POLYMER FOR MINING

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CONTENTS

DOWEX™ Trademark of The Dow Chemical Company
AMBERLIT™ Trademarkk of Rohm and Haas

1. INTRODUCTION

To be sustainable, mining activities need to consider the environmental, social and economic impact. This directs mining companies towards technologies that will have the smallest environmental footprint. For this reason, recovery processes using solid resin beads for recovery is often preferred over the use of to liquid ion exchange for recovery (solvent extraction).

Ion exchange technology is well known and has been used for many years for the recovery of, for example, base metals, and precious metals and of those that are used for energy such as uranium, lithium, thorium etc.

With the dwindling global fossil fuel resources & a strong focus on CO_2 emissions & climate change, nuclear energy is seen as the safest, most viable energy module for the future. The efficient recovery of uranium has thus, once again, become strategic and of prime focus for The Dow Chemical Company.

This paper is a small reflection of some of the recent developments made in functional polymers, commonly called ion exchangers and in particular Strong Base Ion Exchange Resins used primarily in the field of Uranium recovery.

Mining operations such as ore retrieval, crushing/grinding, leaching, solid/liquid separation (CCD) and filtration are often complex and can impact the recovery of the uranium by ion exchange. Whilst all the preceding process engineering steps can be optimized and improved, there are some aspects of the process that are particular to the ore itself. One of these is the affect that a variety of foulents have in the resin performance.

In this paper, two known fouling agents will be used to illustrate how a functional polymer was modified in order to either reduce or eliminate some of the fouling issues.

2. SILICA FOULING [1]

The impact which silica fouling has upon the operating capacity, kinetic performance, elution characteristics etc. of strong base anion resins is considerable. Thus a good understanding of the fouling mechanisms is important if a remedy to decrease these effects is to be sought.

Ion exchange resin technology can be considered as a core system but the application of this core technology varies quite considerably between different recovery techniques. The different recovery techniques such as “In Situ Leach”, “Resin In Pulp”, “Heap Leach” and alkaline or acid leaching need to be considered. Each technique requires a specific ion exchange resin and load/elution technology.

To access the impact which some of these technologies, foulents etc. have upon the ion exchange resin, a simple matrix can be effectively used. Below is an example of a matrix that was used for a resin in pulp process (RIP).

$$\left\{\begin{array}{cccccccccc}
\text{Fe} & \text{V} & \text{Metals} & \text{SO4} & \text{Cl} & \text{Anions} & \text{Silica} & \text{Mechanical} & \text{Loading} & \text{Elution} \\
{++} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & {+/-} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & {+/-} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & {++} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & {++} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & {++} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & {+++++} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & {+++} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & {++} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & {+++}
\end{array}\right\}$$

Figure 1: Resin-in-pulp Process Matrix

Once the most important parameters included in the matrix are rated, the overall impact of all parameters of the resin matrix and recovery efficiency can be measured. This drives the choice of the resin type and hence its formulation.

If the above matrix is represented graphically (effects vs. parameter), the interdependence of each parameter can be more clearly seen. Thus if one resin property is modified to suit or improve a parameter (such as silica fouling for instance), the affect that this modification might have upon another parameter (such as loading or mechanical stability) is clearly visible.

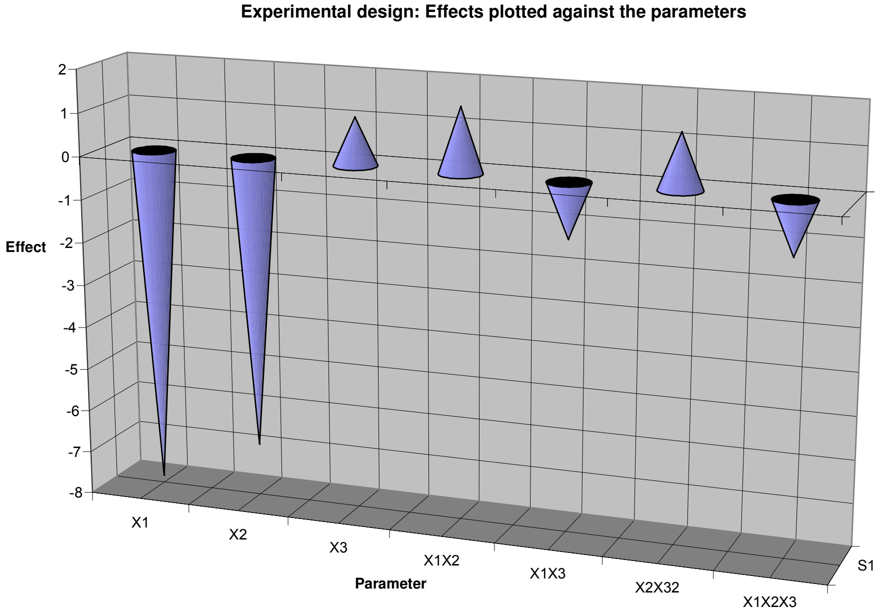


Figure 2: Experimental Design

Once such matrix is solved, the design of an ion exchange resin for the required application becomes possible. Solving such a matrix will also enable one to define a prediction model that will give the performance of the resin according to the parameters present in the leach solution.

Whilst several mechanisms have been presented before, the proposed mechanism was found to be essential in allowing us to design the functional polymer now used today and found to be most suitable for the recovery of uranium in the presence high silica concentration in acid (H_2SO_4) leach.

The solubility of silica is very dependent on the pH of the solution. In acid leach, silica solubility becomes an issue with respect to fouling of the ion exchange resin.
In alkaline leach, silica solubility and fouling of the resin is not an issue.

As can be seen in the graph below, the solubility of silica at pH ~2.00 (acid leach) is approx. 140 mg/l as SiO_2, whilst at pH ~10.00 (alkaline leach), solubility is approx. 600 mg/l as SiO_2. Thus silica tends to precipitate if acid leach concentrations exceed 140 mg/l as SiO_2.

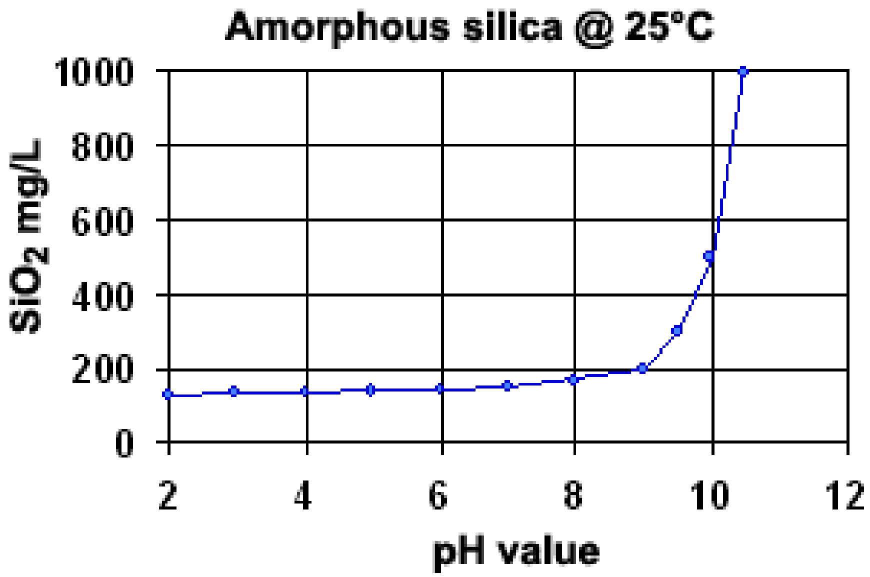
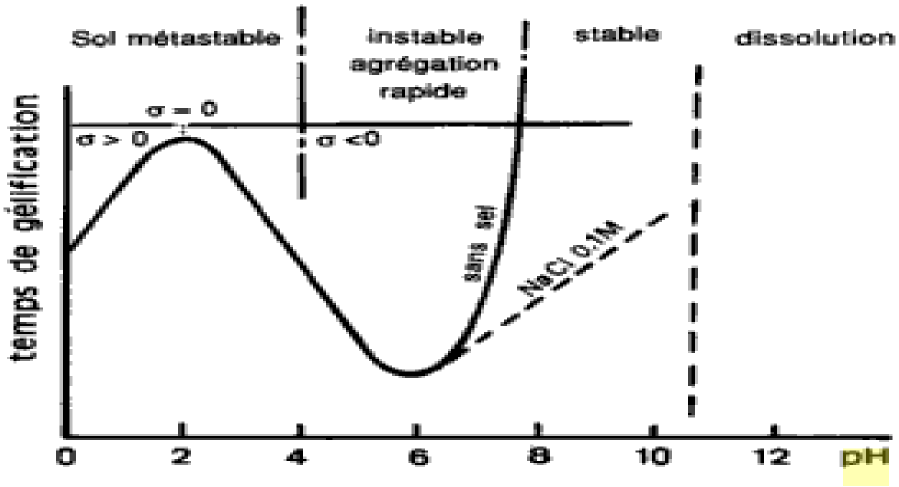


Figure 3: Silica Chemistry

However, another very important aspect which is not reflected in the pH Solubility graph above is the behavior of silica as a function of the pH.

As illustrated in the graph below, the behavior of silica varies as a function of the pH.

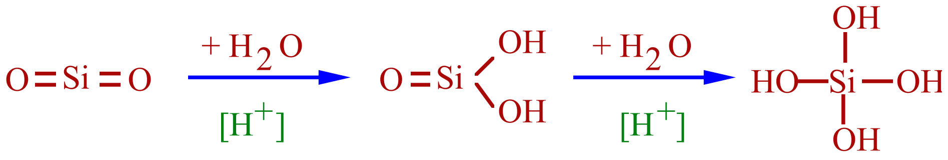


The graph shows the jellification time of silica as a function of the pH. According to this graph, in the acid region, the stability of silica is the best when the pH is around 2 and the worst when the pH is around 5 to 6.

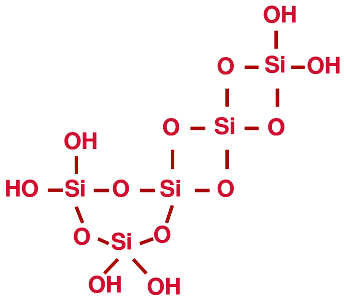
In acidic leach, the optimum pH for the recovery of uranium is around 2 (sulfate concentration of around 0.25 mol/kg in solution). So in principle, in acid leach situations, the stability of silica should be the best at pH 2.00. In practice, silica fouling of conventional resins is known to be extremely rapidly.

Clearly, this goes against what the above graph is showing.

- When comparing the differences between the observed fouling of gel and a marco-reticular resin structure, one theory used to explain this was the fact the silica exists as a polymer in acidic solutions and that the size of the polymer (Oligomeric silica - soluble particles 15 ~ 30 Å)



$$O{=}Si{=}O \xrightarrow[{[H^+]}]{+H_2O} O{=}Si(OH)_2 \xrightarrow[{[H^+]}]{+H_2O} HO{-}Si(OH)_2{-}OH$$



is such that it could easily enter into the macroreticular resin matrix (illustrated here below **[1]**)

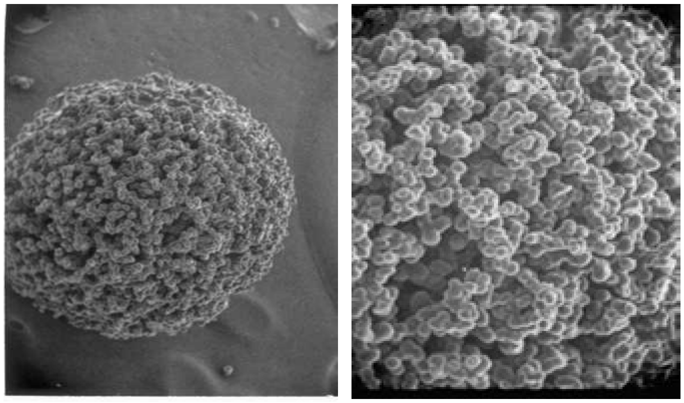


Figure 4: SEM of Resin Morphology

whilst it will not enter into the pores of a gel resin matrix structure.

To confirm this, a large molecule such blue dextran (MW = 2,000,000 g/mol) compared to the assumed silica polymer (MW = ~350 g/mol) was used. These molecules are by far bigger than the assumed oligomeric silica. However, it was clearly seen that this blue dextran molecule could easily enter into the resin gel resin structure and thus, the assumption of having a deposition of silica on the surface of the gel resin due to molecule size alone was excluded.

Therefore this complex silica fouling mechanism required further investigation.

In the quest for an explanation of this silica fouling mechanism, it was necessary to re-analyze and understand all phenomena that are taking place within the polymer matrix.

As previously mentioned, the optimum pH for the recovery of uranium in acid leach is around 2. The equilibrium model graph below shows the ionic form of the uranium molecule as a function of the concentration of sulfate in solution. **[1] [3] [4]**.

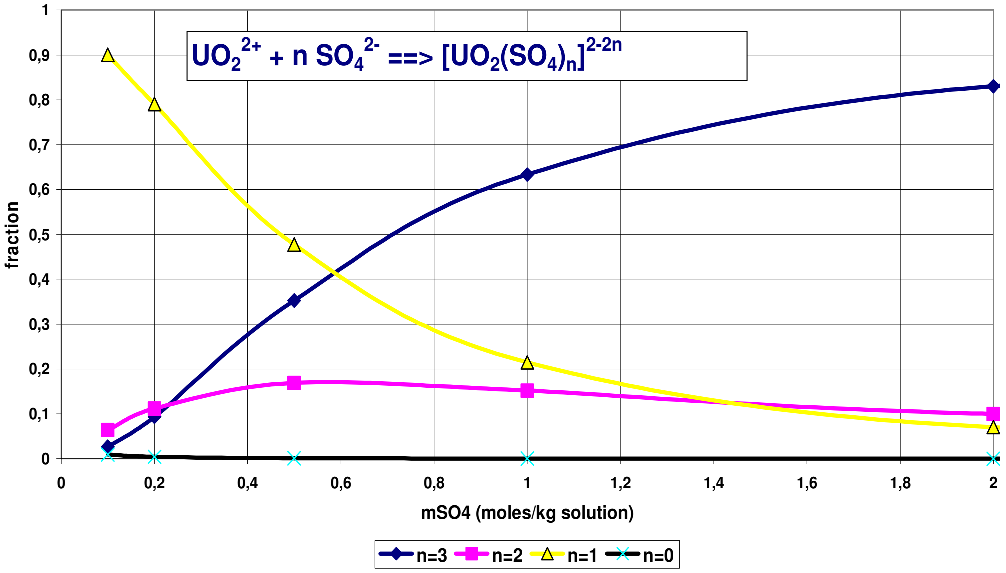


Figure 5: ionic form of the uranyl as a function of the concentration in sulfate

What could be seen is that at sulphate concentrations of 0.25 mol/kg in solution (pH~2), the <u>uranium enters in the resin as neutral species</u>.

At a higher sulphate concentration, the loading of uranium in the resin decreases which corresponds to the point where uranium is in negative charge form **[1] [3] [4]**.

The explanation resides in the Donnan potential concept **[2]**. The Donnan potential (sometimes referred to the Donnan Exclusion potential) has one immediate consequence for electrolyte sorption; it repels co-ions from the ion exchange resin and thus prevents the internal co-ion concentration from rising beyond an equilibrium value, which is usually much smaller than the concentration in the external solution. Thus, only the neutral species can easily enter the resin matrix while charged molecules or ions are repelled.

Silica is a neutral specie so it can enter in the resin matrix **[1]**.

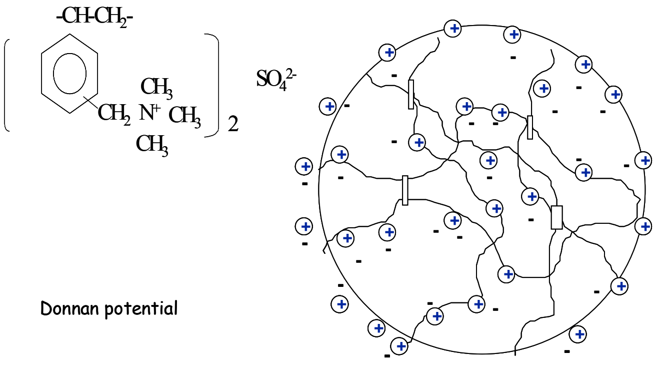


Figure 6: Donnan Potential

From the above we must conclude that silica can enter the resin matrix. However, some SEM pictures of a uranium loaded/silica fouled gel resin clearly show that the silica stays at the surface of the resin **[1]**.

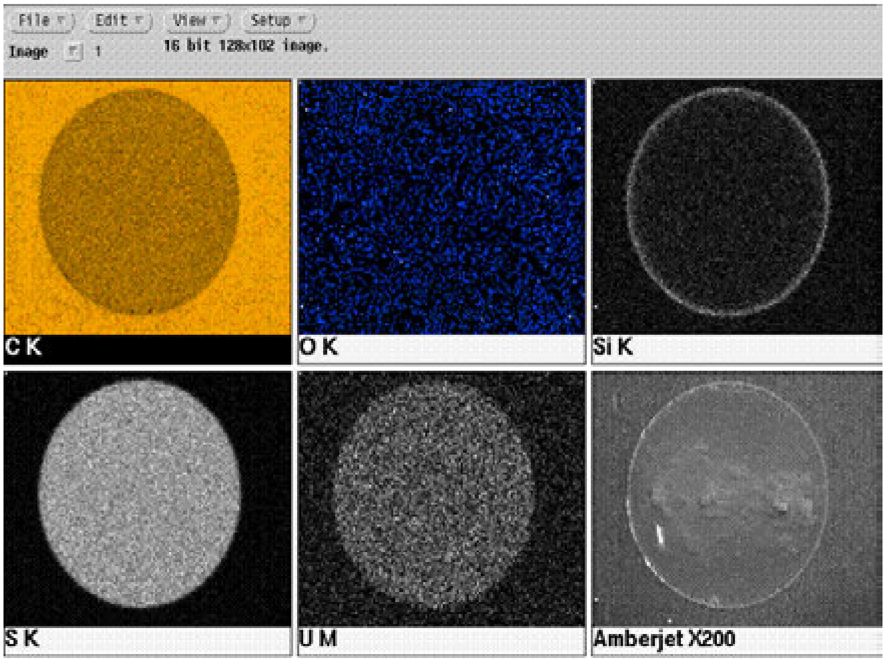


Figure 7: Silica mapping of gel resin

To understand the phenomenon, it is necessary to look at other properties that an ion exchange resin has. In fact, a resin bead is covered by a thin layer of liquid referred to as the Nernst film as illustrated in the picture below **[1]**.

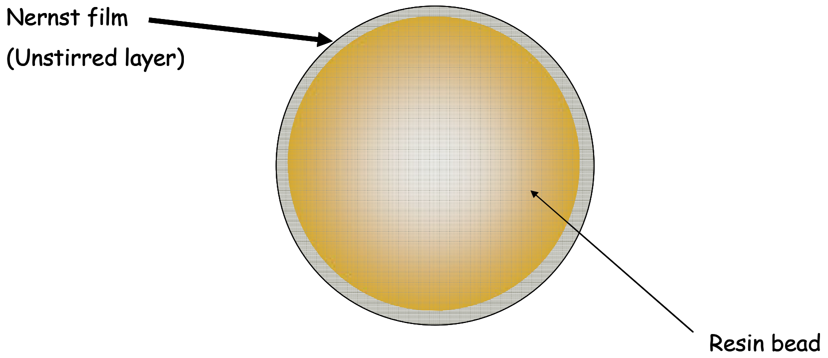


Figure 8: Nernst Film

To understand the phenomena that are taking place in this Nernst film, a simple analogy is made with an ion exchange membrane. Both the ion exchange membrane and the ion exchange resin in solution have this Nernst film and are subjected to the same osmotic forces. Ion exchange membranes can conduct a current so it becomes possible to measure all the phenomena that are occurring in the near vicinity of the Nernst film and at the surface of the membrane.

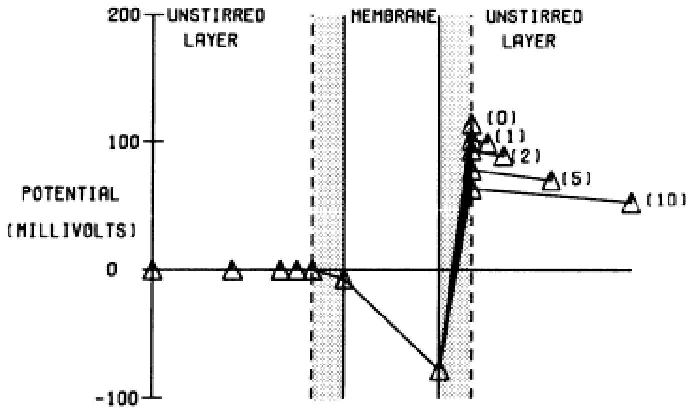


FIGURE 1 Electrical potential profile in the vicinity of a hypothetical ion exchange membrane with 3.0 M of negative fixed charge per liter of membrane water. Internal permeabilities assumed were: cation, 7.619 × 10^{-6} cm s^{-1}; anion, 0.218 × 10^{-3} cm s^{-1}. Bathing solutions contained 5.0 M/liter on the left, and 0.0015 M/liter on the right, of a 1:1 univalent electrolyte. The potential profiles illustrate the effect of assuming unstirred layers of 0, 1, 2, 5, and 10 μm thickness on each side of the membrane. The potential profiles superpose from left to right until they enter the Donnan layer on the low concentration (right) side of the membrane. The thicknesses of the membrane and the Donnan layers are not drawn on the same scale as the unstirred layer thickness. The stippled area indicates the Donnan layer.

Figure 9: Electrical Potential Profile

Based on the measurements it appears that the potential at the entrance of the Nernst film evolves through the thickness of the film.

The potential in the case of the uranium is directly linked to the pH of the leach solution. In fact the protons, which are positively charged, are excluded and hence, according to the Donnan exclusion principle, they are partially excluded from the inside of the resin bead. Thus, the potential can change up to 200mV.

Nernst law (E = -0,059.pH) for acid-basic solutions, links the potential or activity of a solution to the pH. The fact that the protons are excluded (Donnan potential) provokes an increase of the pH inside the resin. Thus for 200mV change in potential, the pH increase is equal to 3.38 units. It means that when the pH of the leach solution is equal to 2, the pH inside a resin immerged in this solution is equal to 5.4.

The picture below is illustrating the increase in of the pH through the Nernst film of the resin **[1]**.

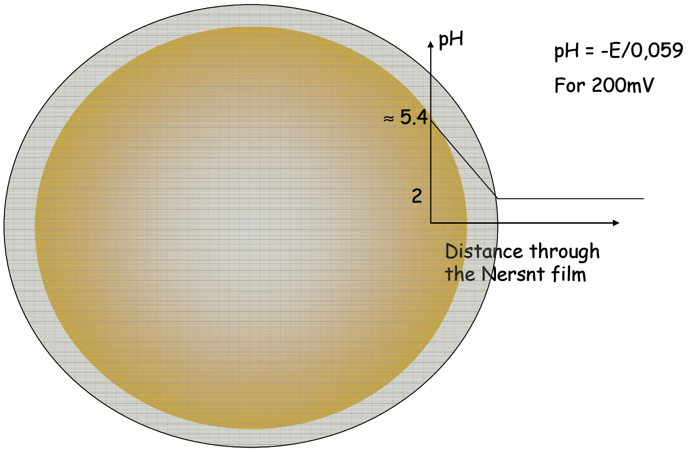
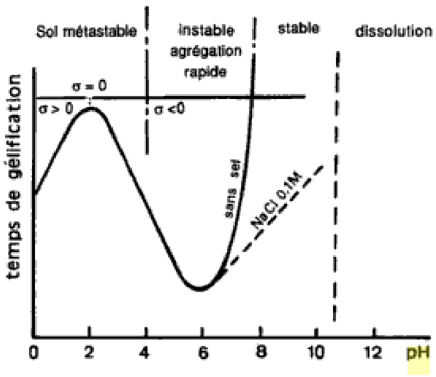


Figure 10: Nernst film and pH

Now, coming back to the stability of the silica as a function of the pH, it becomes obvious that the silica in solution at pH 2 is more stable than when the pH is at 5.4. Moreover, the sudden difference in pH across the Nernst film creates a mixing effect which amplifies the instability of the silica **[1]**.



The above data was used in the manufacture of an ion exchange resin with the aim to limit the change in potential through the Nernst film.

Again, some SEM pictures of a uranium loaded/silica loaded MR resin clearly show that the silica is not primarily loaded to the surface of the resin read but it continues to migrate through the resin bead **[1]**.

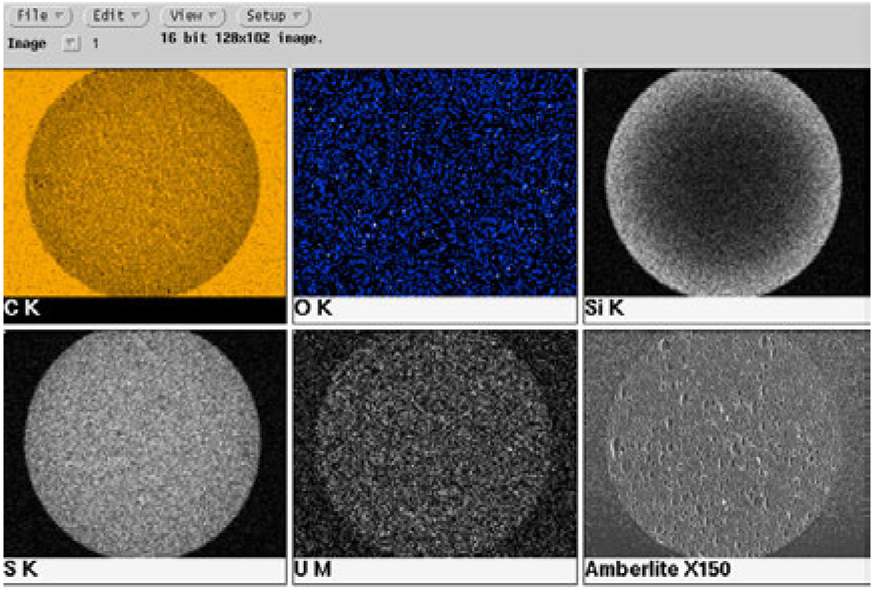


Figure 11: Silica mapping of Ambersep 920 SO4

The silica fouling mechanism is not prevented but retarded. This retardation permits its use in a solution matrix that is high in silica. The fact that silica is not precipitating on the surface of the resin bead allows the resin to continue to load/elute uranium, even when highly loaded with silica.

When the silica concentration in the resin bead becomes excessive, the resin is treated with a special caustic treatment which dissolves and removes the silica and the resin properties are fully recovered.

The frequency or cleaning is depending on the silica concentration in the leach solution.

In the case of a conventional ion exchange resin, the precipitation of the silica at the surface of the resin beads dramatically reduces the loading, results in increasing tails and long/incomplete elution cycles. For these resins, it is advisable to “regenerate” the resins on a much more frequent basis, in some cases, this is done on every load/elution cycle. Moreover, the osmotic stability becomes an issue because of the repeated caustic treatment (acid/base cycling) could lead to resin bead breakage, pressure drop issues and losses. In other words, not only the recovery of uranium is impaired but the whole process is affected.

Note: Other aspects such as the mechanical stability and resistance to attrition were also studied and led us to the formulation of a more resistant ion exchange resin. Such polymer finds its direct application in resin in pulp techniques. The technology that permits the reduction in the silica fouling effect on the functional polymer is an additive technology, also bringing a more attrition resistant polymer.

3. IRON FOULING

Iron is a known contaminant of uranium. It is possible to eliminate the iron from a concentrated eluate by precipitation but in some case the concentration of iron is so high that the precipitation process is difficult.

Unlike silica, the mechanism of iron loading will not be discussed suffice to say, iron (Fe^{3+}) is quite simple; it is loaded simultaneously with uranium. The intention here is to share some information about how the iron issue can be addressed or how the iron contamination on loaded resin (and conc. eluate) can be reduced.

As illustrated in the graph below **[1]**, it is clear that the uranium loading decreases as a function of the concentration of iron in solution.

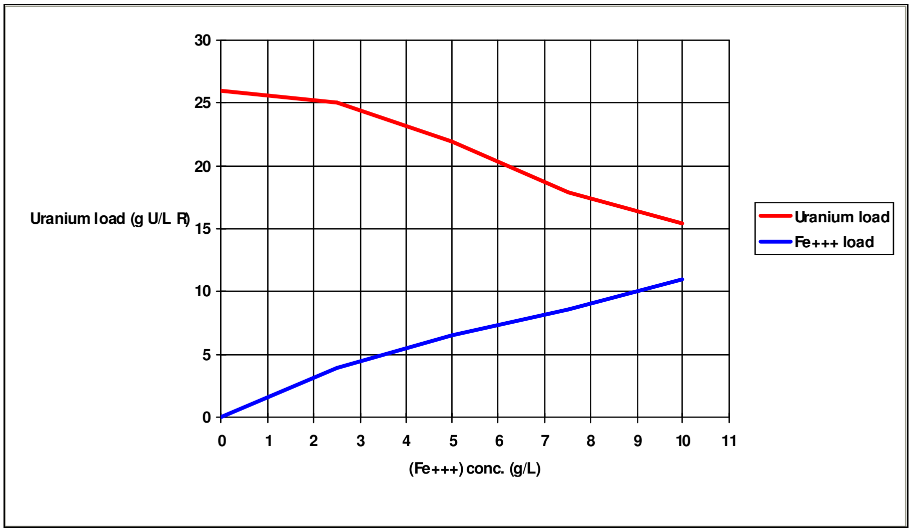


Figure 12: Effect of Fe+++ on Uranium loading

In fact ferric iron makes a complex with sulphate, just like uranium. So the mechanism of fixation of iron is similar to the mechanism of fixation of uranium as previously explained.

There are some possibilities to minimize the interference with iron during the uranium loading. Here again, the comprehension of the mechanism is essential. In fact the ions have all a so called intrinsic affinity. The formulation of the ion exchange resin is extremely important. In some case an ion exchanger can apparently exhibit very good performance in synthetic leach solution matrix but when presented with real/actual plant leach solutions, different behavior patterns are observed.

Below is a graphical illustration of the affinity of ferric iron with some different resin types **[1]**. The affinity can be measured in different manner but the most convenient way is to measure the ratio between uranium and the other element in consideration.

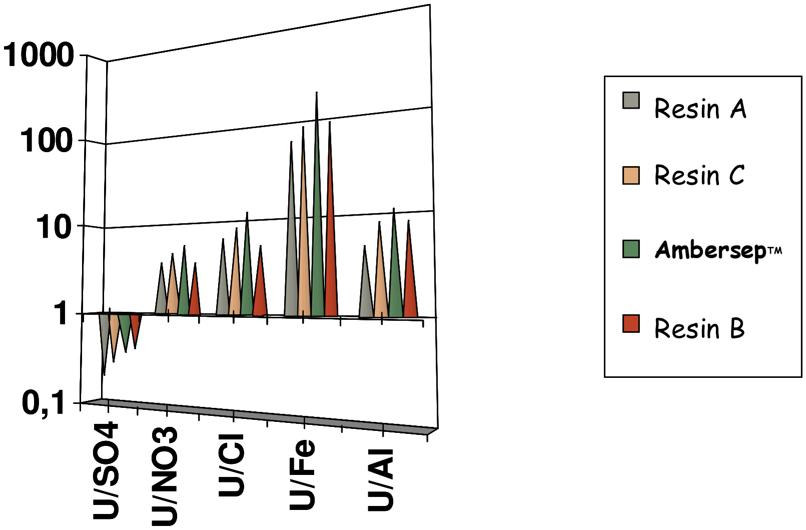


Figure 13: Affinity of verious resins for Uranium vs other common anions

Here again, the new formulation uranium specific MR resin, due to its unique formulation, exhibits the best behavior in the presence of not only iron, but also in presence of most of the known contaminants often present in leach solutions.

Having iron loaded simultaneously with uranium is one aspect. The elution of the iron off the resin is another. In some cases, iron is eluted together with the uranium, in other cases, the iron is irreversibly fixed by the resin. This is irreversible fouling can be explained by the very high affinity that a specific resin can have to the iron. In the SEM below **[1]** the iron is irreversibly loaded in the resin A, reversibly loaded in the resin B and only partly loaded into the new functional MR polymer.

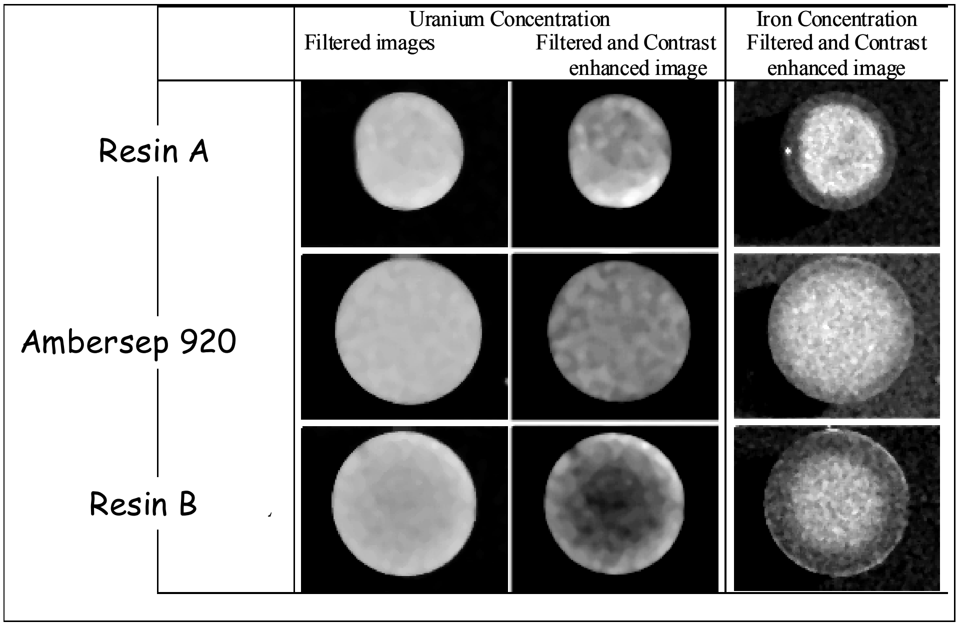


Figure 14: SEM iron mapping

The irreversible fouling of the resin with contaminants such as iron, leads to a constant decrease in of the operating capacity. Hence, the performance of the resin evolves cycle after cycle.

4. FUNCTIONAL POLYMER = COMMERCIAL ION EXCHANGE RESIN

[1] Fouling mechanisms are complex, some more complex than others. In all cases, fouling affects the performance of the ion exchanger which leads to a reduction in productivity, high leakage in the barrens and an increase in the operation cost with an increase in regeneration chemical consumption.

The correct functional polymer formulation should be in total alignment with the end use application.

We have demonstrated that there are some functionalized polymer resins that are currently in use which have been tailored to the application. For this reason, these “smart resins” have found wide acceptance globally for “smart applications” on an industrial scale, such as Resin In Pulp.

Some of the products developed have been tested, evaluated and confirmed by customers and we wish to thank all for their contribution towards this development.

Silica fouling, attrition and mechanical resistance, loading, elution properties are all very important and will remain a challenge and continued future focus as we, The DOW CHEMICAL COMPANY continue to develop functional polymers into commercial ion exchange resins..

5. TOWARDS A SEPARATION TECHNOLOGY

The complexity of uranium leach matrices varies from ore body to ore body necessitating different leach mechanisms such as acid, alkaline, pressure, heap leach etc. The composition of the ore bodies also vary geographically. The ore is leached by these different leach solutions and techniques to solubilise the uranium for extraction by either solid or liquid (solvent extraction) ion exchange systems. The leach is not selective for uranium so the different elements which are extracted can also interfere with the recovery of uranium leading to an overall reduced recovery efficiency. In some cases, the co-leached elements can even make the extraction technology impossible (c.a: iron in some solvent extraction applications).

Because of the complexity of the solution matrix, an alternative technology appears to become essential to address the issue. Separation technology certainly appears hence to be one of the most viable options as we adress these issues in the future.

The aim of this footnote is to share with the mining community some of the latest technology developments we are currently pursuing.

6. SEPARATION TECHNOLOGY [1]

The use of ion exchange resin in water treatment, nutrition, pharmaceutical, catalysis, chemical processing and mining applications is well known.

This wide variety of applications is partly due to the fact that ion exchange resins are made with inert polymers that have no footprint on the environment or health.

This wide range of applications is also spread across a wide range of technology.

In catalysis for instance, ion exchange resin is loaded with a metal ion and then used as a catalyst to facilitate a chemical reaction. Some interesting applications use ion exchange resin as a media which permits the separation of some species without fixing them into the resin. This technology is called chromatography.

Separation technology is often wrongly associated to requiring a very complex technology, requiring high pressure, very small flow rate eg Instrumental analysis using Ion Chromatography etc.

However, the separation technology developed for industrial scale is quite different from what is known in analytical applications.

With the development of new separation techniques, it is now possible to envisage the application of these in the sphere of mining.

In some cases, where solvent extraction (SX)technology is not possible (presence of contaminants), ion exchange technology could be applicable. Consideration of concentration (and recovery) of eluates can be carried out using acid/alkali resistant membranes. This is enhanced when element concentrations increase, placing these leach solutions outside the economical realm of IER and SX.

However, by using the ion exchange resin as a separation media, some appliucations become very viable. Once the separation of the elements is achieved, the recovery process by solvent extraction of electro winning becomes possible or facilitated.

Below is a picture illustrating the separation of several metals with a specific ion exchanger **[1]**. The metals are loaded simultaneously and separation of the metals was achieved by using a very specific eluent solution..

Ion exchanger used as a separation media

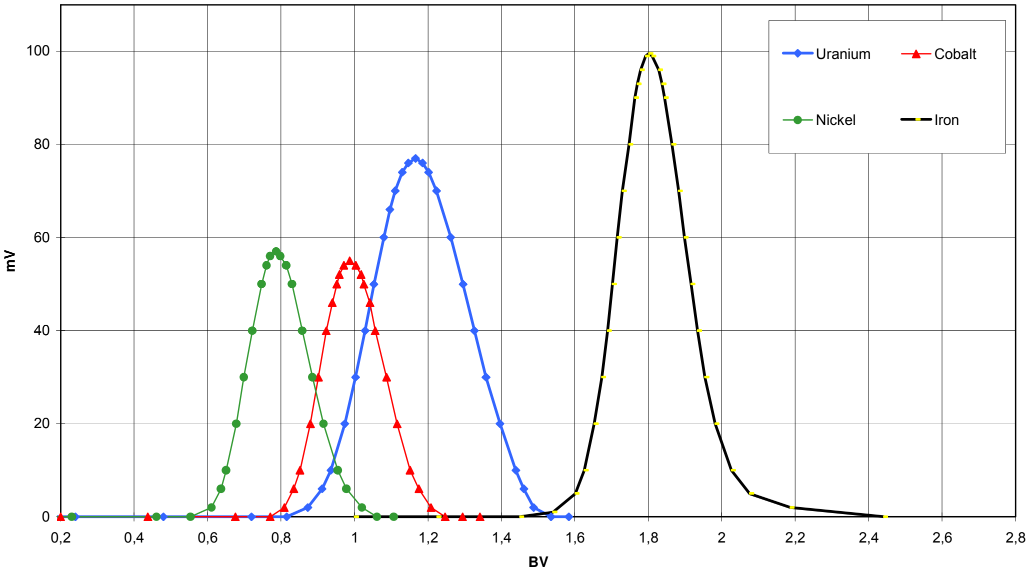


Figure 15: Gradiant pH elution of anion exchange

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THE ADVANTAGES OF TRUE CONTINUOUS COUNTER CURRENT ELUTION IN URANIUM PROCESSING

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CONTENTS

1. INTRODUCTION

Ion exchange is often used for the recovery and upgrading of uranium from sulphuric acid and carbonate leach liquors, especially for low grade solutions. Efficient stripping of the loaded resin is critical to limit equilibrium constraints in the adsorption circuit and ensure that targeted recoveries are achieved. A further objective is to produce an eluate or loaded strip liquor with as high as possible a uranium concentration, as it limits the downstream processing costs as well as determine the quality of the uranium product if direct precipitation from the eluate is considered. In order to target both these objectives simultaneously, a relatively large number of stripping stages as well as adequate strip liquor volume are required when the more common stripping agents are used. Batch, batch-continuous and true continuous counter-current elution processes are being used for stripping of uranium-loaded strong-base resins.

This paper details kinetic and equilibrium stripping data obtained using uranium-loaded strong-base resins and conventional eluants to highlight the contraints around the elution process. It also compares the advantages and disadvantages of different elution strategies, as well as the comparative costing for some of these options.

2. EQUILIBRIUM AND KINETICS OF URANIUM ELUTION

Very little information is available in the open literature that clearly shows the limitations around uranium stripping from a strong-base anion exchange resins using sulphuric acid or bicarbonate as strip liquors. Researchers often refer to uranium stripping as being slow, and hence that stripping periods of 12-30 hours are required for efficient stripping [1, 2].

2.1. URANIUM STRIPPING EQUILIBRIUM

Work done at Mintek shows that stripping of uranium-loaded strong-base anion exchange resins is strongly dictated by the associated equilibrium constraints using conventional eluants. The isotherms are reasonably unfavourable (linear), which indicates that in order to maximise the uranium concentration in the eluate, a large number of strip stages would be required [3, 4].

Figure 1 shows an equilibrium isotherm that was generated for a resin that was loaded to 25 g/L U_3O_8 from an sulphuric acid leach liquor, and using an eluate containing 110 g/L H_2SO_4. A Freundlich model was fitted to the experimental data, and the constants determined were as follows:

$$y = 0.35\ x^{0.89}$$

A McCabe Thiele construction on the stripping equilibrium isotherm indicates that 8 stages would be needed to achieve an eluate concentration of around 4.2 g/L U_3O_8. Increasing the number of stages to 20 would yield an eluate concentration of about 5.7 g/L U_3O_8. In both cases a stage efficiency of 70% was assumed. These results imply that a true continuous counter current elution system, which simulates an infinite number of stages, would be attractive to provide the maximum eluate concentration of 6 g/L U_3O_8 for a resin loaded to 25 g/L U_3O_8.

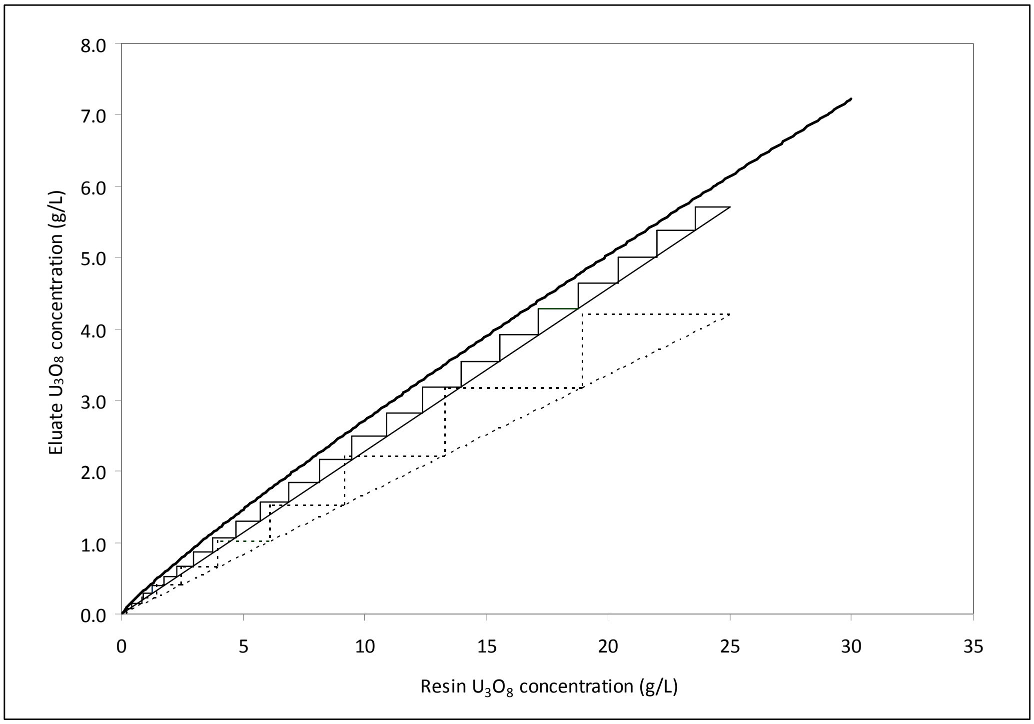

Figure 1: Stripping isotherm using 110 g/L H_2SO_4

Similar results have been obtained for carbonate systems where stripping was done using 1M $NaHCO_3$. Figure 2 shows an equilibrium isotherm that was generated for a resin that was loaded to 25 g/L U_3O_8 from a carbonate leach liquor, and using an 1M $NaHCO_3$ as the eluant. A Freundlich model was fitted to the experimental data, and the constants determined were as follows:

$$y = 0.1\ x^{1.04}$$

The maximum equilibrium eluate concentration achievable was 2.8 g/L U_3O_8 when the resin was loaded to 25 g/L U_3O_8. Figure 3 shows that 20 stages, at a 70% stage effiency, would only yield 2.1 g/L U_3O_8 in the eluate if the resin is to be stripped to a residual U_3O_8 concentration of less than 1 g/L.

Increasing the concentration of the eluate or strip liquor allow the strip equilibrium isotherm to be more favourable, although it was found to remain quite linear for H_2SO_4 concentrations up to 2M (Figure 3). However, a significant increase in the strip liquor concentration would cause higher osmotic shock of the resin and would generally have an adverse effect on the downstream processing costs.

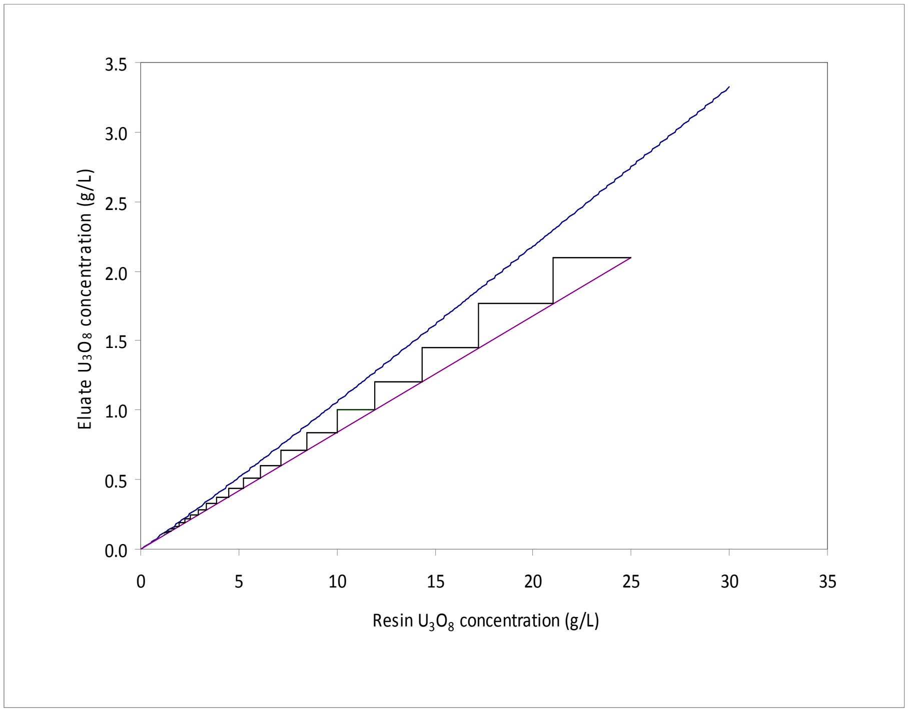

Figure 2: Stripping isotherm using 1M NaHCO3 and 20 stages.

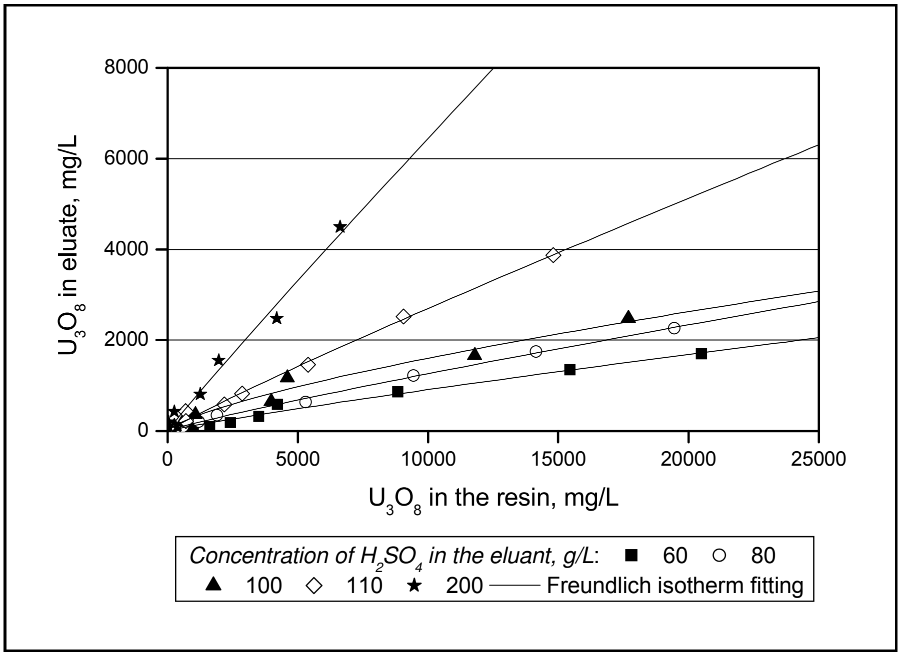

Figure 3: Effect of acid concentration on the stripping equilibrium profile

Stripping reagents containing relatively high concentrations of chlorides or nitrates would enhance the stripping equilibrium isotherm significantly, and would allow considerably higher eluate uranium concentrations to be produced. The stripped resin then would have to be regenerated using sodium carbonate or sulphuric acid prior to being recycled to the adsorption circuit. However, the use of nitrates or chlorides for stripping could potentially cause contamination of the plant waters with nitrates or chlorides, which are difficult to manage across the entire circuit. Once nitrates or chlorides enter the leach and subsequently the adsorption circuits, it would adversely effect the performance of the resin. Furthermore, the materials of construction for these solutions are more costly. Nitrate and chloride-containing eluants might also be environmentally unacceptable for certain applications.

2.2. KINETICS OF URANIUM ELUTION

Kinetic stripping tests were conducted to evaluate the rate of uranium stripping from the resins using 110 g/L H2SO4 as eluant at ambient temperature. Two strong-base resins, one macroporous (Macro) and one gel (Gel) resin, were tested. The mean resin particle sizes for the Macro and Gel resins were 807 µm and 780 µm respectively.

The Macro and Gel resins, fouled with silica to 15 and 9 % (m/m) of SiO_2 respectively, were pre-loaded to 30 g/L U_3O_8. Portions of the resin were contacted with 110 g/L of H_2SO_4 at a solution:resin ratio of 60 under vigorous agitation at ambient temperature in a baffled reactor. Eluate samples were taken after different time intervals and analysed for uranium. After 24 hours, the resin was separated from the eluate, rinsed with water and re-stripped consecutively with 10 BVs (bed volumes) each of 2 M HNO_3 and 1 M NaOH to ensure efficient stripping of uranium and silica respectively. The stripping profiles for the two resins are presented in Figure 4.

Kinetics of uranium elution was similar for both the resins tested. The rate of stripping the gel resin was slightly slower compared to the macroporous resin under the experimental conditions, including the level of silica fouling, evaluated. Uranium desorption was completed in less than four hours for both resins. The relatively fast kinetics of uranium stripping indicate that often the total volume of eluant or uranium equilibrium concentration in the strip liquor, and not elution time, could be the constraining factor for efficient uranium stripping from strong-base ion exchangers.

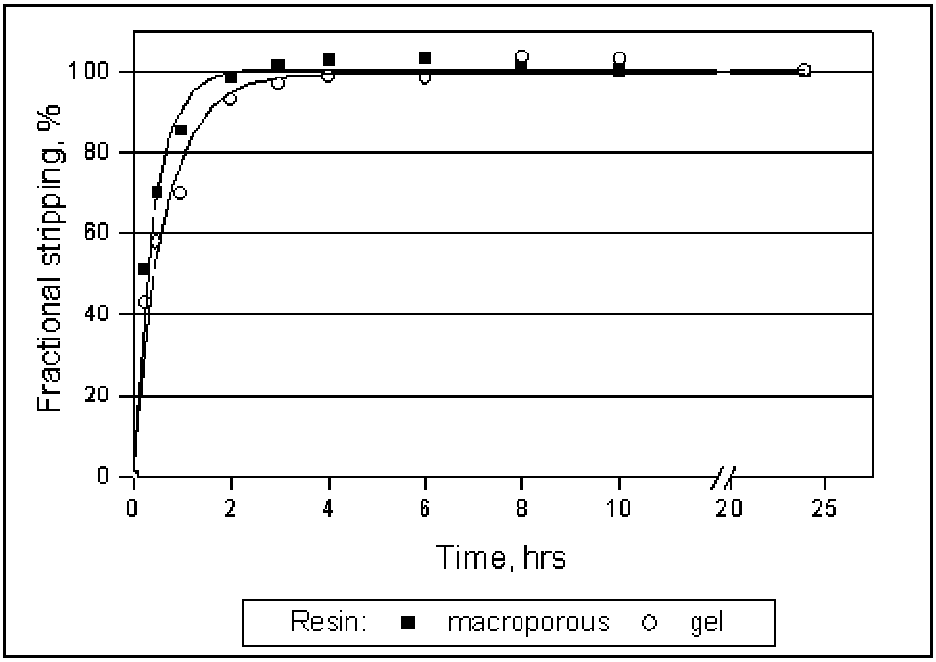

Figure 4: Uranium stripping profiles

2.3. EFFECT OF MODE OF FLOW ON ELUTION PROFILE

In order to accurately evaluate the effect of flowrate on elution it is important to ensure that the resin is loaded to the same level of uranium, hence that a bulk volume of resin is pre-loaded prior to conducting comparative stripping test work. When resin samples containing different levels of uranium are stripped, the results would be different and cannot be compared.

Figure 5 and Figure 6 compare the elution profiles obtained for a gel-type strong-base resin, loaded to 10g/L and 14g/L U_3O_8 respectively, evaluating upflow and downflow modes of stripping. Two different throughputs were evaluated on these resins, namely 6 and 1 BV/hr respectively. Results indicated that there was no significant effect on the elution profile when solution was passed either upflow or downflow through the resin bed at the flowrates indicated.

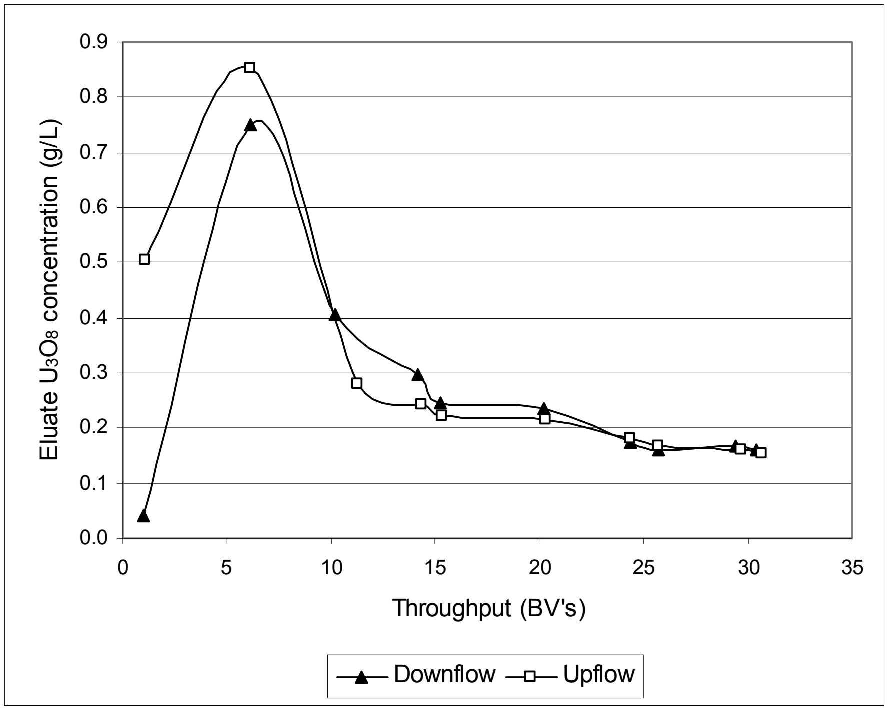

Figure 5: Effect of upflow vs downflow (6BV/hr @ 10g/L).

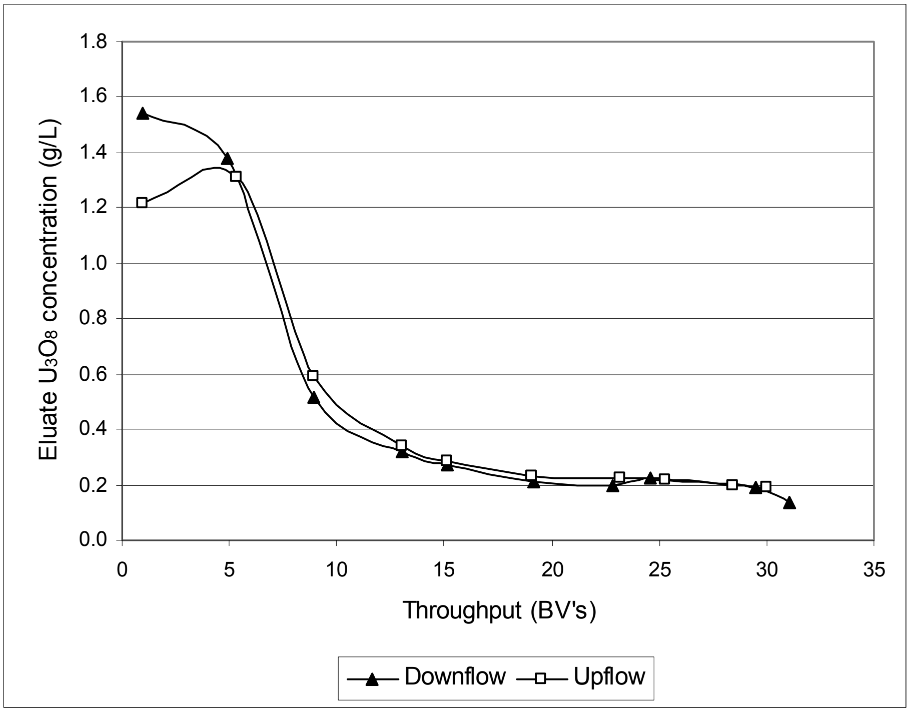

Figure 6: Effect of Upflow Vs Downflow (1bv/Hr @ 14g/L)

For both these tests 400 mL of resin were used. The flowrate employed were 2.46 L/hr (6 BV/hr) at a linear velocity of 5 m/hr, and 0.45 L/hr (1.1 BV/hr) at a linear velocity of 1 m/hr.

It should be noted that for the 1 BV/hr tests, where the initial uranium loading on the resin was higher (14g/L) than for the 6 BV/hr tests (10g/L), higher peaks were observed. For the 6 BV/hr downflow and upflow tests, 3.94g and 4.01g of U_3O_8 were eluted respectively. For the 1 BV/hr downflow and upflow tests, 5.58g and 5.65g of U_3O_8 were stripped respectively. This confirmed that the same amount of uranium was eluted with the same initial resin loading, irrespective of the mode of operation within the limits tested.

At very low linear velocities, gravitational back-mixing of the concentrated eluate might become a problem when flowing upwards through the bed [5].

2.4. EFFECT OF FLOWRATE ON ELUTION PROFILE

Some elution tests were done in order to evaluate the effect of flowrate or eluant residence time on elution efficiency. The flowrates were varied from 0.5 BV/h to 4 BV/h, and the elution was done passing the eluant down through a packed bed of resin. Results shown Figure 7 in indicated that there was no significant difference between the elution profiles vs bed volumes passed through the resin bed within the flowrate range evaluated.

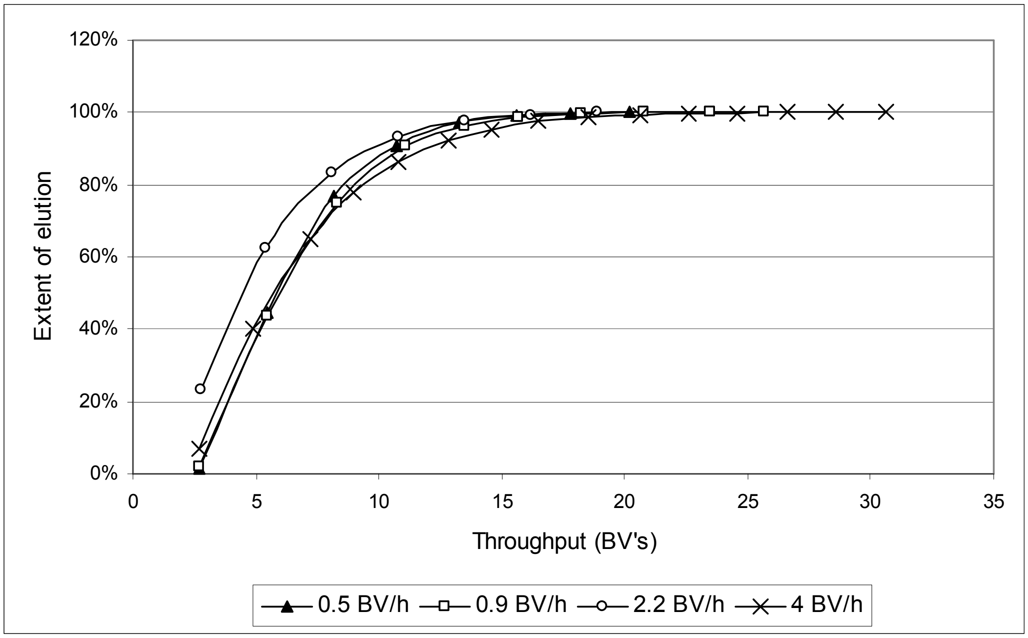

Figure 7: Effect of Different Flowrates on Elution

2.5. SUMMARY OF ELUTION PERFORMANCE

The following can be summarised based on the elution work described:

(i) Stripping equilibria for eluting uranium from strong-base anion exchange resins using conventional eluants (H_2SO_4, $NaHCO_3$) are unfavourable, hence in order to achieve the maximum uranium concentration in the eluate whilst stripping the resin efficiently, a relatively large number of stages would be required;
(ii) The rate of stripping uranium from gel and macroporous resins were relatively fast, with elution being completed within 4 hours (batch contact);
(iii) Downflow or upflow mode of operation provided similar elution profiles under the experimental conditions used, again indicating that the elution profiles obtained was as a result of the equilibrium constraints in the elution system;
(iv) Eluant flowrates of up to 4 BVs/h resulted in similar elution profiles, hence the efficiency of elution was primarily determined by the equilibrium constraints;
(v) In order to strip the resin to < 1g/L U_3O_8, a relatively large total volume (20-30 BVs for uranium loadings >20 g/L U_3O_8) of eluant have to be passed through the resin.

3. POTENTIAL ELUTION SYSTEMS

Once the equilibrium constraints around elution of uranium from strong-base resins were quantified, it was clear that in order to achieve as high a uranium concentration as possible in the eluate or strip liquor whilst still stripping the resin efficiently (<1 g/L U_3O_8 on the eluted resin), more focused attention was given to the design of the elution system. Elution systems can mainly be divided into three categories, referred to as:

(i) batch,
(ii) batch-continuous, and
(iii) true continuous systems.

3.1. BATCH SYSTEMS

Fixed bed elution is an example of a batch elution system. Although fixed-bed systems are hardly used for adsorption of uranium due to blockages when fine solids enter the column, they are still used for elution since there are no solids present in the eluate. The principles of a fixed-bed batch elution system is relatively simple. It requires additional resin holding tanks before and after the actual elution colum to accomondate the continuous adsorption circuit, as well as holding tanks for portions of the eluate to be recycled to build up the uranium tenor [1]. This results in higher capital costs for the holding tanks and for the relatively large resin inventory in the elution circuit. Hence, batch systems are comparatively expensive.

3.2. BATCH-CONTINUOUS SYSTEMS

"Simulated-moving-bed" (SMB) type operations simulate a continuous counter current process by having eluant flowing for a certain period of time through a series of fixed-beds and then periodically stopping the flow of eluant to move the fixed-beds counter-currently to the eluant flow by moving the locations at which streams enter and leave the columns. These systems have found widespread commercial application for liquid seperations in the petrochemical, food, biochemical, pharmaceutical, and fine chemical industries [6].

The Outotec SepTor, Calgon ISEP and IONEX IXSEP-RDA (Rotary Distribution Apparatus) System are examples of such systems and are used to load, strip and wash the resin. There are a number of advantages to these systems, including the fact that they can have a relatively large number of stages (up to 30 mostly) [8, 9, 10]. These stages are usually divided into loading, washing, elution and regeneration duties and can be arranged to operate in parallel or in series [7]. Figure 9 shows the SepTor Continuous ion exchange system. An option would be to utilise the entire system for uranium elution, coupled to any type of adsortion system.

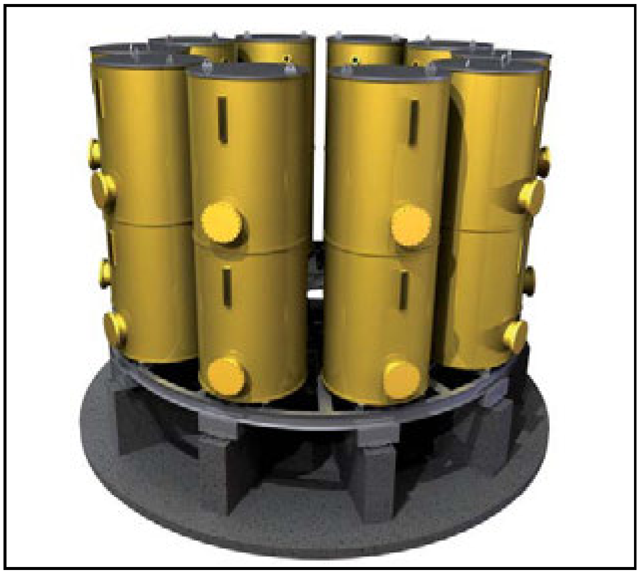

Figure 8: Septor Continuous Ion Exchange System [8]

Other advantages of these systems are that, due to the smaller stages and frequent transfers, a relatively small resin inventory is needed for these systems. The elution and regeneration steps can also be done on the same train, which minimise the overall footprint of the process. The frequent transfer of resin from and to the adsorption circuit would probably make this technology somewhat complicated.

Fluidised bed columns follow the same principles as SMB's. The NIMCIX columns have discreet stages in a column and eluant is passed upflow through the column, fluidising the resin in each stage. Loaded strip liquor or eluate is collected at the top of the column. After a period of time of forward flow, resin is withdrawn from the bottom of the column, thus achieving counter current movement of the resin and solution. Figure 9 shows a typical NIMCIX elution column setup [7].

The main advantages of these columns are that they are relatively easy to operate with significantly less mechanical parts than SMB systems. Here also, the resin inventory needed for the system is considerably less than in fixed-bed operations. The disadvantages are that the number of stages are limited due to height restrictions of the columns (1-m section seen as minimum to allow maintenance to be done inside each section), resin control between the stages could be a problem [1], and generally only a portion of the resin inventory in a stage is transferred. Transfer time is often limited to a minimum of 2 hours for ease of operation.

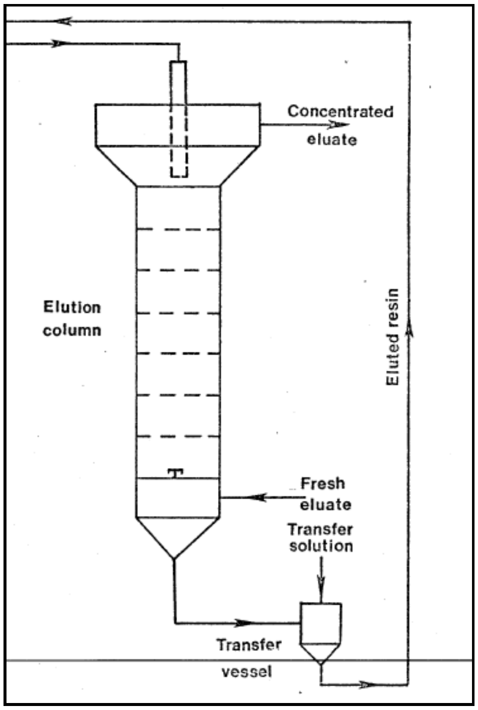

Figure 9: NIMCIX elution column [7]

Porter system is a patented system where pregnant solution is advanced through a series of tanks, each containing a volume of resin. Tanks are fitted with distribution manifolds to ensure good liquor distribution. The solution passes up-flow through the fluidised resin beds (in tanks). Some designs have utilised gravity flow throughout the train of tanks, but inter-stage pumps have been employed. Resin is advanced through the system counter-currently to the flow of pregnant solution. One tank of resin at a time is transferred to the adjacent tank, using an air-lift system. The flow of pregnant solution to the ion-exchange facility is unaffected by the resin transfer operations [7]. Although this system has only been reported for use as adsorption contactors, it can in principle also be used for elution. The disadvantage of this system is that although it is operated as a fluidised bed, it probably reacts as a hybrid mixed reactor and fluidised bed, hence its stage efficiency would be lower.

3.3. TRUE CONTINUOUS COUNTER-CURRENT SYSTEMS

The principle of a true continuous counter-current system is that it would similate an infinite (or very large) number of stages due to its plug flow nature. It also has an important advantage, as it maximizes the average driving force for mass transport. Figure 10, obtained from modelling an uranium stripping operation using a 110 g/L sulphuric acid solution, shows clearly how the overall resin inventory decreases as the number of stages increases.

The system was modeled so that the resin entering the elution column contained 25 g/L U_3O_8 and that the eluted resin should have less than 1 g/L U_3O_8. The resin flowrate was taken at 1 m^3/hr. In all instances the eluate concentration was set at 5 g/L U_3O_8, so the eluate flowrate remained constant at 4.8 m^3/hr with only the stage size and transfer intervals changing. This resin volume calculated includes the resin inventory needed before the actual elution column in each case.

These results indicate that a continuous counter-current system could have significant cost advantages. Because the system is operated continuously, relatively small resin inventories would be needed before and after the column, saving both on resin and capital costs. It would also be possible to achieve higher eluate grades that would be beneficial for direct precipitation, and more efficiently stripped resin to ensure efficient uranium recovery during adsorption.

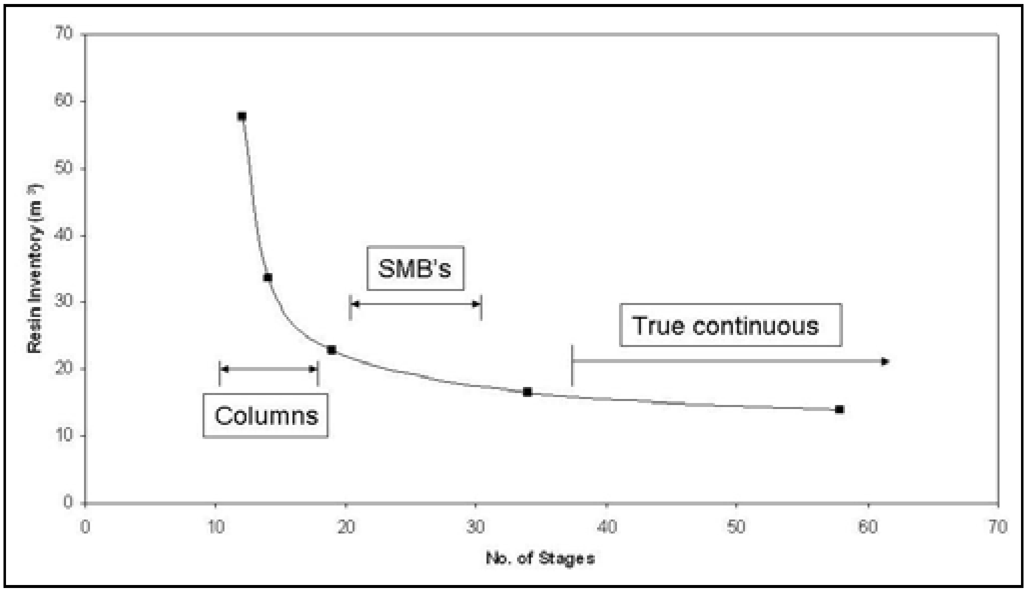

Figure 10: Resin inventory vs. number of stages

Continuous counter-current moving-bed systems, often referred to as “true-moving-bed” (TMB) systems, encounter operating difficulties, mainly due to failure in achieving plug flow of the resin and channelling of fluid through the moving bed [6].

3.3.1. Semi continuous: batch loaded

Himsley loading columns operate in a similar manner to NIMCIX columns, but for elution the Himsley system uses a counter current fixed-bed setup where loaded resin is rinsed and transferred to the bottom of the elution column, displacing an equivalent volume of eluted resin back to the top of the adsorption column. The eluant is passed down-flow through the column, counter-currently to the resin [7].

In certain mines in Kazakhstan a U-shaped column is used, which is operated as a batch continuous elution system. The saturated resin is transferred from the adsorption column and enters the elution column at one end of the U-tube. At every resin transfer, resin is pushed through until it reaches the opposite end, where it leaves the column as stripped resin. The eluant enters from the opposite end to where the resin enters, flowing in a counter current manner. Relatively high eluate grades are being claimed for these operations, but eluants containing nitrate are often used, which provides a sigificantly more favourable strip equilibrium than sulphuric acid [1].

CleanTeQ Ltd markets a patented U-tube elution circuit, called the Clean-iX® elution process, which utilises a counter-current operation to ensure a high uranium concentration in the eluate and a reduced resin inventory. The uranium concentration builds up in the eluate across the one leg of the U-tube and at a point close to the bottom of the U column, a zone exists where uranium on the resin is in equilibrium with a relatively high uranium tenor in the eluate (a concentration that would be allowed by the equilibrium for the specific stripping conditions, i.e resin loading and eluant composition). The eluate is removed at this point. According to CleanTeQ Ltd the eluate can contain a uranium concentration of 10-60 g/L (this would also be a factor of the type of eluant employed). A portion of this eluate is passed to the other leg of the U-tube, where the high uranium concentration in the eluate cause other loaded components/impurities to be displaced off the resin and report to the solution in the upward leg of the U column. Eventually these impurities leave as a waste stream exiting the column at the end where the loaded resin enters. This stream is recycled to the adsorption circuit to recover any uranium [11, 12]. The CleanTeQ U-tube elution column is shown in Figure 11.

Although the resin might be loaded batch-wise into the top of the U-tube, there are not individual stages as in the SMB systems or fluidised column. The resin and solution moves counter currently without disruptions and thus have an infinite number of stages if plug flow of both resin and solution can be assumed.

Figure 11: CleanTeQ's "U" column [11]

3.3.2. Current Mintek developments: true continuous

Mintek realised that, based on the relatively unfavourable stripping isotherm and the fact that as high as possible an eluate uranium concentration would generally be required, continuous counter-current elution would be attractive. Also, Mintek has done extensive work on Resin-in-pulp (RIP) technology that eliminates the need for solid/liquid separation upfront and where adsorption takes place in a true continuous manner. If RIP is to be used with a true continuous elution system followed by direct precipitation huge CAPEX and OPEX savings could be realised.

Mintek has been developing a true continuous counter-current elution system for stripping uranium from strong-base resins. The design of this circuit will remain unpublished until wrapping up of the development. One of the major problems being experienced has been solution and resin bypass. This will have to be minimised in order to ensure efficient performance of the system.

4. ECONOMIC EVALUATION

A basic economic evaluation of the different elution systems discussed above is shown in Table 1.

Table 1: Basic economical comparison of different elution systems.

	Fixed-bed	NIMCIX	Continuous	
Resin flowrate to elution	3	3	3	m^3/hr
Resin loading	25	25	25	g/L U_3O_8
Acid strength	120	120	120	g/L H_2SO_4
Stripped Resin concentration	1	1	1	g/L U_3O_8
Resin residence time	20	20	7	hrs
Elution resin inventory	102	134	72	m^3
Max. eluate grade	3.5	4.5	6	g/L U_3O_8
No. of stages		12		
No of columns	2	2	-	
Column height	4.7	13.7	-	m
Column diameter	2.6	2.0	-	m
Eluate flowrate	20.6	16	12	m^3/hr
U_3O_8 production	1.5	1.5	1.5	m lb/y
Estimated CAPEX	49.1	31.7	26.1	Rm
Estimated OPEX (excl resin loss)	4.65	3.95	3.50	Rm/year

For the continuous elution option, the design and operation of the system being developed at Mintek were used. Thus the design criteria have not been provided.

This analysis indicated that quite a significant CAPEX and OPEX saving could be realised for a true continuous elution system compared to fixed-bed and NIMCIX elution columns.

5. CONCLUSIONS

Test work at Mintek indicated that the stripping of uranium from strong-base anion exchange resins has a reasonably unfavourable isotherm. Kinetics of stripping was relatively fast. These observations were confirmed by elution of loaded resin in a packed bed, where the elution profiles were similar for flowrates of 0.5 - 4 BV/h, using upflow or downflow modes of operation. Hence, the most critical aspect to ensure efficient elution is to maximise the volume of eluant to be passed through any section of the resin bed. This understanding of the stripping of uranium is required in order to optimise the design of the elution circuit.

A true continuous counter current elution system, which is relatively easy to operate and maintain, will have an overall economical benefit for the stripping of uranium from strong-base anion exchange resins. One of the major advantages of a continuous system would be the higher uranium concentration that can be achieved in the eluate, hence downstream processing or direct precipitation of uranium from the eluate becomes more cost-effective. Resin inventories around the elution circuit could be minimised if a continuous elution system is employed, which would result in a significant CAPEX saving.

6. ACKNOWLEDGEMENTS

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A TECHNICAL EVALUATION OF ELUTION TECHNOLOGIES FOR URANIUM RECOVERY

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CONTENTS

1 INTRODUCTION

Ion exchange resins have been widely used for extraction and purification within the uranium industry for many years. Traditionally, batch ion exchange (IX) systems were widely used, however the last 30 years has seen the introduction of continuous countercurrent IX systems into the marketplace. This paper investigated the commercially available elution technologies for sulphuric acid leach environments to determine the ideal elution technology for each different uranium elution flow sheet. The study focused on 4 different commercially available elution technologies, namely:

Clean-iX® Continuous Straight Column Elution: Clean TeQ's continuous moving packed bed elution systems, where solutions are contacted with resin in a continuous counter-current mode.

Clean-iX® Concentration Desorption U-column Elution: Clean TeQ's U-column utilises a concentration desorption process to maximize product concentrations and minimize impurities.

Carousel/Batch Elution: The carousel elution system consists of 3 columns in series with two columns in operation and one column loading/unloading resin.

NIMCIX® Elution: Originally developed by the National Institute for Metallurgy (NIM), the NIMCIX elution occurs in a series of fluidised stages inside a column.

For each elution technology, a process flow diagram and mass balance was developed based on a typical uranium acid leach design criteria. From the mass balance a high level mechanical design was completed to allow comparison of the following parameters:

- OPEX/CAPEX
- Performance (uranium recovery and iron scrubbing)
- Operability (maintenance requirements, availability, etc)

A separate study was undertaken to determine the optimum combination of elution technology to a commercially available product recovery route for yellow cake production. The main unit processes considered in this analysis were:

- Elution (U-column and Straight/Carousel)
- Neutralisation (lime, magnesia and sodium hydroxide)
- Precipitation (peroxide and ammonia)
- Eluex (ion exchange/solvent extraction [AMEX])

A mass balance was constructed to estimate the reagent consumption for each unit process to allow a comparison to be completed. This paper summarises the available alternatives for each unit process to determine the potential optimum flow sheet.

2 ACID ELUTION SYSTEM COMPARISON

2.1 ELUTION PROCESS DESCRIPTION

For each system it was assumed uranium in the form of uranyl sulphate complex is stripped from an SBA (Type II) resin in the elution circuit and the eluted resin in the sulphate form is returned to adsorption. The adsorption system was assumed to be a carousel resin-in-pulp (RIP) plant, and therefore, suitable buffering capacity is required upstream and downstream of the elution system to allow for sufficient resin to be received and sent to RIP. While an RIP adsorption circuit was assumed, it should be noted that each elution technology can also be used in Heap Leach or ISL applications.

The uranium recovery for each elution was assumed to be the same for all technologies, at 98%. Each technology was designed to achieve this result. In the case of the U-column, there is a small amount of uranium that slips with the waste solution (0.5-1%) but the size of the elution plant has been increased to account for this. Other size adjustments were made based on the availability of the Elution column in "operation" mode due to its operating philosophy.

2.1.1 Clean-iX® Continuous Straight Column Elution

Clean TeQ's Continuous Straight Column Elution system utilizes continuous movement of the resin counter-currently to the flow of solution to ensure the driving force of reaction is maximised and reduces the resin inventory required in the system. The resin is intermittently transferred in and out of the column in small batches via an airlift. In each column, resin enters the top and is transferred from the bottom. Solution is pumped into the bottom of the column and overflows into a launder or through a screen. The following is a basic schematic demonstrating the flow of resin through the elution system:

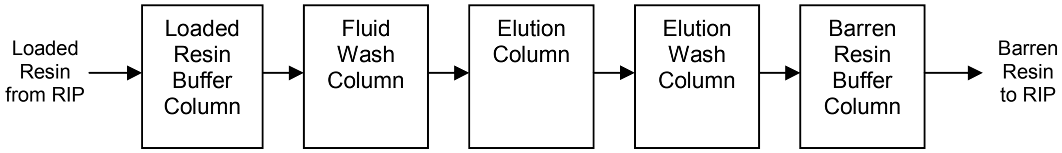

Figure 1: Block flow diagram of continuous straight elution

A brief description of the elution process is as follows:

1. Resin enters the Loaded Resin Buffer Column via a loaded resin screen, where it is separated from slurry and washed to remove any solids entrained with the resin. The column is sized to hold one batch of resin contained in an RIP tank.
2. Every 30-60 minutes a small batch of resin is transferred via an airlift from the bottom of each column into the top of the next column. The resin transfer sequentially starts from the end of the elution system (Elution Wash Column) and progresses back through the elution system one column at a time. During this transfer no solution is being pumped into the column. Once the transfer from that column is complete, the column returns to a run mode and solution resumes pumping. Therefore the "offline" time of each column is only 1-2 minutes.
3. The Fluidised Wash Column elutriates any fine solid particulates remaining on the loaded resin after screening by passing water up the column to momentarily fluidise the resin bed.
4. The Elution Column contacts clean loaded resin counter currently with fresh eluent to remove uranium and remaining impurities from the resin and return the resin to its sulphate form according to the equation:

   $$R_4[UO_2(SO_4)_3] + 2SO_4^{2-} \rightarrow 2R_2SO_4 + [UO_2(SO_4)_3]^{4-}$$

   Loaded resin enters the top of the column, where the solution with the highest concentration of uranyl sulphate complex is discharged. Fresh eluent solution (H_2SO_4) enters the bottom of the Elution Column counter currently to the flow of the loaded. As the eluent solution flows up the column, uranium as uranyl sulphate complex ion is stripped off the resin. Concentrated eluate solution (uranyl sulphate complex) overflows from the top of the column.
5. The Elution Wash Column uses raw water to wash excess eluent (sulphuric acid) from the resin. The overflow from this column is sent to an eluent make up tank. This ensures any entrained acid on the resin is recovered to eluent make up to minimise reagent consumption.
6. The Barren Resin Buffer Column holds one batch of barren resin for transport back into the adsorption circuit. After an RIP tank has been emptied and cleaned, the column is pressurised using air to push the resin from the bottom of the column into a resin distribution manifold, allowing resin to enter any one of the RIP tanks.

2.1.2 Clean-iX® Concentration Desorption U-Column Elution

The concentration-desorption process is different from a conventional Carousel or Straight column elution as it uses the selectivity of the resin for uranium and continuous nature of the process to produce a high tenor, high purity, concentrated eluate solution. In all other elution systems, there is a dilution effect on the product eluate from elution. Typically the concentration of uranium is reduced by a factor of 2-5 times in the product eluate when compared to the loaded resin capacity (a dilution "factor" of 2-5). The concentration-desorption process occurring in the U-column typically has a dilution factor of 0.5-1.0. The benefit of this is all downstream unit process size and reagent costs can be reduced.

Figure 2 shows a basic schematic demonstrating the flow of resin through the elution system:

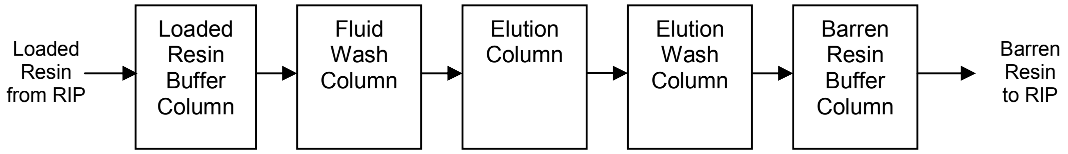

Figure 2: Block flow diagram of continuous U-column elution

A diagram of the U-column is provided in ***Figure 3***. Loaded resin enters the top of the left hand side (LHS) of the U-column as a moving packed bed and is transferred periodically out of the right hand side (RHS) by pressurising the LHS with plant air. Eluent in the form of sulphuric acid is pumped into the RHS of the U-column counter-current to the resin flow.

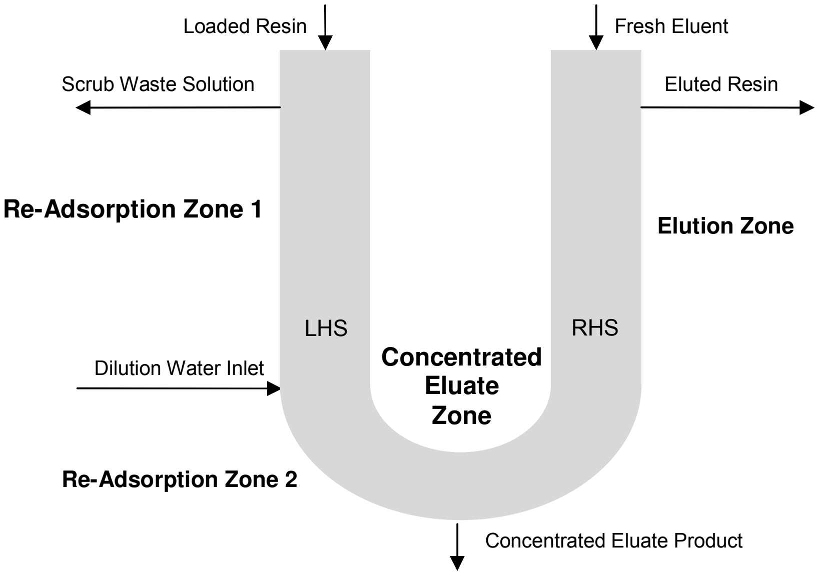

Figure 3: Stream nomenclature for the U-column

The following is a description of each of the areas of the U-column:

<u>Re-Adsorption Zone</u> 1	Resin in this area will be subjected to favourable adsorption conditions through the addition of dilution water. To ensure adsorption conditions are maintained in this section of the column, the sulphate concentration must be less than 50g/L. Under these conditions, the resin will selectively adsorb uranium in preference to the more poorly selected species, which have loaded under more favourable conditions in adsorption, i.e. such as Fe(III). As uranium replaces these ions they are displaced into the scrub waste solution. The use of water injection into the column is optional and is only required when high eluent concentrations are used to ensure adsorption conditions are achieved.
<u>Re-Adsorption Zone</u> 2	Resin in this area will be exposed to a high uranium concentration in solution created by the concentration effect at the bottom of the column.

	As the resin is exposed to a higher uranium concentration in solution than compared to adsorption, the resin will load to a higher capacity as predicted on the adsorption isotherm. The majority of impurities are chromatographically pushed off in favour of the uranyl sulphate complex.
Concentrated Eluate Zone	Resin is partially desorbed and is bathed in a highly concentrated eluate/eluent solution. This is the point of highest concentration of uranium in solution and is the point for product extraction.
Elution Zone	Resin in this area has exchanged all the adsorbed metals for sulphate functional groups and the resin is restored. The restored resin is now fully eluted and in the sulphate form.

2.1.3 Carousel Elution

While the stages of elution remain the same for both Carousel and Continuous elution modes, the main difference is a batch of resin is transferred from RIP and enters a column, where it remains for the entire duration of the elution cycle.

Each Elution Column holds 1 RIP tank volume (12-24 hours) of resin. Each column is a closed system where liquid travels in an *upflow* direction and exits via a "candle stick" drain to a valve manifold. From the drain manifold the solution is discharge to a corresponding inventory tank depending on the sequence in the elution cycle. All three columns are identical in design.

Once the resin has been loaded in the RIP circuit it is screened and washed to remove all the entrained slurry from the RIP circuit. Clean resin falls by gravity or transferred via a water eductor into one of three Elution columns. Once the column is full with loaded resin the elution sequence commences as outlined below.

Figure 4 is a basic schematic demonstrating the flow of resin through the elution system:

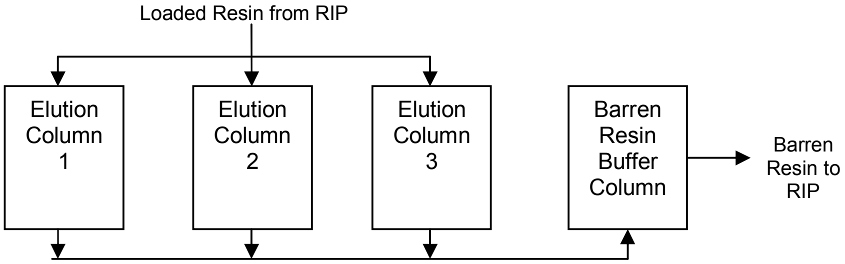

Figure 4: Block flow diagram of Carousel elution

Two columns are operating in series through steps 2 to 4 while one column is unloading and reloading resin. The elution sequence is described by the following steps:

1.	Resin Filling	Resin is pumped from the RIP tank via the loaded resin screen.
2.	Displacement	Eluent is passed up the column remove the water from the resin bed, limiting the dilution of the product eluate stream.
3.	Elution	The Elution process step contacts loaded resin with eluent to remove uranium and remaining impurities from the resin and return the resin to the sulphate form. The elution sequence is divided into three stages where fresh eluent is repeatedly passed through the column to build the uranium concentration in solution.
3a.	Product Elution	Eluent, which has already been passed up through the preceding column (steps 3b and 3c) is passed up the column to partially strip the resin and to build the concentration of uranium in the solution stream to its maximum. The solution exiting the column during this step is product eluate.
3b.	Recycle Elution	Eluent previously passed up the column (step 3c) is recycled through the column to further strip the resin and build the concentration in the solution stream. This solution is used for product elution.

3c.	Final Elution	Fresh eluent (H_2SO_4) is passed up the column to fully strip the already partially eluted resin. Solution exiting the column in this step is used for recycle elution. The resin after this step is now fully eluted.
4.	Elution Wash	Raw water is passed up the column to remove any entrained eluent in the resin bed. Solution exiting the column is sent to the eluent make-up tank.
5.	Resin Unloading	After washing, the resin is transferred to the Barren Resin Buffer Column for transportation into the RIP circuit.

2.1.4 NIMCIX Elution

The operation of a NIMCIX column is similar to that of a straight moving packed bed column with the key difference being the use of a series of fluidised stages, created by perforated trays in the column, forming discrete resin stages for ion exchange.

Due to the design parameters of a NIMCIX column design, it was found that operating two NIMCIX columns in series reduces the volumetric flow of the eluent (H_2SO_4) and product eluate considerably (see Section 2.2.2). Both single and two-stage NIMCIX elution options have been considered in this paper. The operation of both NIMCIX columns in the two-stage scenario are similar, therefore only the single stage NIMCIX process description is discussed below.

Figure 5 is a basic schematic demonstrating the flow of resin through the elution system:

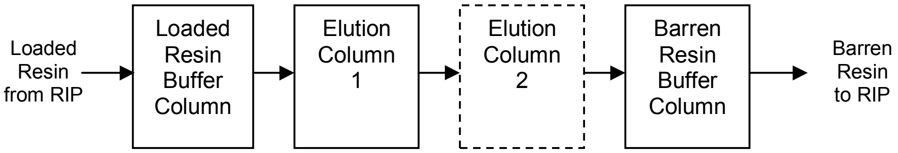

Figure 5: Block flow diagram of NIMCIX elution

Clean loaded resin enters the Loaded Resin Buffer Column and is transported at regular intervals into the Elution Column via airlift. The Elution cycle is comprised of 5 steps:

1.	Forward Flow	Eluent solution flows up through the column, counter-currently to the flow of resin. The flow of solution fluidises the beds of resin contained in each stage of the column, ensuring effective mixing of resin and solution. Once the solution has passed through all stages it overflows in to a launder where it flows by gravity to a tank.
2.	Settling	The solution flow is turned off allowing resin to fall through the perforations in each tray to the stage below. Depending on the settling characteristics of the resin in the solution, this only takes a short amount of time.
3.	Reverse Flow	A fixed volume of solution and resin is removed from the bottom conical section of the column into a resin transfer vessel using a pump. During this time, resin continues to settle from one stage to the stage below through the perforated trays.
4.	Delay and Flush	Solution is circulated through the conical section at the bottom of the NIMCIX column and the Resin Transfer Vessel, flushing any resin that may be contained in these sections into the resin transfer vessel.
5.	Resin Transfer	The Resin Transfer Vessel is isolated from the NIMCIX column. Hydraulic pressure in the Resin Transfer Vessel, created by the resin transfer pump, is used to transfer the resin into the top of the succeeding column. Typically this resin/solution stream passes over a dewatering screen. The dewatered resin enters the top of the next column and the underflow returns to the solution tank.

As dewatering screens are used after the NIMCIX columns, there is no elution wash step. As the NIMCIX column can tolerate higher solids in solution, a fluidized wash step is also not required.

2.1.5 Regeneration

Regeneration is required if there is a significant build up of impurities (e.g. silica) reducing the performance of the resin. Typically a dilute sodium hydroxide solution is used to reduce the silica content of the resin to acceptable levels. For the purposes of this paper, regeneration was not included in any of the technology designs.

2.2 RESULTS AND DISCUSSION

The following section discusses the relative advantages and disadvantages of each elution technology, focusing on hydrometallurgical performance, design, capital cost, operating cost and operability.

2.2.1 Performance

Loaded Resin Washing and Particulate Removal

Packed resin beds act as highly efficient particulate filters, capturing fine particles in the solution stream as it comes in contact with the bed. Batch/Carousel systems are particularly vulnerable to particulates, as the resin bed is moved very infrequently as it is exposed to a much higher volumetric flow rate of solution before it is transferred. Typically a TSS of <5ppm is acceptable in solutions entering into Carousel systems ensuring the pressure increase across the resin bed is minimised. In the case of the Carousel system in this study the resin is removed every 72 hours Therefore it is likely that higher TSS can be tolerated in solutions (~10ppm).

The Clean-iX® Straight and U-column elution technologies intermittently move the resin (30-120 mins). Therefore any solids built up in the resin bed are removed into a fluidised wash column for particulate removal. Typically, these technologies can tolerate up to 100ppm TSS in solutions before performance and operation of the column is affected.

The NIMCIX column operates as a fluidised column, and therefore the effect of particulates is greatly reduced. Typically NIMCIX columns can operate with up to 3% solids before operation and performance is affected. While this is an advantage for its use as an adsorption column, there can be no solids entering the downstream SX and uranium precipitation circuits. Therefore it is likely that the use of the NIMCIX column as an elution column will require some form of filtration to ensure any solids carried on the resin do not enter into downstream product recovery. It should also be noted that impurity metals present in solids can continue to leach out into the solution phase in IX feed and through the column. Therefore there is a risk that the impurity levels can continue to rise if solids are not completely removed from the loaded resin. The potential effect of this can be established during lab scale testwork.

Eluted Resin Washing

The methods for washing the eluted resin differ for each technology. Both the Straight and U-column elution technologies use continuous counter-current washing of the resin in a moving packed bed column to wash the resin. The Carousel column washes the resin bed volume after elution using *upflow* washing. The NIMCIX column utilises a static screen to wash the interstitial solution from the resin.

Incomplete washing of the resin can affect its performance in adsorption and therefore should be considered during detailed design. Washing with sprays or on screens (as in NIMCIX elution) will only remove the eluent that is carried with the resin. During the elution process, eluent is diffused throughout the entire resin bead, and therefore, time is required to allow for the majority of this to diffuse out.

Effect on Downstream Unit Processes

There are several different product recovery alternatives that can be considered for a uranium acid system. The two main process routes are direct precipitation (peroxide/ammonia) or SX followed by precipitation.

The suitability for direct precipitation over SX/precipitation is determined by the volumetric flow and uranium tenor of the product eluate stream from Elution. If the uranium tenor is sufficiently high enough, the reagent consumption in neutralisation prior to uranium precipitation is minimised and the direct precipitation option becomes the most economic alternative. Because of the concentration effect occurring in U-column elution, the product eluate volumetric flow is much smaller than the other elution technologies. Typically U-column product eluate flow rates are one third that of Straight, NIMCIX or Carousel elution technologies.

The suitability of direct precipitation over SX is also dependent on the impurity levels in the product eluate stream. In particular for an acid system, iron is of specific concern. Typical Yellow Cake product specifications suggest a composition of 75% uranium and 0.15% iron. Based on these values the uranium concentration must be 500 times higher (a U/Fe impurity ratio of 500:1) than iron to meet this specification.

If the iron concentration is less than 500mg/L in the product eluate and the U/Fe ratio in solution is ideally above 500:1, then the use of SX is not required, as the concentration multiplier is acceptable for final product specification. Compared to the typical performance of elution technologies, U/Fe ratios with U-column elution tend to be 1.5-2 times higher than other elution technologies. This is because U-column elution utilises re-adsorption, where additional scrubbing occurs as the re-adsorption conditions displaces iron for uranium on the resin. Therefore this higher level of scrubbing in the U-column gives a much higher purity product. The concentration effect occurring in the U-column elution also increases the uranium concentration relative to iron, further increasing this ratio.

If the purity of the product eluate from U-column elution is not sufficiently high, SX will be required before precipitation to ensure product quality. If this is required, the Straight Column elution option would be the preferred option in an Eluex arrangement. High uranium concentrations in the product eluate have the potential to cause high viscosity in the organic phase in SX loading. This causes a third phase to form, which is removed with the raffinate. Therefore the product eluate from U-column elution would have to be diluted, negating its benefits.

2.2.2 Design Considerations

Continuous vs. Carousel

In continuous moving packed bed elution systems, the resin is intermittently moved down the column. Every transfer, a volume of resin is removed from the bottom of the column and a fresh amount enters the top of the column. Assuming the column has a residence time of 12 hours, there would be 12 discrete bed volumes of resin in the column. The solution entering the bottom of the column contacts the bottom bed volume first, with this liquid continuing to contact the 2nd bed volume, 3rd, and so on. Therefore in this column there are 12 bed volumes (BVs).

In Carousel operation, the resin is not moved until the cycle is complete. Therefore there is 1 bed volume in a Carousel column.

In both cases, the same amount of solution will be used. If 3BV/hr is required to elute the resin for 12 hours, continuous operation will use a total of 36BVs. Similarly the Carousel column will use 36BVs to elute the loaded resin.

The difference lies in the solution management for both systems. Because a bed volume resin for a Carousel system is so much larger than in Continuous column (12 times in this example) the eluent, product eluate and wash water tanks have to be significantly larger to have this solution available.

One way to reduce this effect is to increase the number of elution columns in a Carousel system to reduce the size of the bed volume in each, and therefore, the flow rate required. Either the solution can be pumped through succeeding columns (i.e. the overflow from column 1 enters the bottom of column 2) or intermediate tanks and pumps can be used. The benefit of using intermediate tanks is that the pressure required to pump the solution through the columns is reduced as the pump has to pump through one column rather than multiple columns. The other benefit is that if these tanks are made to be larger than just a surge tank, if there are any fluctuations in resin loading, the variations of uranium concentration can be normalised.

One other notable point is that the more stages that are available, the higher the efficiency of mass transfer. Therefore continuous systems will always be more efficient than Carousel systems, unless the number of bed volumes in a continuous column is matched by the number of Carousel columns in series.

To equal the efficiency of a Continuous system, 12 columns would be needed in series. While there would be a reduction in the flow rate requirements through the system, the capital and operating requirements would likely to be much higher than a single continuous counter current column.

NIMCIX Column Mechanical Design Considerations

The primary drivers of elution design are governed by the strength of eluent, the flow rate of eluent and the residence time of the resin required. All three of these variables are interconnected and can be determined during feasibility lab-scale testing. No matter which elution technology is used, these three process parameters are required to be met.

The mechanical design parameters that become secondary are:

- The aspect ratios of the column ensuring adequate theoretical transfer steps are created.
- The superficial velocity of the solution through the resin bed to ensure plug flow and enough turbulence to reduce the size of the film layer (not too slow) and to ensure the resin bed does not expand (not too fast).
- The height of the column to ensure pressure on resin is not too high.

In a moving packed bed column design (such as Straight Column and U-column Elution), there is a trade-off between the aspect ratio used and the superficial velocity. Typically if the superficial velocity of the column is between 1-20m/hr there will be minimal bed expansion due to the height of the resin bed and the use of pressurised columns.

In NIMCIX systems, the superficial velocity becomes much more important. In each stage in a NIMCIX column, there is a resin bed with a height of 0.5-1m. Solution travelling up the column causes the resin bed to expand in each stage. An increase in superficial velocity can fully fluidise the resin bed, causing resin to travel up through the perforated plates in each stage, “mixing” the discrete resin beds. This mixing of the resin beds will reduce the overall performance of the column due to short circuiting.

A further complication is caused by the density difference of loaded versus eluted resin. When the loaded resin enters the top of the column, it is denser than the eluted resin at the bottom. Therefore at a fixed superficial velocity the bed at the bottom of the column will expand more than the bed at the top. For SBA resins which require higher concentrations of sulphuric acid (150-200g/L) to completely elute the resin, the density differential between the resin and the acid becomes small, reducing the superficial velocity required to fluidise the bed. The consequence of this is the elution column must be very wide to ensure the superficial velocity is kept low for fine bead resins and that the bed height is lower than typically designed. The opposite is also true, whereby larger bead resins require a much higher superficial velocity to expand the bed. These considerations are required to be addressed in the design stage to ensure no operational issues. Also because of this the turndown of the NIMCIX column is very small, as it effects the physical movement of the resin in the column.

By designing two NIMCIX columns in series the column diameter can be reduced and allows the required superficial velocity to be reduced in order to expand the bed. While this has made the NIMCIX column more competitive from a performance point of view, the capital and operating costs are higher than that of Straight and U-column technologies.

Availability

Within each of the elution system control philosophies there are process downtimes as resin is transferred in the Continuous technologies, or there is change of step in the Carousel elution.

In both Straight and U-column elution, there is typically a 2 minute transfer period where the resin is airlifted out of the column over a 60 minute period. Therefore the maximum availability of the elution systems is 96.7%.

In Carousel elution system, one column remains offline for loading and unloading of resin. There is also a 30 second delay between each sequence step. Therefore the availability of a single column is 46%, while the overall system has a plant availability of 99.1%

For the NIMCIX system, the column typically takes 10-12 minutes to transfer eluted resin with a total elution cycle time of around 170 minutes. Therefore the availability of the NIMCIX column for elution is 92.9%.

Therefore in terms of plant availability, the Carousel elution system has the largest period of downtime, which must be accounted for in process design.

Operability and Maintenance

The following is a summary of the maintenance issues unique to each elution technology:

- NIMCIX: The main maintenance issue in a NIMCIX column is the fouling on the interstage perforated plates. Typical NIMCIX mechanical design allows for a man-hole at each stage level to allow for access to the perforated plates during downtime. The column must be emptied to a point below the perforated plate in order to service it and due to nature of the column; it is typically classified as a confined space. Access also can be an issue with either permanent scaffolding or stairs required to get access to all levels.
- Carousel: Due to the nature of design, there is a large amount of automated valves required at the top and bottom of each column to allow automation of the circuit. Typically there are 8-10 automated valves per column. Normally the Carousel column is operated at pressure to hydraulically transport resin after a complete cycle. Due to the pressure required to transport the resin the columns may be deemed as a pressure vessel and therefore will be subject to AS1210/ASME8 pressure vessel code.
- U-column: The concentrated eluate is extracted from the bottom of the column from a mesh screen. Typically if there are solids with the resin, they will settle in the bottom section. Typical design is to have the take-off point on the side of column (on the U) with provision for a second take-off next to it, in case there are any blockages.

  Due to the pressure required to transport the resin the U-column it may be deemed as a pressure vessel and therefore will be subject to AS1210/ASME8 pressure vessel code.
- Straight: Similar to the U-column, the moving packed beds utilise candle stick screens as the drain points at the tops of the columns. There is potential for these screens to block, but each screen is removable and readily accessible from the top of the column and would require a minimal maintenance window to change out or clean.

2.2.3 Operating Cost

The following table is a summary of the relative operating costs for each of the technologies.

Table 1: Relative operating cost comparison (200g/L H_2SO_4)

Item	U-column	Straight Column	Carousel Column	NIMCIX 1 Column	NIMCIX 2 Column
Consumable (Variable) Costs	0.85	0.85	0.88	1.81	0.94
Fixed Costs	0.15	0.16	0.17	0.17	0.17
Total OPEX	**1.00**	**1.01**	**1.05**	**1.97**	**1.11**

It can be seen from ***Table 1*** both Straight and U-column elution give the lowest operating cost with the NIMCIX 1 Column system giving the highest.

Sulphuric acid was by far the largest single contributor to operating cost with the overall operating cost sensitive to the sulphuric acid consumption rate. The cost can be directly related to the amount of eluent used in each technology, with both NIMCIX columns coming out the highest due to the higher eluent flow rates required.

The eluent strength considered was 200g/L, which is high when compared to other IX circuits operating on uranium elution around the world as it was assumed that a particularly strong base resin was used. Alternative resins may be eluted with 120-150g/L acid, significantly reducing this portion of the operating cost. Table 2 shows the new reagent costs using an eluent concentration of 150g/L. While overall the operating costs for all plants would be reduced, there is only a marginal change in the relative operating costs between systems.

Table 2: Relative operating cost comparison (150g/L H_2SO_4)

Item	U-column	Straight Column	Carousel Column	NIMCIX 1 Column	NIMCIX 2 Column
Total OPEX	1.00	1.01	1.06	1.92	1.11

2.2.4 Capital Cost

The following is a summary of the capital cost for each technology:

Table 3: Relative capital cost comparison for elution plant

Technology	**U-column**	**Straight Column**	**Carousel Column**	**NIMCIX 1 Column**	**NIMCIX 2 Column**
Total Equipment Cost	0.34	0.30	0.50	0.32	0.36
Total Discipline Installation Costs	0.66	0.47	0.82	0.62	0.71
Total Direct Cost	**1.00**	**0.77**	**1.32**	**0.94**	**1.07**

Table 3 shows that the Straight Column system is the cheapest, with the NIMCIX 1 elution the second most. This is due to:

- The straight elution column is a smaller column all other columns.
- Due to the resin expansion requirements and the number of man-holes to service the interstage plates, the NIMCIX columns are more expensive than other columns. But because there are fewer columns in the system when compared to U-column or Straight Column, the NIMCIX system is cheaper.
- While the process tanks for all continuous options are similar, due to the larger inventory of solution required for the Carousel Column operation, the tank cost is significantly higher.

Overall the Carousel system is the most expensive due to the high tank costs. The least expensive is the U-column with the Straight Column and NIMCIX single column options display similar prices.

3 URANIUM PRODUCT RECOVERY COMPARISON

3.1 PROCESS DESCRIPTIONS

3.1.1 Direct Precipitation

Depending on the elution technology if the concentration is sufficiently high enough then direct precipitation becomes a viable recovery process. In the case of the U-column, direct precipitation is feasible via neutralisation with lime, caustic or magnesia followed by precipitation.

Figure 6 shows the block flow sheet used in all precipitation unit processes:

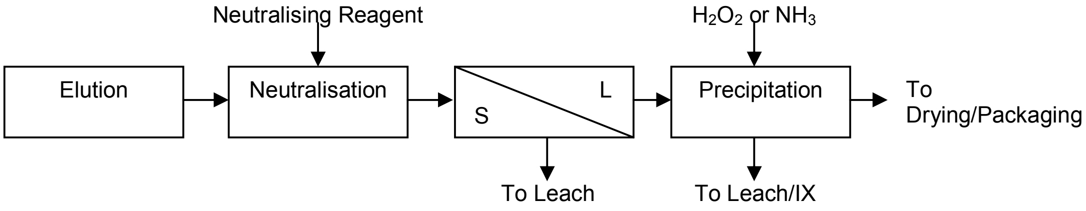

Figure 6: Typical precipitation flow sheet

3.1.2 Ion Exchange-Solvent Extraction (Eluex)

In some instances where the uranium tenor from elution is not sufficiently high enough for direct precipitation or there are deleterious elements still present then solvent extraction (SX) is required. The process where IX is combined with solvent extraction (SX) is known as Eluex. Traditional batch ion exchange systems require high eluent volumes to fully elute the resin and typical strong base resins are not selective towards uranium over other metals.

The Eluex process uses the relative strengths of each unit process and combines them to produce a high purity product. While there are several options available for stripping of the organic solution, the most popular is the use of ammonia/ammonium sulphate because when it is paired with ADU precipitation, several of the streams can be recycled through the process to minimise reagent costs. The Eluex flow sheet integrates the elution and solvent extraction unit processes. A typical flow sheet is shown below:

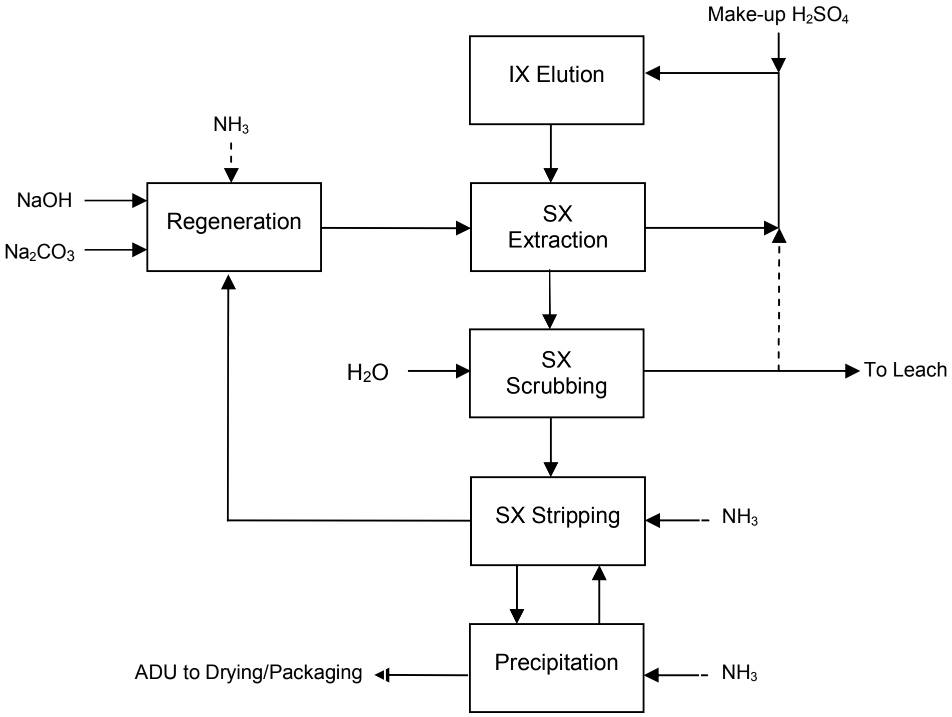

Figure 7: Typical Eluex flow sheet

The product eluate from elution enters into the SX extraction stage, where the amine extracts the uranyl sulphate complexes. The raffinate returns to eluent feed, with make-up sulphuric acid to replace acid consumed in elution and SX extraction.

While the recycling of acid reduces the overall acid consumption of the plant, the free acid in the IX product eluate can affect the performance of SX. Higher acid concentrations increase the level of bisulphate ions in solution, which directly compete with uranyl sulphate complexes on amine extractants. Therefore it is preferred to reduce the acid concentration in the product eluate to give a better performance in SX. This can be done by resin selection and elution optimisation.

Overall the net benefit of the Eluex process is the large recycle streams of both acid and ammonia to reduce total acid and ammonia consumption, giving a net result better than IX or SX alone.

3.2 RESULTS AND DISCUSSION

3.2.1 Comparison Direct Precipitation and Eluex

A high level model was developed to analyse the operating costs for each system. It was assumed that the uranium production through each system was the same.

Direct Reagent Costs

The main reagents consumed in direct precipitation are:

1. H_2SO_4 for elution
2. $Ca(OH)_2$ for neutralisation

3. NH_3 for precipitation
4. Resin replacement

The main reagents consumed in the Eluex process are:

1. H_2SO_4 for elution and extraction
2. NH_3 for stripping
3. Solvent replacement
4. NH_3 for precipitation
5. Resin replacement

As the uranium throughput was the same for both systems, it can be assumed that the ammonia consumption in ADU for is the same. Therefore the main process variables to be investigated were:

- Acid strength in elution
- Uranium loading capacity
- The dilution factor in elution. For all elution systems (with the exception of the U-column) the concentration of uranium is lower in the product eluate than on the loaded resin (i.e. a dilution factor >1). In U-column elution, the concentration of uranium in the product eluate is often equal to or greater than the loading on the resin (i.e. a dilution factor of <1) due to the concentration effect. The lower the dilution factor, the less product eluate is being sent downstream and therefore the smaller the downstream processes and the lower the amount of acid required to be neutralised.

A high level mass balance was completed for both direct precipitation and Eluex to determine the estimated reagent costs for different variable set points. Direct precipitation consisted of elution, neutralisation with lime and precipitation with ammonia. Eluex consisted of elution, solvent extraction and precipitation with ammonia. Each of the three variables listed above were analysed to determine their relative effect on the reagent cost. For each variable, the dilution factor was used as the main variable for comparison, with the effect of the other variables relative to this analysed. The mass balance was designed to assume a fixed uranium throughput.

Figure 8 gives the total relative reagent costs for both direct precipitation and Eluex with changing acid concentration in the eluent. The reagent cost for solvent extraction is only marginally affected by the eluent acid strength and the dilution factor. As the majority of the acid in the product eluate is recycled back to eluent after solvent extraction, the only acid consumed is for uranium extraction (solvent protonation) and therefore remains relatively stable.

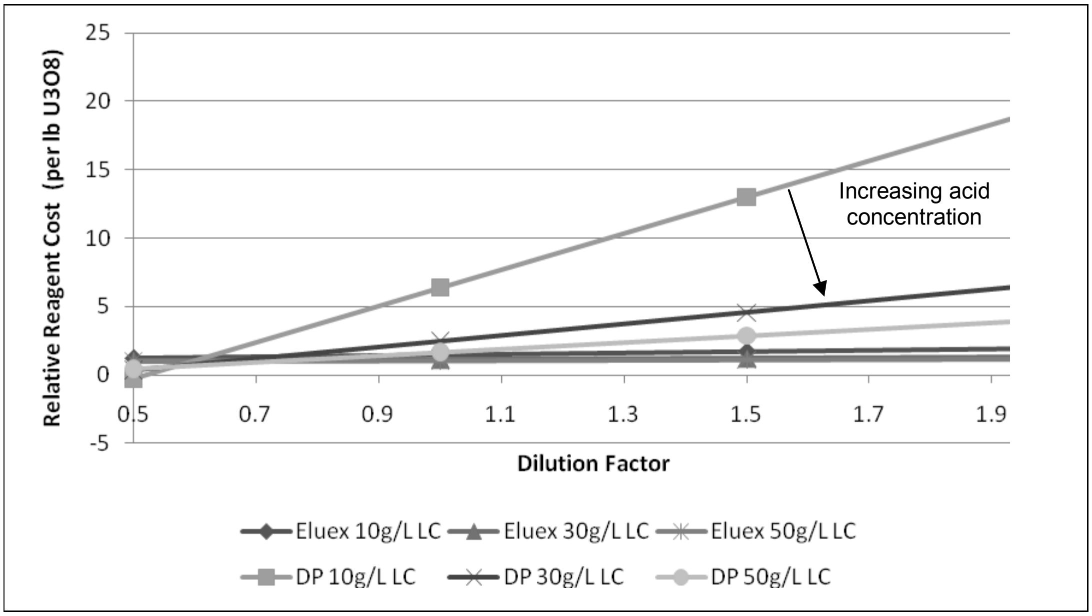

Figure 8: Relative reagent costs with changing acid concentration (50g/L U_3O_8 resin loading)

Conversely direct precipitation is sensitive to both variables. Decreasing the dilution factor causes more of the eluent solution (still containing high amounts of acid) to travel up the left hand side of the U-column and discharge at scrub waste. As this solution is sent back to leach, this acid offsets the acid required for leaching. Therefore this acid can be counted as a credit in the whole flow sheet, reducing the relative cost. A higher dilution factor means that more acid is being sent to neutralisation, increasing lime consumption and increasing the amount of acid required to be replenished.

Also a higher acid concentration in the fresh eluent increases the acid concentration in the product eluate, requiring more acid to be neutralised (increased lime cost). Therefore the overall reagent cost increases.

The other variable investigated was uranium loading capacity. Uranium loading changes the amount of eluent used in elution and the amount of acid required for solvent extraction. It can be seen from ***Figure 9*** that the reagent cost for direct precipitation is relatively sensitive to the uranium loading, as the main reagent cost is in neutralising the acid. Decreasing the uranium loading increases resin flow rate required to maintain the uranium throughput, which increases the size of the eluent flows required.

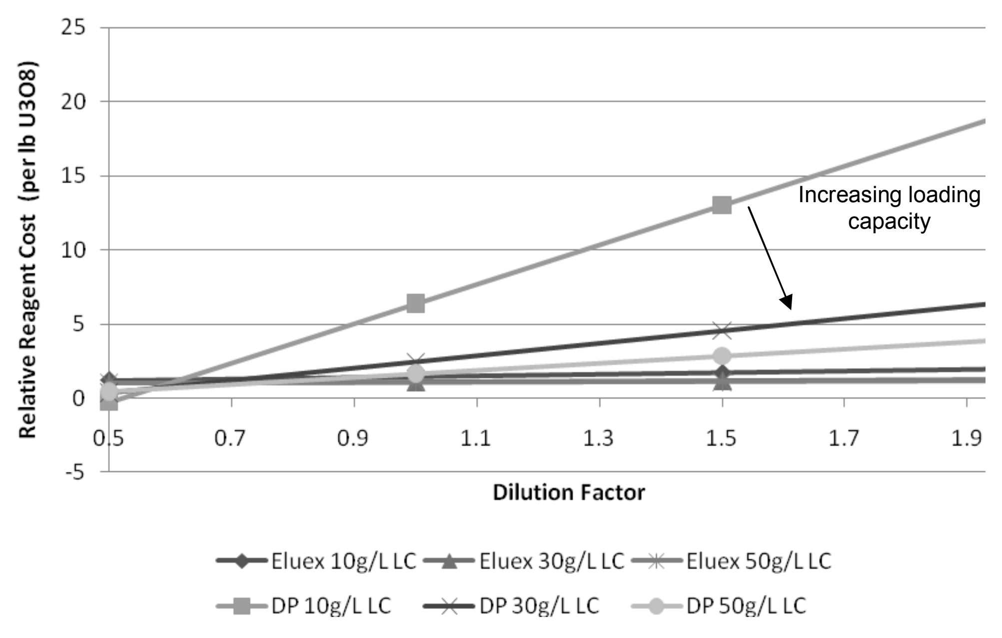

Figure 9: Relative reagent cost with changing uranium loading (150g/L H_2SO_4 in eluent)

There are other effects on solvent extraction that have not been quantified but should be noted.

While the amine groups are relatively insensitive to the acid concentration compared to SBA resins, there is an effect on performance as the acid concentration increases. Previous work (Mackenzie, 1997) has shown that as the acid concentration increases, the performance of the extractant decreases. Therefore a larger system with more extractant or a system with more stages is required to ensure the overall performance of SX is not affected. For example, increasing the acid concentration from 100g/L to 140g/L in the eluate can decrease the solvent loading by up to 15%.

Conversely the reagent cost for SX is not greatly influenced by the uranium loading, as the main consumption of acid in SX is through uranium extraction, which has been assumed to be fixed. Acid consumption for scrubbing decreases with increasing loading capacity as the increasing loading capacity reduces the flow of resin and consequently the product eluate flow to SX. Acid is used to adjust pH of the scrub solution to pH 1. Reducing the overall size of the SX plant reduces the scrub flow rate required and hence reduces the acid required.

It can be determined that direct precipitation becomes more cost competitive at higher uranium resin loadings, as the resin flow rate is reduced through the system, reducing the eluate flow rate and the acid flow to neutralisation.

Taking into consideration these additional operating costs, it is likely that the cross over point between SX and direct precipitation is a dilution factor of 1-1.5. Less than 1-1.5, direct precipitation with U-column elution is likely to be the lower cost option. Above this range, Straight column and

Carousel systems are better suited to Eluex, as the concentration effect of the U-column holds no performance advantage with SX.

The model only quantified the reagent costs associated with each of the unit processes. It did not take into consideration the additional capital and indirect operating costs associated with SX. It is likely that when all of these items are factored in, the relative operating cost differential between Eluex and direct precipitation would be reduced, such that the cross over point from SX to direct precipitation would be in the range of 2-3.

Based on reagent costs, if U-column elution operates at a dilution factor of 1 or less, it will be the most economic option. At dilution factors greater than 1, Eluex tends to be the most economical process route for this study. Therefore straight column or Carousel column elution technologies can be utilised here.

4 CONCLUSIONS

4.1 URANIUM ELUTION TECHNOLOGY

Based on the design criteria used as the basis for design in this report, the following conclusions can be determined:

For the use of direct precipitation for uranium product recovery, the U-column is the most cost effective elution technology due to reduced sulphuric acid neutralisation costs.

For the use of SX downstream of elution, the Straight Column is the most cost effective elution technology as a high uranium concentration product eluate is not desirable in SX and Straight Column elution is the cheapest elution alternative.

The Carousel elution is the least efficient form of elution. Carousel systems are more suited for ground water remediation, where the movement of resin is extremely low.

While the NIMCIX Column is as efficient as the Straight Column for uranium extraction, due to mechanical design constraints, the NIMCIX system is larger and more expensive in both capital and operating costs. For unclarified solutions of 2-3% solids, it is likely that the NIMCIX Column will be the optimum process. The NIMCIX system also has minimum plant turndown capacity and must operate near the designed eluent flow rate.

4.2 URANIUM ELUATE NEUTRALISATION

The three reagents investigated were lime, magnesia and sodium hydroxide, all of which have been used in uranium mines historically. Reagent cost analysis showed that lime precipitation was by far the cheapest option for neutralisation of acid. The relative costs of neutralisation with changing product eluate flow, eluent acid concentration and uranium flow rate remained insensitive, suggesting that at all process conditions for elution, lime neutralisation would be the most cost effective.

4.3 DIRECT PRECIPITATION AND ELUEX

Based on the reagent costs, Eluex would be the most cost competitive option. A dilution factor of 1--1.5 or less is required for direct precipitation to be the cheapest option. In acid elution, this is only possible with a U-column. Based on operating plants, a dilution factor of 1.0 is typical of sulphuric acid plants, with nitrate elution having a lower ratio. To eliminate SX from the flow sheet, U-column elution is required (It is assumed that impurity levels in the product eluate from U-column elution are sufficiently low for direct precipitation). If Eluex is used, it is recommended a Straight column system is utilised, as the operation of these units is simpler compared to a U-column.

When the cost of capital is taken into consideration, it is likely that the cross-over point for SX/direct precipitation is 2-3, due to the larger capital cost of the SX plant.

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SELECTING THE OPTIMUM IX SYSTEM FOR URANIUM RECOVERY

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Presented by

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CONTENTS

DEFINITIONS

Acronym	Definition
ADU	Ammonium diuranate
CCD	Counter current decantation using thickeners in a staged arrangement
CCIX	Continuous counter-current ion exchange, including in many cases fluidised resin bed or moving bed configurations
Eluant	Solution used to elute (strip) the loaded uranium from the resin
Eluate	Product solution resulting from the elution operation
FBIX	Fixed bed ion exchange
ISR	In-situ recovery – also referred to as ISL (in-situ leach)
IX	Ion exchange
MTZ	Mass transfer zone: refers to the active front in a resin bed where ion exchange is occurring
NIMCIX	NIM stands for the former South African National Institute of Mining, now Mintek; CIX refers to counter-current ion exchange
ORP	Oxidation reduction potential
PLS	Pregnant leach solution
Regeneration	Process to recover resin kinetics and capacity lost due to semi-irreversible loading of certain species, especially silica, on the resin
RIL	Resin in leach
RIP	Resin in pulp
Scrub	Process used prior to elution to selectively remove impurities from the resin
SDU	Sodium diuranate
SX	Solvent extraction

1. INTRODUCTION

The selection of a flowsheet for uranium recovery is largely dictated by the mineralogy and nature of the host rock, in particular its acid consuming capacity. Leaching is commonly undertaken with sulphuric acid and, less often, with alkaline carbonate solutions.

The principal technologies used for final separation and recovery of uranium include solid ion exchange with resins, solvent extraction and precipitation. These processes may be adopted either alone or in combination depending on the nature of the project and the concentration of impurities in the leachate. Importantly, solid ion exchange is the purification technology of choice for the recovery of uranium from alkaline (sodium carbonate/bicarbonate) liquors since solvent extraction is not possible with presently available extractants.

The early extraction plants commonly used solid ion exchange in either a packed bed mode for liquor treatment or resin-in-pulp (RIP) mode for slurry treatment. These RIP plants used baskets of resin that were moved counter-currently to the pulp flow. In the late 70's and early 80's fluid bed technology was developed as a means of improving extraction from solution. These systems reduced the required resin inventory, provided a means of operating continuously (unlike packed bed systems) and generally reduced the cost of the unit operation. Fluid bed technology found application largely in combination with solvent extraction (SX) in the so-called *Eluex* process, particularly for the treatment of large flows of low-tenor leach liquors. Lately packed bed systems have also moved towards more continuous configurations and the Beverley project in South Australia has selected an innovative version of moving packed bed technology for the treatment of high flowrates of acidic in-situ leach liquor.

Recently there has been a resurgence of the RIP process driven largely by the fact that it obviates the need for solid-liquid separation. The technology has been instituted on the Kayelekera uranium project in Malawi that is treating ore containing mudstones and it has been proposed for an expansion of Langer Heinrich that is treating relatively slow-settling alkaline slurry. It is also being developed for some of the Western Australian alkaline leach projects that exhibit poor solid-liquid separation characteristics such as Wiluna and Lake Maitland.

Whilst SX and possibly direct precipitation technologies are viable and economic in specific circumstances, resin ion exchange, particularly fluid bed and RIP, are also flowsheet contenders. The objectives of this paper are therefore:

- To identify in general terms the advantages of resin ion exchange and its applicability within the uranium extraction flowsheet.
- To provide some general guidelines with respect to the potential cost advantages of resin ion exchange.
- To identify key resin characteristics and important selection criteria.
- To examine the design aspects of the unit operation with respect to adsorption, elution and other processing steps.

2. SELECTION OF THE OVERALL URANIUM RECOVERY FLOWSHEET

A detailed discussion of the overall selection criteria for a uranium recovery flowsheet is outside the scope of this paper. However, the choice of the flowsheet will be influenced by a number of criteria including:

- The mineralogy of the uranium species that will determine the ease of leaching and the need for high temperature and/or oxidising conditions.

- The nature of the host rock that will determine the acid consumption and the selection of an acid or alkaline leach process.
- The ability to pre-concentrate the ore by size, radiometric properties, gravity concentration or flotation techniques.
- The grade of the deposit and the planned throughput that will influence the volumetric flow and tenor of the PLS.
- The ease of solid-liquid separation.
- The nature and concentration of co-leached impurities.
- The amenability of the deposit or ore to in-situ leach or heap leach.
- The availability and cost of water and key reagents.
- Health, safety and environmental considerations.

The key factors influencing the selection of an ion exchange process can be summarised as follows:

- Fluidised-bed systems are economically more attractive at high flowrates and low uranium feed tenors. In such situations the fluid bed system can be combined with solvent extraction (Eluex). This will give improved selectivity and also conserve the acidic eluate that can be recirculated between SX and CCIX.
- Fluid-bed processes are more tolerant of a high suspended solid content in feed liquor than packed bed systems. Solution with up to 2% (w/w) solids can be accommodated (Streat & Naden, 1987; IAEA, 1994).
- Ion exchange resins are less selective over impurities, such as ferric iron, than solvent extraction. This may be offset by the use of an impurity scrubbing step within the flowsheet or the use of a more selective precipitation process such as hydrogen peroxide.
- Ion exchange technology provides the opportunity to have a central elution and recovery plant receiving loaded resin from a number satellite leach / adsorption circuits. This would be an advantage in the case of projects exploiting multiple and relatively small deposits.
- The competition from chloride for ion exchange sites represents an issue for both amine extractants and anionic resins. It may be possible to offset this by the use of cationic extractants/resins.
- The use of RIP can be economically advantageous, particularly so in the case of projects where the leach pulp exhibits poor sedimentation and filtration characteristics. This is invariably the case with alkaline leach pulps especially those emanating from the treatment of calcrete ores.
- Uranium recovery from phosphoric acid can be undertaken using SX or IX. The SX process necessitates extensive steps for organic removal with associated cost. The use of a phosphonic acid chelating resin could eliminate the need for organic removal, providing a significant capital cost benefit (Streat & Naden, 1987; Soldenhoff, Tran, & Griffith, 2009).

3. COST ADVANTAGES OF ION EXCHANGE PROCESSES

3.1 ELUEX VERSUS DIRECT SX

The Eluex process comprises primary uranium recovery using ion exchange with sulfuric acid elution, followed by solvent extraction from the eluate. Acidic raffinate can largely be re-used as eluant, thereby conserving reagents. The direct SX process extracts uranium directly from the PLS. This obviates the need for an ion exchange circuit but inevitably requires a larger SX circuit.

An important difference between the two options is the superior tolerance of the Eluex process to suspended solids in the PLS. As discussed in Section 6.2, several IX contactors are capable of treating high PLS solids. The direct SX process is much less tolerant of suspended solids and clarification of PLS is required to allow stable operation and maintain an acceptably low crud associated solvent loss.

The Eluex process increases the uranium tenor ahead of SX, thereby reducing the size of the SX circuit. In this situation the minimum size of the SX contactors are generally constrained by the organic flowrate, which due to a largely fixed loading constraint, is proportional to uranium mass flow. As a result, the capital and operating costs of the SX circuit in an Eluex flowsheet are largely proportional to uranium mass flow.

In comparison, the size of the extraction circuit for the direct SX process is determined by the PLS flow. The PLS flowrate will also determine the entrained organic losses.

Based on the above discussion the benefits of IX in the Eluex process can be summarized as:

- Elimination of the need for thorough PLS clarification
- SX capital cost reduction
- SX operating cost reduction, primarily due to lower organic loss

These benefits are offset by the additional capital and operating costs associated with the IX circuit, which are generally less sensitive to PLS flow.

Recent work by AMEC Minproc has shown that for liquors containing less than 350 mg/L U_3O_8, the Eluex process is generally the preferred option, primarily due to a lower proportion of operating costs being driven by PLS flowrate.

On the other hand, for liquors containing in excess of 700 mg/L U_3O_8, Direct SX is generally preferred.

Between 350 and 700 mg/L U_3O_8 the choice of process becomes less obvious and factors other than PLS tenor must be considered in greater detail. For a given PLS tenor, a larger PLS flowrate tends to favour the Eluex process and Eluex is normally preferred for flow rates above 2000 m^3/h.

3.2 RIP VERSUS SOLID/LIQUID SEPARATION AND RECOVERY

In a recent AMEC Minproc study it was concluded that the hydrometallurgical flowsheet capital cost for a RIP-SX circuit will be about 30% less than the CCD-SX alternative. However, RIP-SX has higher operating cost that is equivalent to about 5 to 10% of the capital outlay (when discounted to present value). The RIP-SX circuit provides the additional advantages of a much smaller footprint and a potentially higher uranium recovery. Net present value sensitivity testing showed that initial capital cost uncertainty was the main risk driver, followed by resin cost uncertainty (both price and ongoing loss).

It is difficult to provide a ‘rule of thumb’ to define the relative advantages of RIP-SX and CCD-SX. The selection is determined by a number of processing issues, in particular:

- The optimum grind size for uranium recovery coupled with the cost of milling. RIP can currently accommodate the treatment of solid particles up to about 300 microns in size.

- The sedimentation rate and the number of CCD thickeners required.

- The liquor available for CCD washing.
- The need in alkaline leaching to recover the sodium carbonate leachate.
- The leach temperatures.
- The potential to combine the leach and RIP steps.

4. ION EXCHANGE CHEMISTRY AND RESIN SELECTION

Ion exchange functions both to concentrate and purify uranium from leach liquors. Merritt (1971) gives an exhaustive account of the chemistry of uranium recovery by ion exchange and the associated elution process options, and only the main aspects are summarised here.

4.1 RESIN PROPERTIES

Ion exchange resins comprise polymeric beads, usually of crosslinked styrene-divinylbenzene (DVB) type. Resins can be in the gel or macroporous form, with the latter having a high resistance to organic poisoning, greater mechanical strength than standard gel resins, and providing a potential reaction kinetics benefit due to a higher macro-pore content. Gel-type resins, on the other hand, are generally less affected by silica fouling from acidic leach liquors (Streat & Naden, 1987) and have higher capacities (IAEA, 1994). Quaternary amine resin functionality is most commonly used in uranium ion exchange. The ionised functional group converts the oil-swellable styrene-DVB copolymer to a water-swellable structure. The relative amount of water in the swollen resin bead is an important property and has a direct bearing on equilibrium, kinetic and mechanical characteristics. The average particle size, degree of cross-linking, degree of functional substitution and macroporosity therefore determines resin properties such as strength, kinetics, selectivity and active capacity (Schweitzer, 1988).

A number of polyacrylic anion exchange resin products are also currently available, being in general more robust than the styrene-DVB resins against attrition, however, with poorer load / elution kinetics performance.

4.2 ADSORPTION

Acid leaching: Dependent on the sulphate content of the leach liquor, the uranium complexes that load on the resin are $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$. The main competing anions include Cl^-, HSO_4^-, SO_4^{2-}, $Fe(SO_4)_2^-$ and other anions or anionic complexes specific to the application. At pH levels below 2.5 uranium loading is significantly depressed due to the strong resin selectivity for the bisulphate ion.

Alkaline leaching: Dependent on the carbonate content of the leach liquor, the uranium complexes that load on the resin are $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. The main competing anions include Cl^-, HCO_3^- and CO_3^{2-} and other anions or anionic complexes specific to the application.

4.3 ELUTION

The usual elution mechanism for uranium ion exchange involves the use of a high concentration of a readily exchanged anion such as bisulphate or chloride. However, the selection of the type of eluant needs to be carefully done considering downstream processing options, reagent cost and reuse. Sulphuric acid eluant is common for acid leach ion exchange circuits as it is relatively cheap, does not introduce any new species and is compatible with a combined ion-exchange solvent extraction circuit (Eluex). Elution by salts is employed where the intention is to directly precipitate the uranium from the eluate; for acid leach circuits sodium chloride is the most common, while for alkaline leach circuits sodium chloride, sodium bicarbonate or sodium carbonate can be employed. Although ammonium or nitrate containing salts are very effective eluants, their use is less preferred due to environmental implications.

4.4 REGENERATION

Regeneration is required to counter the effect of the semi-irreversible loading of certain species such as silica, molybdenum, polythionates, sulphur, organics, titanium, zirconium and thorium. For acid leach liquors, silica is usually one of the main “resin poisons” and the regeneration step usually comprises a dilute caustic pre-wash to pre-neutralise the resin and prevent silica re-precipitation, followed by 2 to 5% caustic regeneration and post-wash. Resins fouled with titanium, zirconium, thorium and organics could require a strong sulphuric acid (6M) regeneration step to remove these species (IAEA, 1994).

5. THE DESIGN OF THE ION EXCHANGE PROCESS

A typical ion exchange process comprises the following steps:

- Adsorption, in which the uranium is extracted from the feed liquor by the resin.
- Resin washing to remove the feed liquor and associated solids from the resin, preventing downstream contamination.
- Optional scrub of the resin to remove co-loaded impurities (such as iron and vanadium) and improve purity.
- Elution, in which the uranium in stripped from the resin.
- Optional post-elution wash to remove the eluant from the resin prior to re-contact with the feed liquor.
- Optional resin conditioning to an ionic form compatible with adsorption.
- Periodic regeneration of the resin to remove adverse species, such as silica, which are not removed by scrub/elution and impair resin kinetics and loading capacity.

From a process configuration perspective, the adsorption process can be selected and designed independently of the other unit operations that comprise the washing, elution and regeneration cycles.

6. ION EXCHANGE OPTIONS FOR ADSORPTION

The process requirements for the uranium adsorption unit operation have been described by Streat & Naden (1987) and include:

- Good contact between the resin and feed liquor.
- Independent movement of resin and feed liquor to facilitate a much longer residence time of the resin than the feed liquor, which allows the process to achieve high resin loadings.
- Minimisation of the feed liquor residence time, compatible with high recovery, in the interest of a compact design and associated low capital cost.
- Accurate stage-wise resin inventory measurement, control and transfer.
- Strict separation of the adsorption and elution sections in order to minimize reagent losses and product contamination.
- Minimisation of mechanical stress on the resin, which leads to resin attrition and loss.

Various process configurations have been developed to meet these criteria and can be classified into three major types: packed bed, fluid bed and RIP.

6.1 PACKED BED

Packed bed ion exchange requires clarified feed liquor and this necessitates the inclusion of both primary solid/liquid separation and clarification in the flowsheet. It comprises one or more packed columns. Due to the plug-flow nature in the bed, high loadings and low barren tenors are achievable. However the quantity of resin employed to achieve this outcome is significantly greater than that of fluid bed or RIP and this represents a further disadvantage of the process. For adsorption, the most common packed-bed configurations include multi-column (i.e. carousel FBIX, as in Figure 1) and “multi-stage” single column (as in Figure 2) systems.

For the FBIX multi-column configuration, resin handling is eliminated by use of a valve arrangement that advances columns to the appropriate stages in the process sequence. Elution is usually performed in the same column as adsorption, thereby eliminating resin handling. The single column multi-stage moving bed configuration is usually run up-flow with slugs of resin periodically discharged from the bottom and recharged at the top. Packed bed ion exchange is intrinsically cyclic with associated surge capacity allowance to be made for the feed and barren discharge solutions. This surge requirement can be minimised by using semi-continuous moving packed bed systems or loading FBIX columns in parallel with elution.

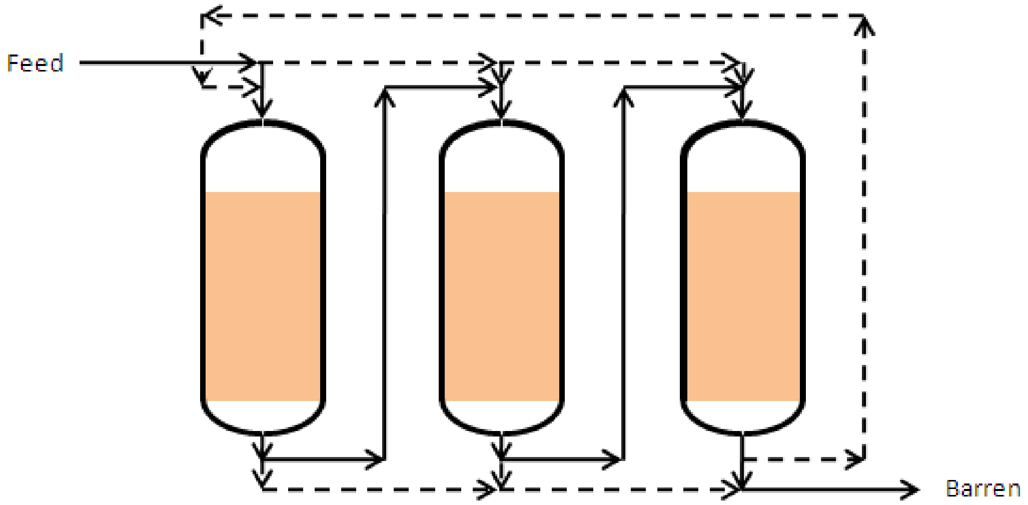

Figure 1 Carousel fixed bed (FBIX) arrangement

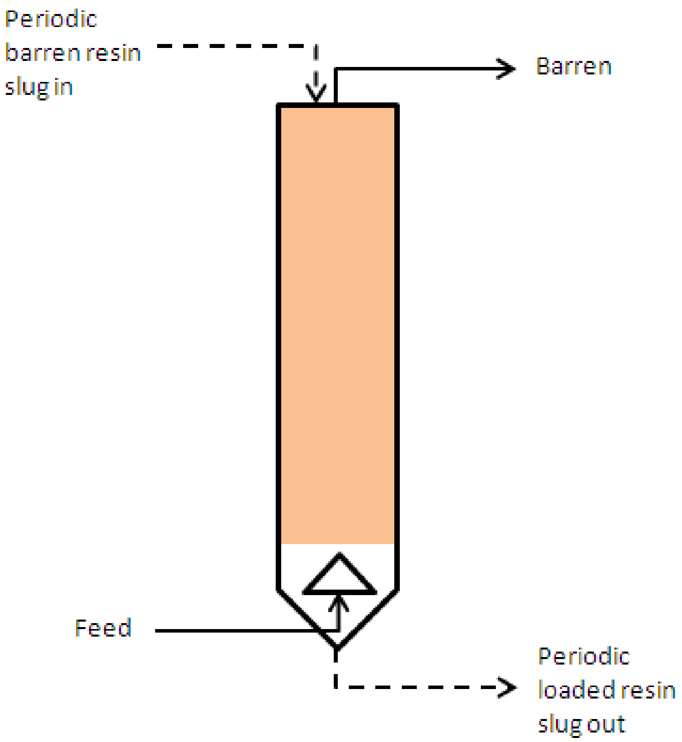

Figure 2 Single “multi-stage” packed-bed column

6.2 FLUID BED

Fluidised bed ion exchange can accommodate unclarified feed liquors containing solids (up to 2%(w/w)). For any specific duty the fluid bed configuration will employ a lower resin inventory than a packed bed and this, coupled with the multi-stage design, will reduce the capital costs of the process. The two main fluidised bed ion exchange configurations that have been employed commercially include the column type and multiple horizontal tank type, both of which use some form of mechanical separation between stages. Except for periodic short stops to allow resin transfer, these units are continuous systems improving resin utilisation efficiency and limiting the feed / discharge solution surge capacity requirements. The NIMCIX contactor (Figure 3) is an example of the column type fluidised bed contactor. Rössing Uranium employs the Porter system which comprises multiple horizontal tanks.

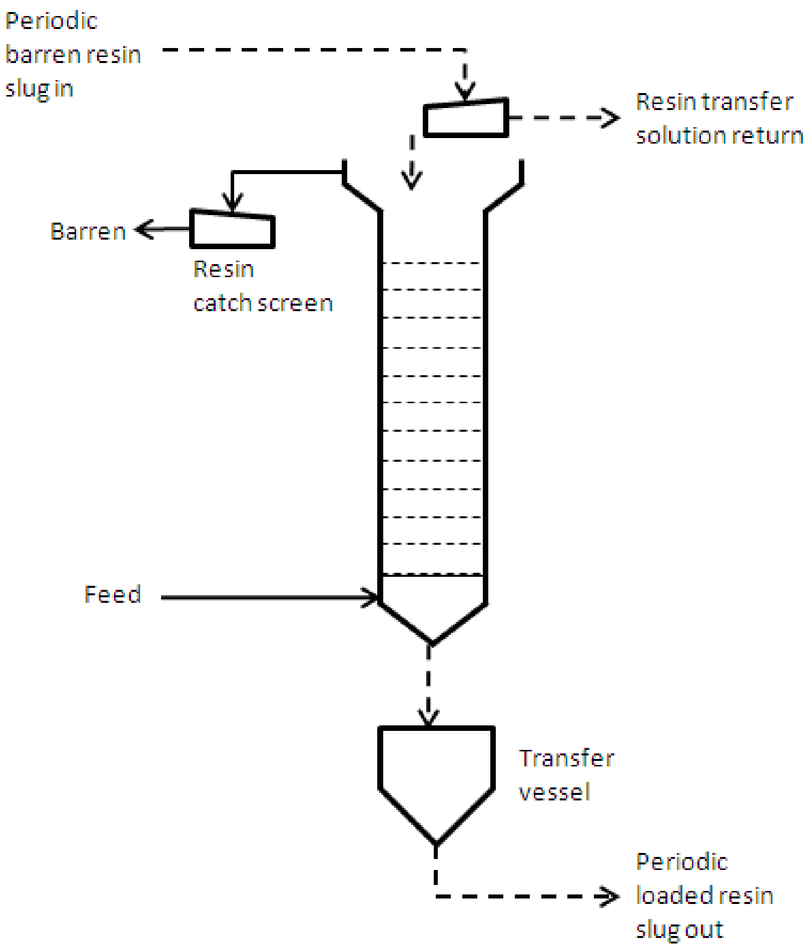

Figure 3. NIMCIX adsorption column

6.3 RESIN-IN-PULP

RIP is applied to desanded leach pulps having a high solids content. The system typically comprises a series of agitated tanks, with interstage screens to facilitate the independent movement of resin and slurry (Figure 4). Factors critical in the design of RIP circuits are the proper selection and sizing of interstage screens, and the agitation and resin transfer systems to minimise resin attrition. RIP contact can be performed in a continuous or carousel fashion, eliminating or minimising the feed liquor surge requirement. Efficient loaded resin washing is required to prevent solids transfer to elution.

The Kemix Pump-Cell system (Rogans & McArthur, 2002) could be employed as a carousel RIP contact arrangement. This system uses a combined agitator and pumping interstage screen mechanism in each stage, which provides a compact design. The mechanically swept interstage screen(s) could alternatively be used in isolation, with a dedicated agitator; this would typically be done for applications with higher uranium tenor, and therefore higher resin flow rates, which result in larger screen area requirements.

Resin-in-Leach (RIL) is an extension of the RIP concept with the leach and adsorption circuits combined or overlapped, reducing the overall pulp residence time and therefore providing a capital saving. For RIL to be considered the leach conditions need to be compatible with the presence of resin: temperature, particle size distribution, and agitation intensity are the main factors requiring consideration. Typical quaternary amine resins can withstand process temperatures up to 80°C, as well as redox potentials up to 600 mV (Ag/AgCl).

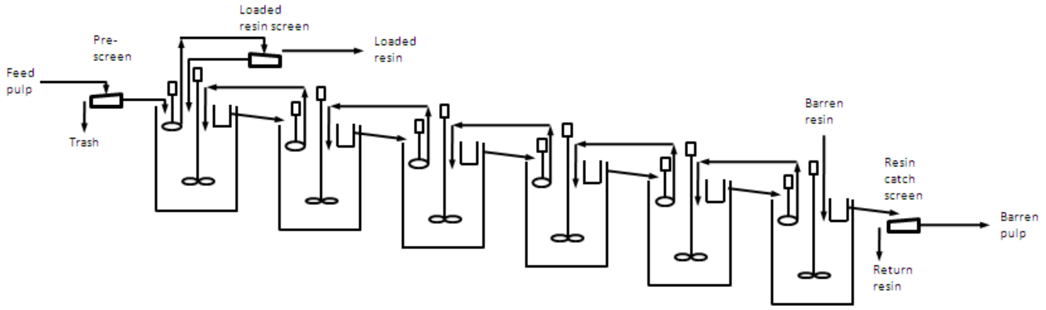

Figure 4. Typical continuous RIP flowsheet

6.4 COMPARISON OF ADSORPTION OPTIONS

Table 1 compares these three major IX configurations.

Table 1
Comparison of IX Options for Adsorption

	System		
Parameter	**Packed Bed**	**Fluid Bed**	**RIP**
Feed solids content	Low solids content required (less than 20 ppm).	Compatible with up to 2% (w/w).	Compatible with high solids content; up to 40% (w/w) in previous commercial applications.
Feed preparation	Requires CCD and / or filtration / clarification. Feed degassing could be required, especially for ISR.	Requires CCD / filtration if feed solids exceed 2% (w/w). Dedicated feed settler for removal of particles with similar fluidisation properties to resin. Feed degassing could be required, especially for ISR.	Removal of sand fraction to prevent screen blocking and excessive resin wear. Trash removal / pre-screen required to prevent resin contamination.
Resin properties	Robust beads for moving bed systems; fast kinetics required. Bead size selected to give acceptable pressure drop.	Robust resin beads, preferably in narrow size distribution range to aid fluidisation distribution; larger, high density beads could be required, which is usually associated with lower capacity / slower kinetics.	Requires larger (> 600 micron), more robust resin beads, preferably in narrow size distribution range. Maximum ore particle size around 300 microns.
Resin loss	Low (5 to 15%/year) Note 1	Intermediate (10 to 20%/year)	High (15 to 50%/year) Note 2

Resin containment	Resin retaining screens in columns.	Density differential between feed liquor and resin – resin retention in fluidised bed.	Interstage screens – internal or external.
Resin flow rate & inventory control	Absolute for FIX. Moving packed bed systems require bed level measurement in the column to measure slug size and a resin surge vessel or buffer column.	Resin transfer or slug measuring vessels required for transfer from adsorption to elution and for transfer from elution to adsorption.	Absolute for carousel arrangement. Continuous system requires barren resin surge vessel and flow measuring device (e.g. measuring hopper).
Pre-elution wash	Wash step only required where feed solids are significant (> 20 ppm) and poses contamination problems in elution.	Intermediate resin washing required – dedicated wash step (i.e. screen wash).	Extensive resin washing required – dedicated wash steps – multi-screen and / or column wash.
Overall resin utilisation efficiency	Low – at any instant only the resin in the loading front is performing useful work. The resin utilisation is improved in moving bed systems by reducing inactive resin bed volume.	High	High
Susceptibility to scaling	Higher: pressure drop over resin bed could induce scale precipitation; scaling in compact bed could lead to channelling and high pressure drop.	Intermediate: resin movement limits resin scaling and open bed reduces risk of column plugging. However accumulation & compacting of solids on the distribution plates has occurred in previous plants.	Low: solids attrition and resin movement reduces equipment and resin scaling; scaling of screens could impair operation.

Notes:

1. This is a typical resin loss range; actual performance would depend on the specific application. Resin loss numbers, presented as the fraction of total resin inventory lost per year, from earlier studies are as follows: IAEA (1994) indicates less than 5% for fixed packed bed systems and 10% for moving packed bed systems
2. This is a typical resin loss range; actual performance would depend on the specific application. Resin loss numbers, presented as the fraction of total resin inventory lost per year, from earlier studies are as follows: Streat & Naden (1987) and IAEA (1994) indicate 20 to 30%; Yahorava (Mintek; 2009) using the MetRIX pilot rig indicates 50% or 100% for tests on two different resins; Wyethe (2002) and Makhubela (2006) indicate 50% as typical.

7. ION EXCHANGE OPTIONS FOR ELUTION

The process requirements for the uranium IX elution unit operation are similar to those for the adsorption with the following exceptions:

- Independent movement of resin and eluant is required to obtain low residual uranium on the resin, while using a minimum volume of eluant. This will maximise the uranium concentration thereby reducing the size and cost of downstream processing.
- Minimisation of the elution residence time or maximising resin utilisation efficiency, in order to achieve a compact design and associated low capital cost.
- Minimisation of mechanical and osmotic stress on the resin, which in turn will minimise resin attrition and loss.

The main elution configurations include packed bed, moving packed bed and fluidised bed. The elution process dictates the size of the downstream circuits, is closely associated with final product purity and form, usually represents the main point of reagent consumption in the recovery flowsheet. These factors will therefore dictate elution process selection.

7.1 PACKED BED

Packed bed elution is the most commonly applied system. It facilitates plug flow and accurate stage resin volume control for a typical multi-step batch elution and is compatible with multi-column FBIX adsorption systems. In a multi-column FBIX system, proper sizing of the columns allows the loaded column to be taken off-line for elution, while the remainder of the columns continue in adsorption duty. Adsorption is therefore only interrupted for valve change-over, which minimises PLS surge requirements. However, in a single column elution system, the amount of resin actively involved in the elution process at any given instant is very small, resulting in low resin utilisation efficiency and associated high capital cost. Furthermore, in order to obtain an acceptable eluate tenor and improve resin utilisation, the eluate has to be recycled (i.e. split flow elution) or a counter-current, multi-stage arrangement is required. This can be attained by using multiple columns similar to that shown in Figure 1 but with eluant in-stead of feed liquor. Such a multi-column system introduces additional complexity, but reduces the individual column size and increases resin utilisation. There is therefore a capital cost trade-off which determines the optimum number of columns. The Outotec SepTor® system is an example of the multi-column arrangement which uses an innovative valving system to direct flow between columns.

7.2 MOVING PACKED BED

Alternatively, multi-stage moving bed or deep packed bed elution can be employed. Moving packed bed configurations have been developed and usually comprise a column arrangement where eluant and resin move counter-currently. The resin is usually moved along by some form of pulsing or jigging mechanism. These systems are versatile and can combine multiple stages in a single column – such as scrub and elution (Figure 5). The counter-current plug-flow nature of this configuration provides high resin and eluant utilisation and allows internal strip-reload zones to form, resulting in relatively high eluate tenors. The U-tube is an example of this system, currently in operation at several uranium operations in Kazakhstan (Patrin, 2005).

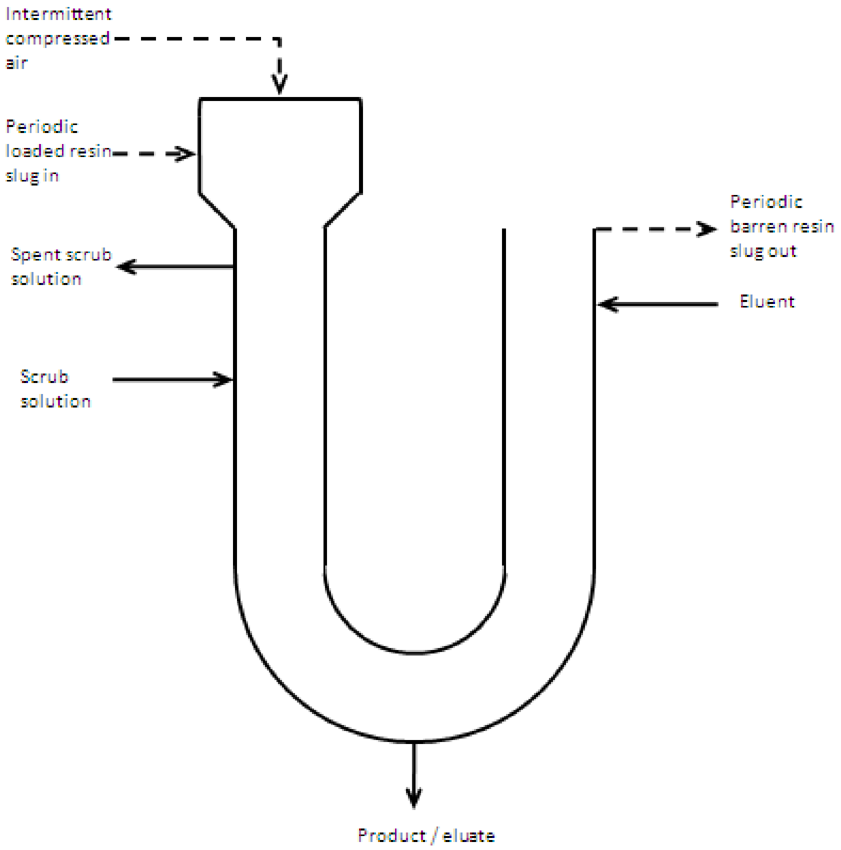

Figure 5. Typical U-tube arrangement

7.3 FLUID BED

Fluidised bed elution systems are usually of the column type and are selected due to their continuous nature and compatibility / standardisation with the adsorption system. The counter-current operating mode provides better resin utilisation and upgrade than obtainable in a single packed bed elution configuration. However, proper stage resin inventory control is important. Furthermore, this system can only be applied where the resin-eluant density difference is sufficient – this could limit the practical eluant concentration. The NIMCIX elution column (Figure 3) is an example of this configuration.

7.4 COMPARISON OF ELUTION OPTIONS

Table 2 compares the three major configurations.

Table 2
Comparison of IX Options for Elution

	System		
Parameter	**Packed Bed**	**Moving Packed Bed**	**Fluid Bed**
Upgrade ratio / reagent utilisation efficiency	Poor, but can be improved by eluate recycle or multi-column arrangements.	Relatively high upgrade ratios attainable.	Intermediate due to counter-current arrangement.
Resin utilisation efficiency	Poor, but can be improved by multi-column arrangements.	High	Intermediate
Continuity	Batch, with multi-column systems semi-continuous.	Continuous, except for resin transfer pause.	Continuous, except for resin transfer pause.
Complexity	Complex valving arrangement on multi-column system.	Simple, except for resin pulse / movement arrangement.	Simple, except for resin stage inventory control.
Resin transfer / movement	None – stage advance facilitated by valve arrangement.	Pneumatic / hydraulic pulsing.	Hydraulic pulsing / backflow.
Susceptibility to scaling	Intermediate – precipitation of salts during elution could plug column, cause channelling or result in excessive pressure drop.	High – precipitation of salts during elution could plug column, cause channelling or result in excessive pressure drop; super-saturated zones could develop due to strip-load mechanism.	Low due to open bed and low pressure drop.

Factors to consider in process configuration selection for both scrub and regeneration are similar to that for elution.

8. OPTIONS FOR RESIN WASHING

Effective resin washing is required to facilitate the strict separation between the adsorption and elution circuits.

Pre-elution washing has the objective of removing feed liquor and associated solids from the resin. In the absence of solids, for a packed bed elution configuration, washing could be performed in the elution column and therefore would not require separate equipment. However, when solids removal is a requirement, a dedicated wash step is usually dictated and is either of the screen or column type. For screen washing, the screen could incorporate “wash pockets”, which allow some stir-up and redistribution of the resin over the screen surface. Screen washing has the inherent draw-back of very low contact residence times, which results in high wash ratio requirements to obtain efficient washing. Alternatively, a counter-current expanded bed column wash arrangement could be used.

For circuits with a solids removal requirement, it is advisable to include a wash water clarification step which allows water reuse and minimises overall water requirements.

Post-elution washing has the objective of removing eluant from the barren resin in order to avoid reagent losses or the transfer of unwanted species to the adsorption circuit (e.g. chlorides where sodium chloride elution is employed).

9. INTEGRATION OF IX INTO THE OVERALL PROCESS

The uranium recovery process is not stand-alone and forms part of an integrated plant. The following potential interactions between the IX circuit and the rest of the plant need to be considered during process selection:

- Leach process: The leach oxidizing agent can affect the downstream uranium loading by introducing competing ions. Chlorate, for example, reacts to form chloride ions in solution, whereas ferric iron in sulphate leach liquor forms the ferric bi-sulphate anion; both species compete with uranium for resin loading. Resins are fairly robust extractants and can handle leach liquors at temperatures up to 80°C and relatively high ORP without deleterious effects.

- Reverse leach for gold ores: The presence of cobalticyanides in IX feed liquor permanently poison resins, and performing the uranium leach prior to the gold leach is therefore advisable, with the additional benefit of increasing subsequent gold recovery (Streat & Naden, 1987).

- Alkaline leach process: Requires a minimum level of bicarbonate in the leached liquor to avoid uranium reprecipitation as SDU. However, the carbonate and bicarbonate anions load on anion-exchange resins, so the concentrations of these species in the leach liquor need to be limited to maintain downstream IX resin capacity.

- Resin in leach: Should be considered where the leach conditions and solids are compatible with the resin. The overall number of leach and adsorption stages could be reduced with associated capital cost saving. In some instances, reprecipitation of uranium could occur in the later leach stages and RIL would provide a recovery benefit. In some instances clays in the solids acts as weak anion exchangers, adsorbing some of the uranium – the application of RIL or RIP has been found to recover this fraction as well as improving overall recovery (IAEA, 1994).

- Elution: Resin elution needs to be performed with an anion that is compatible with the rest of the plant. For circuits with significant barren liquor recycle, the eluting ion will build-up in the leach-adsorption circuit and could affect the performance of these circuits. For example, a chloride elution would introduce chloride into the barren liquor and should this build-up it will suppress uranium resin loading.

- Eluant recovery: For some acid elution applications there could be a cost incentive to recover part of the sulphuric acid in the eluate by nano-filtration, especially where high concentrations of acid are employed followed by direct precipitation (Soldenhoff, Emett, & Tran, 2009).

- By-product recovery: When molybdenum or vanadium is present an integrated flowsheet to recover these elements should be considered whilst meeting the uranium product specification (Soldenhoff, Emett, & Tran, 2009).

10. CONCLUSION

Solid ion exchange is a versatile process that has found application in many uranium recovery flowsheets, especially for cases with high PLS flow rate and / or difficult solids-liquid separation.

Future improvements in resin properties (especially robustness and selectivity) and associated contact equipment would expand the application of the unit operation.

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