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Proceedings

Uranium-REE Conference

12th Annual Uranium Event

ALTA Metallurgical Services, Melbourne, Australia

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PROCEEDINGS OF
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Alan has over 40 years' experience in the metallurgical, mineral and chemical processing industries in Australasia, New Zealand, North and South America, Africa, Asia and Europe. He has worked in metallurgical consulting, project development, engineering/construction, plant operations, plant start-up and technology development. Projects and studies have involved copper, gold/silver, nickel/cobalt, uranium and base metals.

Since 1985, as an independent metallurgical consultant, Alan has as undertaken feasibility studies, project assessment, project development, supervision of testwork, flowsheet development, basic engineering, supervision of detailed engineering, plant commissioning and peer reviews and audits. Clients have included a variety of major and junior mining, exploration and engineering companies throughout Australia and overseas.

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Uranium-REE Proceedings

Project Development

SO YOU HAVE FOUND A URANIUM DEPOSIT – NOW WHAT

By

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ABSTRACT

Uranium exists in a seemingly myriad of minerals (>150 known), further complicated by different valencies. While there may be one or two dominant species in a deposit, there are often a variety of minor minerals which need to be treated in order to achieve a high recovery. On top of this, uranium minerals occur in a wide variety of host rocks.

STEP ONE MUST BE TO carry out initial thorough and systematic geological and mineralogical studies and detailed chemical analyses of drill samples in order to classify the ore deposit versus other known types of deposits and Identify ore types within the deposit with potentially different metallurgical properties.

STEP TWO – SOMETIMES OVERLOOKED - IS TO benchmark the deposit against other past and present commercial operations and/or projects attaining feasibility study level for similar deposits to gain information on successful and unsuccessful geological interpretation, resource assessment, and mining and treatment methods.

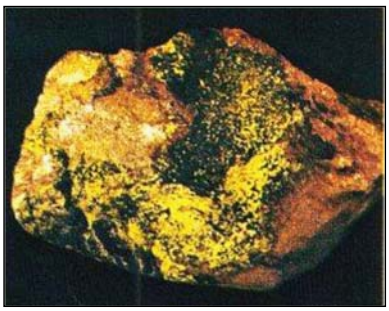
THIS LAYS A SOUND FOUNDATION FOR STEP THREE which is undertake a THOROUGH Scoping Study covering ALL aspects of the project to make a decision whether to move on to a Prefeasibility Study (PFS), undertake further scoping level work, bring in a partner, sell the project, or walk away.

If proceeding with a PFS, the recommendations should specify the preferred or short listed mining methods and treatment processes, incorporate metallurgical and mineralogical input to the procedures for the drilling program and geological model, and prepare a project development plan, schedule and cost. Sometimes there are opportunities for by-products, such as vanadium, molybdenum, base metals, REEs which may add value.

Finally, the temptation to take short cuts SHOULD BE AVOIDED AT ALL COSTS!

Keywords: Uranium Deposits, Project Development, Process Selection, Scoping Study, Prefeasibility Study, Key Steps

Carnotite



Uraninite

?

- Uranium exists in a seemingly myriad of minerals (>150 known).
- Further complicated by different valencies.
- While there may be one or two dominant species in a deposit, there are often a variety of minor minerals which need to be treated in order to achieve a high recovery.
- On top of this, uranium minerals occur in a wide variety of host rocks.

So Step One must be to:

Carry out initial geological and mineralogical studies, and detailed chemical analyses of drill samples to:

- Classify the ore deposit versus other known types of deposits.
- Identify ore types within the deposit with potentially different metallurgical properties based on chemical and physical properties of gangue and uranium minerals.

Step Two – sometimes overlooked - is to:

Benchmark the deposit against other past and present commercial operations and/or projects attaining feasibility study level for similar deposits to:

- Gain information on successful and unsuccessful geological interpretation, resource assessment, mining and treatment methods, metallurgical testwork and scale-up strategies, climatic effects, logistical, political and social issues, and performance data.

- Activities can include site visits, searching for available reports and published papers, and talking to personnel and consultants involved.

This lays a sound foundation for Step Three:

Undertake a THOROUGH Scoping Study covering ALL aspects of the project including:

- Initial resource tonnage and grade estimates at various cut-offs.
- Identification of potential ore types.
- Development of conceptual mining strategy and costs.
- Identification of most likely treatment methods.

- Identification of potential impurity problems and/or by-product opportunities.
- Assessment of ore upgrading potential.
- Development of conceptual flowsheets.
- Development of preliminary strategies for disposal of waste, residue, tailings or solution bleed streams.

- Identification and preliminary assessment of potential water sources.
- Preliminary testwork for most likely processes based on mineralogy, grade and benchmarking.
- Conceptual flowsheet, key equipment sizing, conceptual layout.
- Preliminary assessment of logistics and infrastructure.
- Preparation of order-of-magnitude capex and opex.

- Identification of possible climatic, environmental, social and political issues.
- Preliminary marketing study.
- Preliminary economic and risk analysis covering all aspects of the project.
- Selection of preferred or short listed mining methods and treatment processes.

Then make a decision whether to:

- Move on to a Prefeasibility Study (PFS).
- Undertake further scoping level work.
- Bring in a partner.
- Sell the project.
- Walk away.

Factors influencing decision include:

- Marginal economics due to refractory ore, low grade or insufficient ore reserves.
- Lack of funding.
- Lack of reliable water supply
- Major environmental issues.
- Remote location and/or difficult logistics.
- High risk social and/or political issues.

If proceeding with a PFS:

- Specify preferred or short listed mining methods and treatment processes for the PFS.
- Incorporate metallurgical and mineralogical input to procedures for drilling program and geological model.
- Prepare project development plan, schedule and cost.

Factors to consider when selecting possible treatment routes include:

- Basic processes are virtually unchanged from the previous uranium boom in 50s – 80s.
- Various process steps and equipment were “borrowed” from the initial uranium flowsheets and further developed in the treatment of copper, gold and nickel-cobalt ores. These developments can now be transferred back into the new wave of uranium operations.
- There are also some new innovations which can be considered.

Also…

- Current deposits are typically lower grade and/or more mineralogically complex. (except of course the very high grade Canadian deposits).
- Environmental and decommissioning regulations are generally more stringent.
- On the positive side – Uranium price is higher.

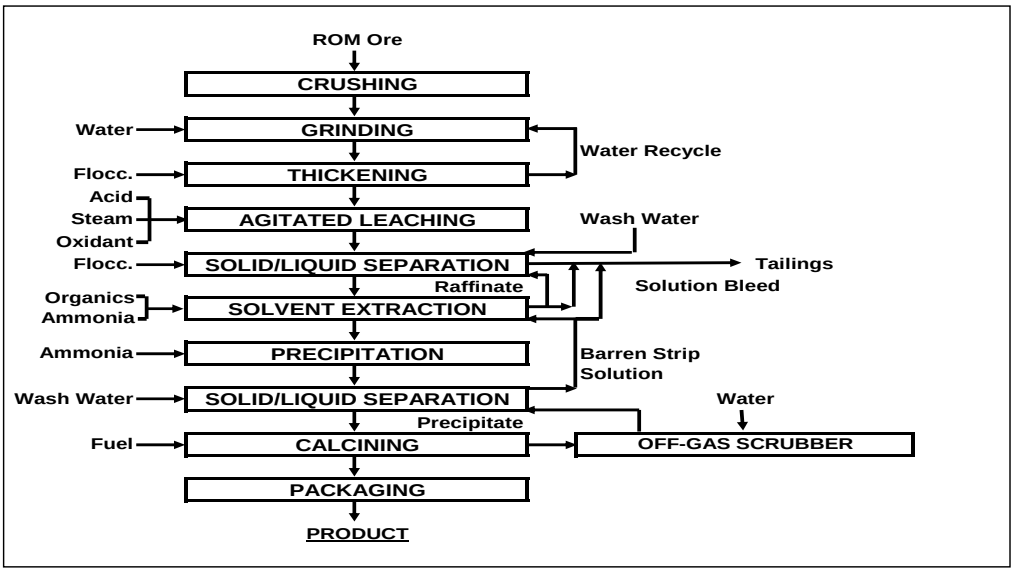
Basic processes are:

- Agitated leaching with sulphuric acid solution at atmospheric pressure and low to medium temperature.
- Agitated leaching with sodium carbonate-bicarbonate solution at atmospheric pressure and medium to high temperature.
- In-situ leaching with sulphuric acid or bicarbonate solution.

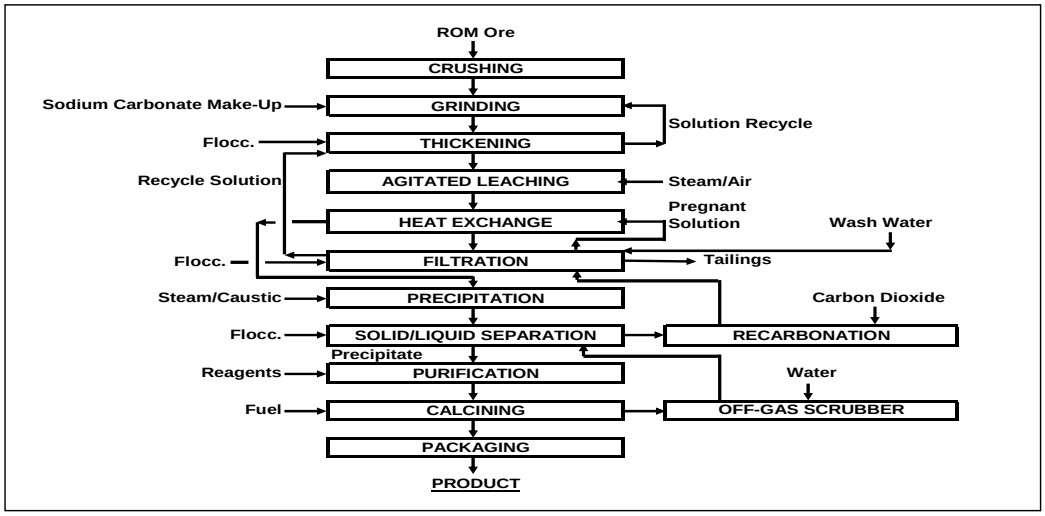
And…

- Strong acid pugging and curing.
- Pressure leaching with sulphuric acid or bicarbonate solution.
- Heap leaching with sulphuric acid or bicarbonate solution.
- Vat leaching with sulphuric acid solution.

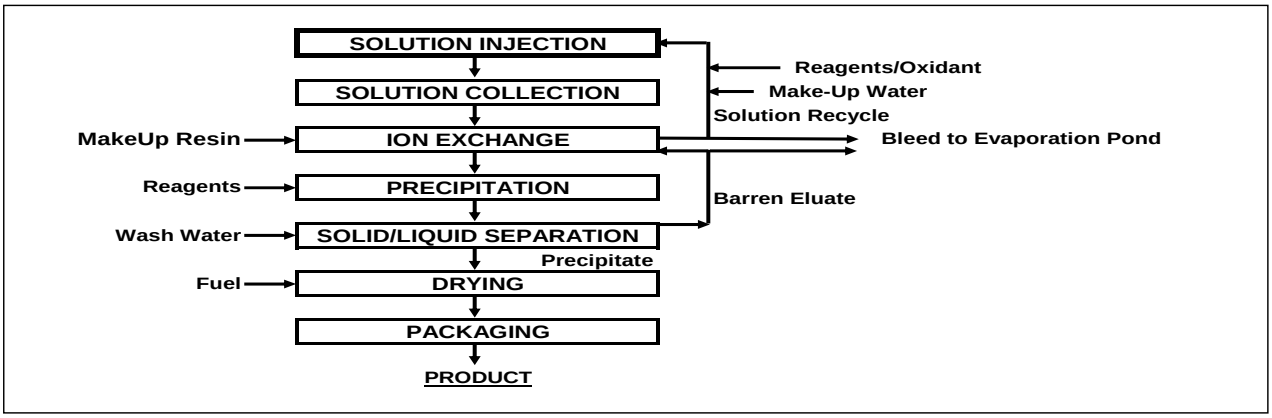
Agitated Atmospheric Acid Leach Flowsheet



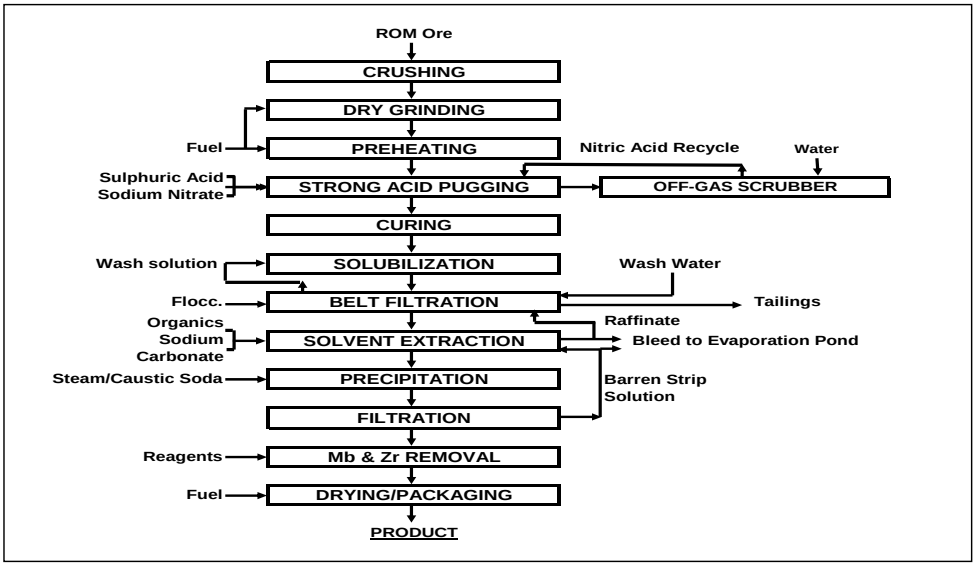
Agitated Atmospheric Carbonate Leach Flowsheet



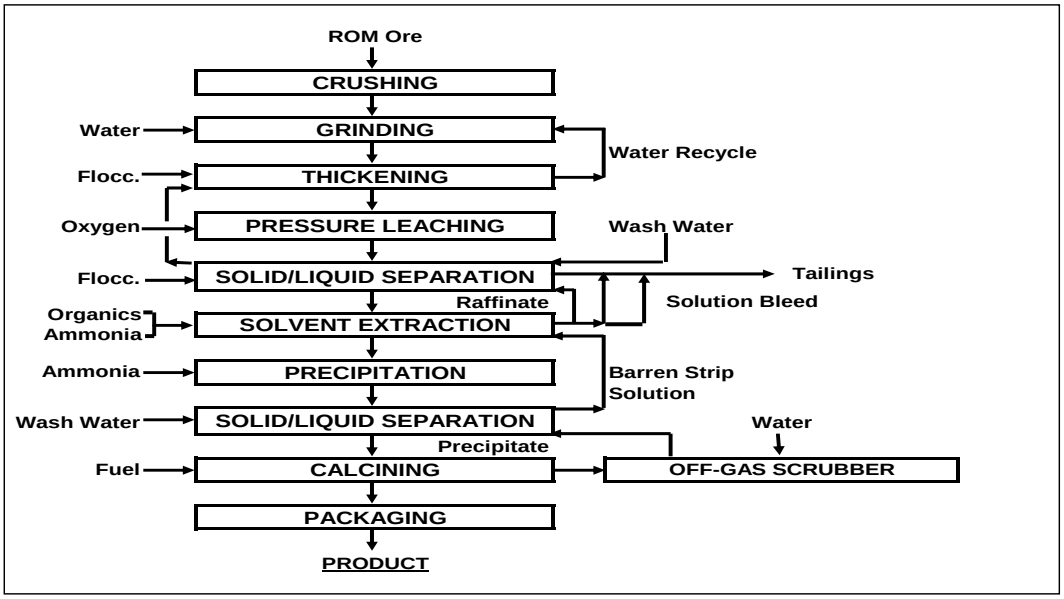
In-Situ Leaching Flowsheet



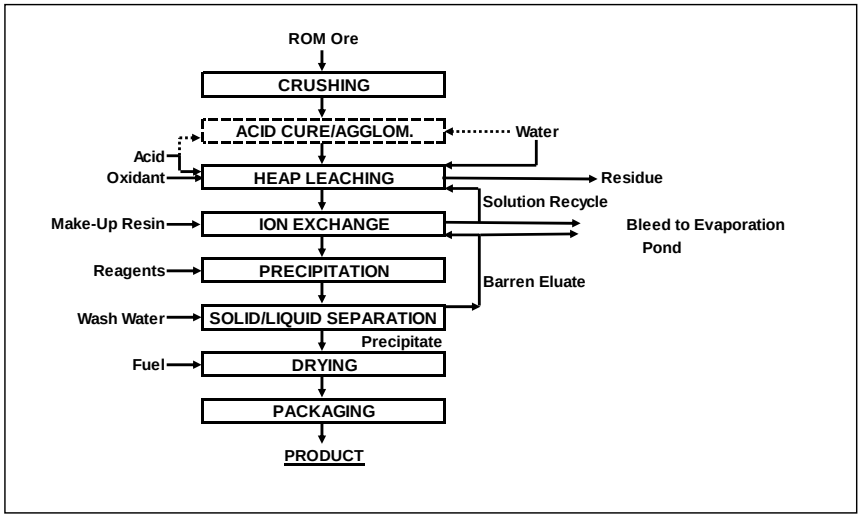
Strong Acid Pugging Flowsheet (Somair, Niger)



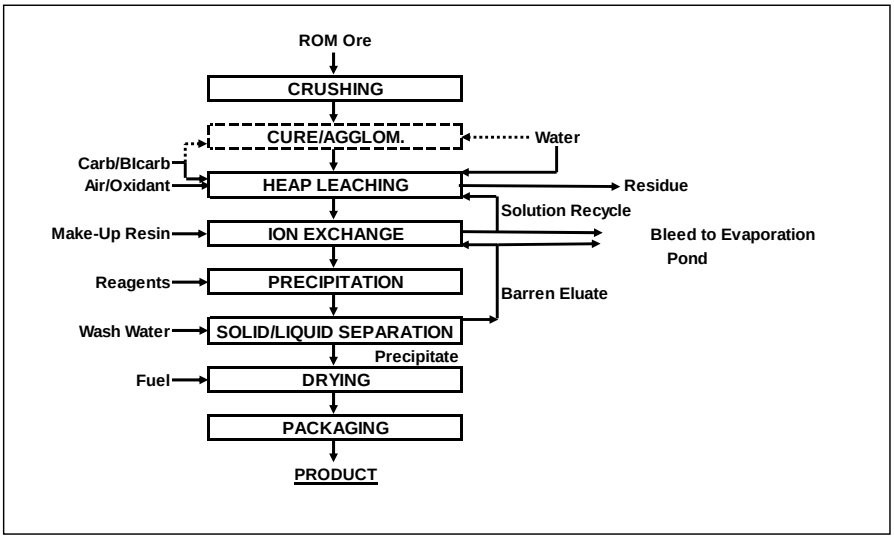
Pressure Acid Leach Flowsheet



Typical Uranium Acid Heap Leaching Flowsheet



Typical Uranium Carbonate Heap Leaching Flowsheet



Pre-concentration or pre-treatment can sometimes be used, including:

Radiometric Ore Sorting to:

- Increase grade and possibly reduce acid consumers.

Flotation to:

- Produce sulphide concentrate for leaching.
- Reject sulphides prior to carbonate leach to avoid high carbonate consumption.
- Produce sulphide conc. to reject acid consuming carbonate gangue minerals.
- Reject consumers in a flotation concentrate.

Sizing for:

- Sand/slime separation with rejection or separate leaching of sands.
- Attrition grinding followed by classification, with screens or cyclones
- Dry grinding and air classification.

Magnetic Separation for:

- Dry beneficiation for arid regions.

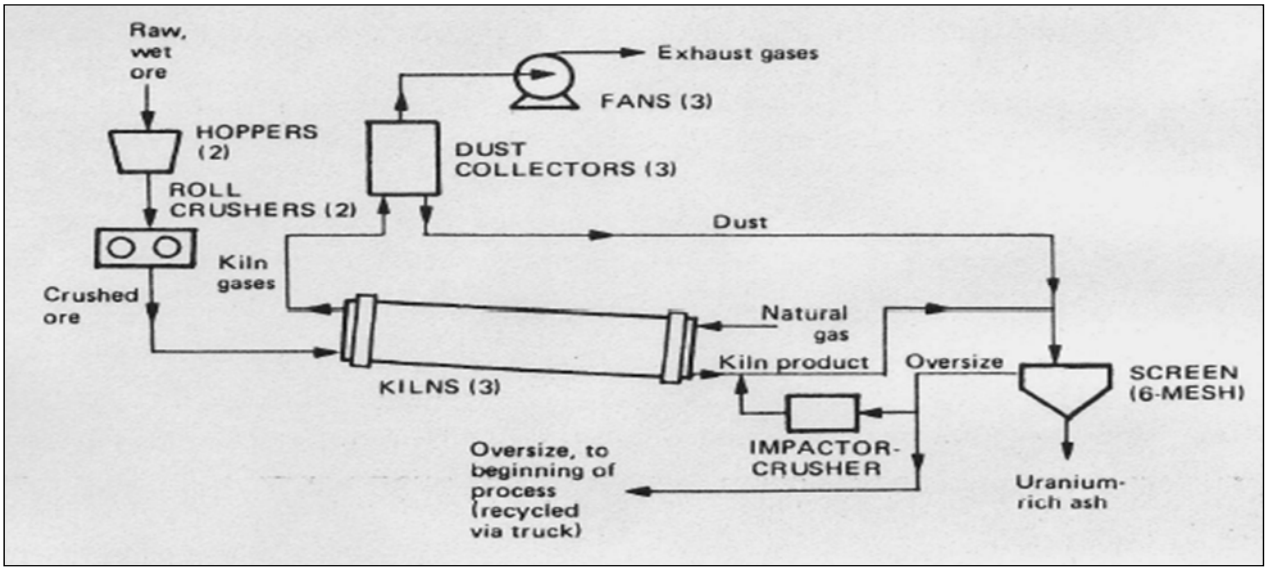
Gravity Separation to:

- Make sand/slime split to produce a sand reject.
- To produce HG uranium conc. With separate treatment of tails.
- To scavenge base metal float tails.
- Methods used include jigs, spirals, Reichert cones, tables, and heavy media,

Pre-roasting sometimes used including:

- Salt roasting with sodium chloride to improve recovery of vanadium from carnotite ores.
- Oxidizing roast to improve uranium recovery from tetravalent minerals.
- For clayey ore to improve solid-liquid separation characteristics after leaching (utilized before availability of effective flocculants).
- To remove troublesome carbonaceous materials.
- To pre-treat uraniferous lignites to produce U rich ash for further treatment.

Lignite Calcination Flowsheet



Warning: Leaching testwork must be carried out with upgraded or pre-treated ore

not always easy!!!

Sometimes there are opportunities for by-products, such as:

- Vanadium
- Molybdenum
- Base metals
- REEs

A starting point for recovery can be gained from benchmarking against previous operations.

Finally,

the temptation to take short cuts should be avoided at all costs!

PROCESS DEVELOPMENT FOR THE MULGA ROCK PROJECT

By

Chad Czerny, Xavier Moreau and Tony Chamberlain

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ABSTRACT

The history, geology and development of the Mulga Rock Project, one of Australia's largest undeveloped uranium resources is outlined with focus on the process development. The Mulga Rock Project is located approximately 240 km ENE of Kalgoorlie in the Great Victoria Desert of Western Australia. The Project will have the capacity to produce around 1,360 tpa of U_3O_8 for up to seventeen years. A Pre-feasibility Study was completed in Q4 of 2015. Vimy Resources Limited is presently engaged in a Definitive Feasibility Study (DFS) which is scheduled for completion in Q1 of 2017.

The metallurgical testwork undertaken to develop the current process flowsheet is summarised and the implications of the results for the process selection for beneficiation (by gravity separation) of uranium-bearing lignite, lignitic clay/shales and carbonaceous sands, and for downstream hydrometallurgical recovery of uranium are discussed.

The beneficiation plant proposed for ore processing comprises of a ROM ore mineral sizer, logwasher for ore slurrying and attritioning, slimes removal using hydrocyclones, and upgrading of a middlings fraction by mass rejection of between 50 and 60% barren quartz sands using two stages of Upward Current Classification (UCC), to produce a uranium-enriched concentrate, and a tail containing low concentrations of uranium (typically <60 ppm U_3O_8). Upgraded ore (by a factor of 2 to 2.5) is milled and thickened to produce a leach feed slurry.

Uranium is recovered from the beneficiated ore by agitated tank sulphuric acid leaching at atmospheric pressure and temperatures of 50 to 70^{o}C. Due to the 'preg-robbing' nature of the carbonaceous ore, uranium recovery from the acidic pulp is achieved using resin-in-pulp (RIP). The eluate obtained by resin stripping is further processed by micro-filtration/nano-filtration followed by direct precipitation using hydrogen peroxide to produce a uranyl peroxide hydrate ($UO_4.xH_2O$) intermediate.

Continuous piloting campaigns are currently in progress, and will be briefly outlined. Around 20 dry tonnes of blended ROM ores obtained from two open cut test pits excavated at Mulga Rock is being processed in these programs.

Results from this program will be supplemented by an extensive Geometallurgical program underway, aiming to capture natural ore heterogeneity and process implications with regards to beneficiation (upgrade factor and uranium recovery), deportment of chlorides to the slurry and leach variability.

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Vision and Mission

Our Vision:

Mining a cleaner tomorrow

Our Mission:

To become a **reliable** and **respected** uranium producer

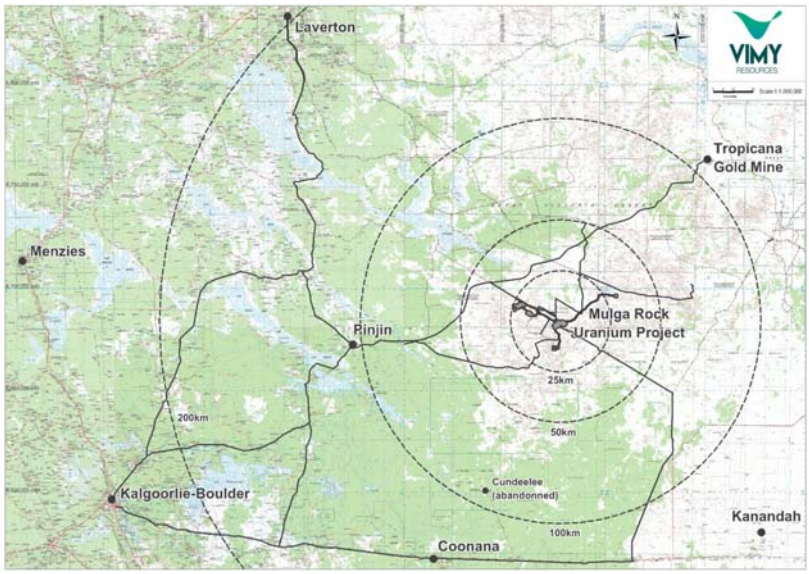
Presentation Outline

- Project Location & History
- Project Overview
- Geology & Mining
- Process Development /Metallurgical Testwork
  - Beneficiation
  - Hydrometallurgical Processing
- DFS Pilot Plant Testwork

Where is Mulga Rock Project?

- 240km ENE of Kalgoorlie in the Great Victoria Desert
- Remote, arid location
- The deposits are covered by granted Mining Leases
- Access is via the Tropicana Mine Road – AngloGold Ashanti

Location (240 km ENE of Kalgoorlie)



Landscape

- Simple, self-repeating dunal / interdunal landscape
- Yellow Sand Plain
- No surface water (sheet flow into topographic depressions)
- Unallocated Crown Land

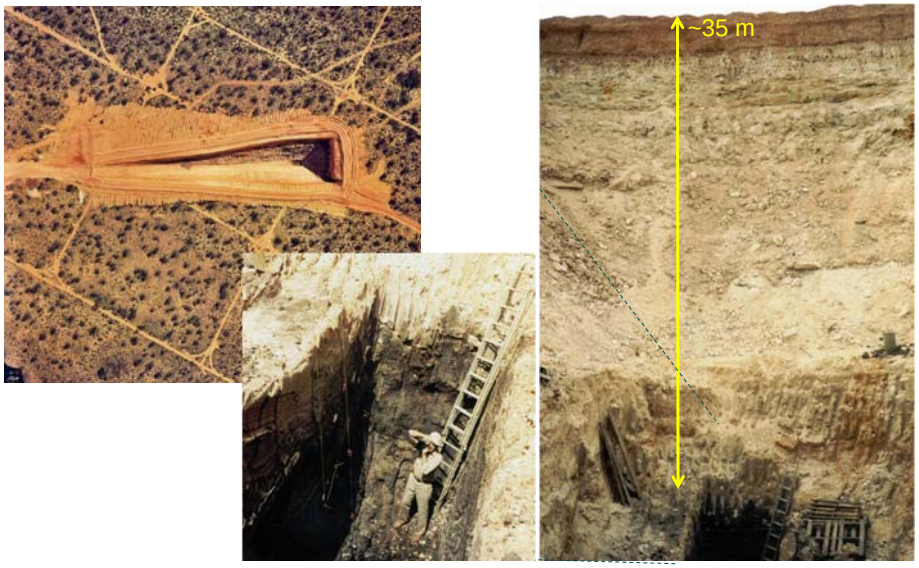
Low shrubs →

Mallee, tall shrub woodland →

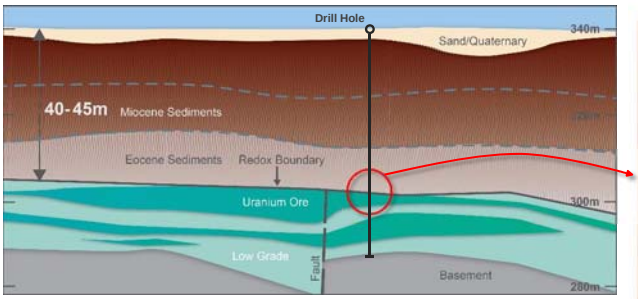
History of the Mulga Rock Project

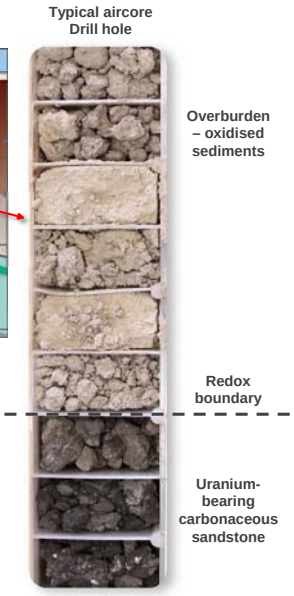
- Robertson Research commissioned by the Power and Nuclear Co of Japan (PNC) to investigate the potential for the east Yilgarn to host sedimentary uranium deposits
- Exploration by PNC started around 1978
- Mulga Rock Deposit (MRD) discovered: 1981 – 1984 (3 deposits)
- Continued exploration & Shogun test pit by PNC (1984 – 1989)
- Eaglefield Holdings acquired MRD in 2000
- MRD acquired by Energy and Minerals Australia (EMA) in 2007
- 2014 EMA becomes Vimy Resources Limited
- Backing by Forrest Family Investment (Minderoo Group), RCF and Macquarie Bank

History of the Mulga Rock Project (Test Pit (box cut) at Shogun Deposit)



Geology : Carbon-rich sedimentary host rock





- Hosted within deeply weathered sediments comprising carbonaceous sandstone; silt; sandy lignites
- Mostly **Uraninite (UO_2)** associated with carbonaceous material and lignite – no complex silicate minerals
- Deep weathering = *soft friable rock*
- Deep pit voids to provide tailings disposal and waste dumps

Geology – cont.

- Sediment hosted U and Base Metals (Ni, Co, Zn, Cu)
  - 2 mining centres:
    - Mulga Rock East: Ambassador, Princess
    - Mulga Rock West: Shogun, Emperor
- Life of Mine = 16 years (Targeting > 20 years)
- Shallow, large deposits
  - Total pit area = ~ 900ha;
  - Depth = 40 – 60m below ground level
  - Open cut, strip mining techniques
  - Similar to mineral sands mining

Mineral Resource and Reserves

Deposit / Resource	Classification	Cut-off Grade (ppm U_3O_8)	Tonnes (Mt)[4]	U_3O_8 (ppm)[5]	U_3O_8 (Mlb)
Mulga Rock East					
Princess	Indicated	150	1.3	690	1.9
Princess	Inferred	150	2.5	380	2.1
Ambassador	Indicated	150	13.2	750	21.7
Ambassador	Inferred	150	16.1	460	16.3
Sub-Total			**33.1**	**580**	**42.0**
Mulga Rock West					
Emperor	Inferred	150	28.4	450	28.1
Shogun	Inferred	150	4.1	550	4.9
Sub-Total			**32.5**	**460**	**33.0**
Total Resource			**65.6**	**520**	**75.0**

- As released to the ASX on 17 September 2015

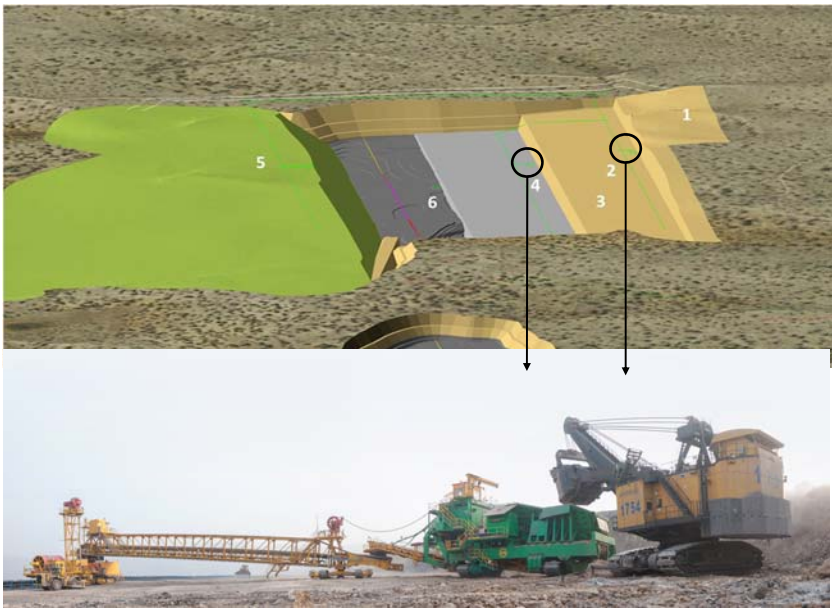
Deposit / Resource	Classification	Cut-off Grade (ppm U_3O_8)[5]	Tonnes (Mt)[4]	U_3O_8 (ppm)[5]	U_3O_8 (Mlb)
Mulga Rock East					
Princess	Probable	150	1.3[1]	639[1]	1.8
Ambassador	Probable	150	13.8[1]	663[1]	20.2
Total Reserve			**15.1**[1]	**520**[1]	**22.0**

- As released to the ASX on 29 March 2016

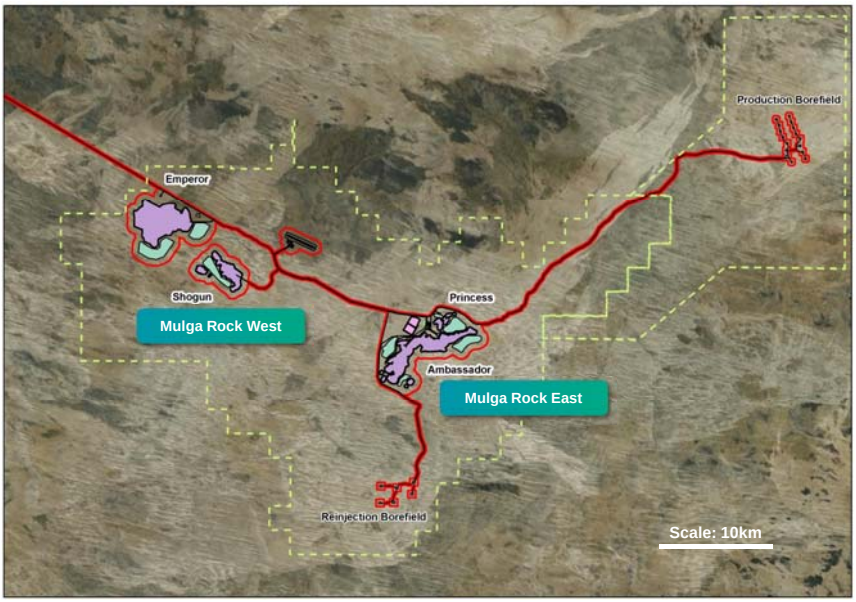
Proposed Mining Method (Mechanised)

- Life of Mine = 16 years (Targeting > 20 years)
- Shallow, large deposits
  - Total pit area = ~ 900ha;
  - Depth = 40 – 60m below ground level
  - Open cut, strip mining techniques
  - Similar to mineral sands mining
  - Overburden: ore strip ratio = ~ 15:1
- Advanced Dewatering (submersible bores ahead of mining front)
- Overburden removal – Mobile IPCC (up to 40m thick)
- Ore - Truck and shovel (typically 5-10 m thick)
- Development envelope = 9,998ha
- Disturbance footprint: Total = 3,787ha; Real Time < 1,000ha

Mining: Mechanised



Ore Deposits and Proposed Site Layout



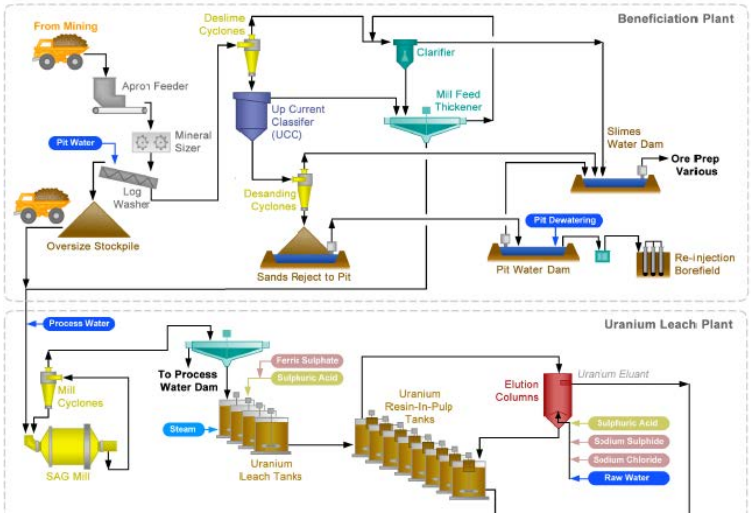
Process Flowsheet

- Polymetallic ore – U (as predominantly uraninite), with associated base metal sulphides (Co, Cu, Fe, Ni, Zn)
- Beneficiation Plant
  - Uranium contained in fine grained carbonaceous clays, lignite/lignitic shales and carbonaceous sands
  - Gravity separation to remove sand/quartz (~ 50-60% mass rejection expected; approx. 4% U loss to tails)
  - Breakthrough ore beneficiation results obtained in large-scale testwork at AML in 2015 using Spirals and Up-current Classifier (UCC) – incorporated into flowsheet
  - DFS Pilot-scale demonstration testwork using UCCs; evaluation of UCC configuration: Rougher – Scavenger and Rougher - Cleaner

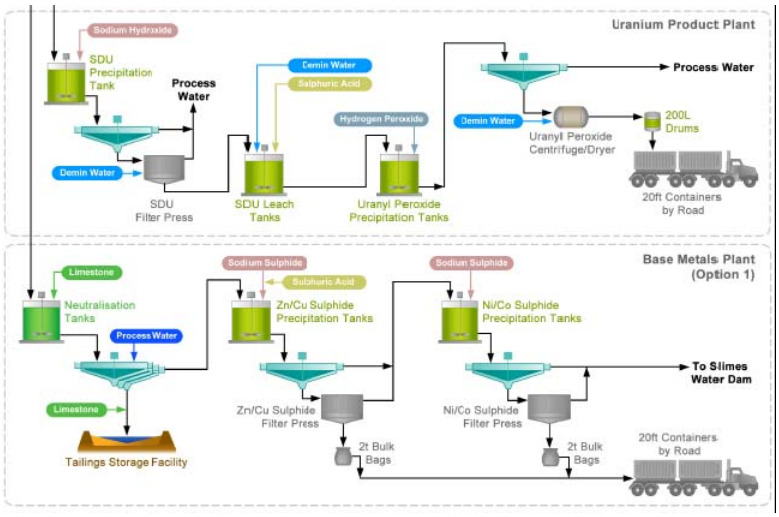
Process Flowsheet – cont.

- Uranium Hydrometallurgical plant
  - Simple acid leach (1atm, 6-12hrs, 50-70^{o}C; low acid req.)
  - U recovery via Resin-in-Pulp Circuit
  - Nano-filtration (NaCl recycled to elution)
  - Direct precipitation of Uranyl Peroxide Hydrate with H_2O_2
  - Centrifuge drying/packing: ~ 1,360 tpa contained U_3O_8
- Base Metals plant
  - U-barren slurry neutralised with limestone
  - CCD washing/thickening; CCD underflow (tailings) are neutralised
  - Base metals recovered from CCD overflow by precipitation as sulphides using Na_2S

Beneficiation and Uranium Leach/RIP/Elution - Schematic Process Flowsheet



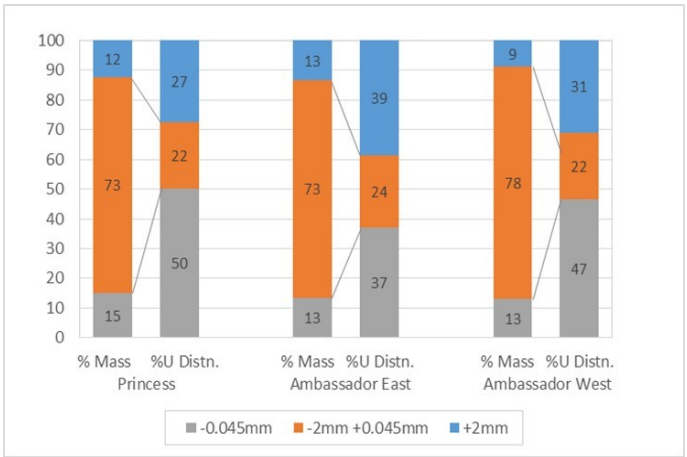
Uranium Precipitation and Base Metals (Cu, Zn, Ni, Co) Recovery - Schematic Process Flowsheet



Beneficiation Testwork

- Uranium resource contains a large portion of coarse silicate sand that contains relatively low grades of uranium mineralisation; up to 65% of the ore is silica-rich sand.
- Uranium mineralisation is associated with light carbonaceous and clay minerals
- Size by assay analysis of “as received” ore and attritioned ore showed that the coarse fraction (+2mm) is consistently concentrated in uranium compared to the overall head assay.
- Attritioned ore, whilst finer and containing significantly less mass in the coarse fraction, retained too much mass and uranium to be acceptable as a tailings reject.
- The fines fraction (-45µm) is concentrated in uranium, and the deportment of mass and uranium is increased significantly by attritioning.

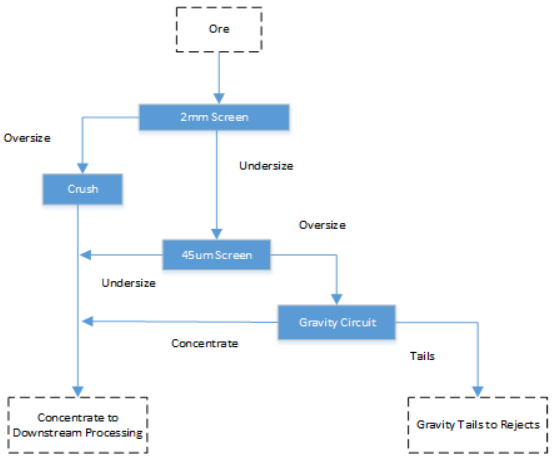
Mass and Uranium % Distribution Results for Princess, Ambassador East and West Composites



Beneficiation Testwork – Diagnostic HLS tests

- Diagnostic Heavy Liquid Separation (HLS) testwork demonstrated that, below 4.75mm, uranium minerals are sufficiently well liberated that they can be separated from the majority of gangue minerals using a liquid specific gravity (SG) separation at 2.0
- Lignite typically has SG of 1.3 – 1.5, and lignitic shale ~ SG 1.7, compared with quartz SG of approx. 1.6 – 1.7
- A beneficiation flowsheet was developed to take advantage of the concentration of uranium in the coarse and fines, and the fact that the intermediate size fraction can be concentrated by gravity separation

Ore Beneficiation - Conceptual Flowsheet Evaluation



Beneficiation Testwork – Summary

Ore Body	Gravity Circuit Configuration	Calc Head U_3O_8 ppm	Beneficiated Product			Mass Rejection %
			U_3O_8 ppm	Upgrade Ratio	U_3O_8 Recovery %	
Princess	UCC Rghr / Spiral Clnr	652	2,252	3.5	95.4	69
	Wilfley Table	722	2,011	2.8	97.7	65
Ambassador East	Spiral Rghr / Spiral Mids Clnr	723	1,980	2.7	95.9	65
	Wilfley Table	826	2,149	2.6	97.4	63
Ambassador West	Wilfley Table	836	1,802	2.1	96.9	55

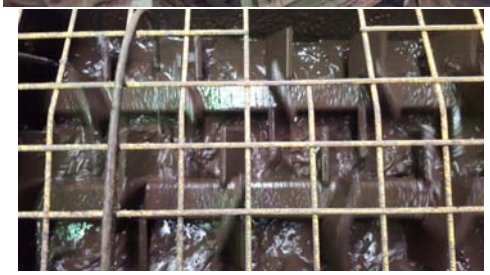
Beneficiation Testwork – Key Findings

- Wilfrey table was used as a laboratory technique to test gravity spiral or UCC
- UCC and Spiral gravity separation produced similar results to laboratory Wilrey Table with scale up.
- UCC achieves a more effective separation of uranium from the bulk mass compared to the spiral.
- A simple beneficiation flowsheet has been developed that can achieve uranium grades in beneficiated ore 2.1-2.8 times the original grade
- Mass rejection of 55-65% to beneficiation tailings
- Uranium recoveries of 95-98% to beneficiated concentrate achieved

Ambassador East – Excavation of Bulk Ore sample #1 for Piloting (17th February 2016)

Ambassador East – Excavation of Bulk Ore sample #1 for Piloting (17th February 2016)

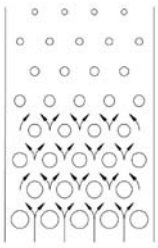
Pilot Logwasher (~160 dry kg/h)



- Approx. 12-15% of mass reports to O/S
- Approx. 40% of U reports to O/S, and is recovered

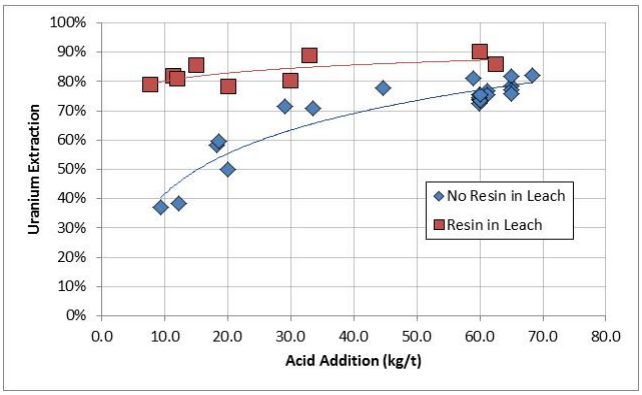
Pilot Upward Current Classifier (UCC)

- Approx. 50-60% of mass reports to UCC U/F (Tails)
- Approx. 4% of U reports to the UCC Tails



A teeter column of sand showing the dispersion of the various sizes

Sulphuric Acid Leach Tests
(High Grade ROM Ore; ~2000 ppm U_3O_8)

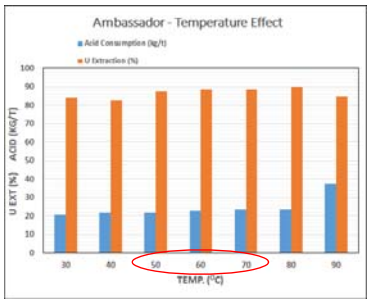


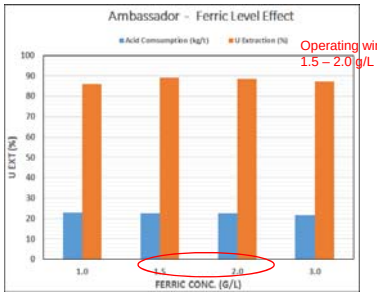
- Decreased uranium extraction in tests without resins, attributed to presence of carbon (lignite) in the Mulga Rock ore
- Solubilised uranium believed to re-adsorb onto the carbon – effectively "preg-robbing" the leached uranium

Resin-in-Leach Optimisation Tests
(Beneficiated Ores)

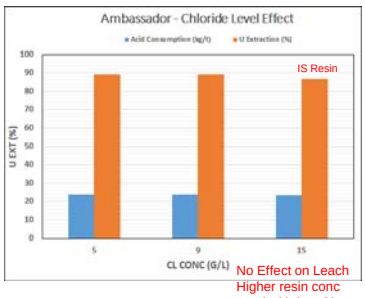
- Resin-in-Leach (RIL) batch tests (~50 completed; 3L stirred heated vessels)
- Parameters examined:
  - Temperature: 30 to 90 ^oC
  - Residence time: up to 12 hrs *(plus 30hrs at 30 ^oC)*
  - Oxidant (Ferric) Addition: 1 to 3 g/L Fe^{3+}
  - Feed density: 25 to 40% w/w solids
  - Sulphuric Acid addition: 20 to 40 g/t
  - Chloride conc.: 5 to 15 g/L
- Base-line Test conditions:
  - 60^oC, 2 g/L Fe^{3+}, 9 g/L Cl, 30 kg/t acid, 8hrs (T>70), 12hrs (T<70)
  - Resin conc.: 10% v/v IX resin
  - Feed density: 35 - 40% w/w

Leaching of Beneficiated Ores - Ambassador East Results



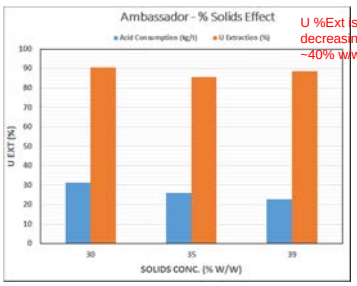


Operating window:
1.5 – 2.0 g/L



IS Resin

No Effect on Leach
Higher resin conc
need with inc. Cl.



U %Ext is not improved by
decreasing feed density;
~40% w/w viable

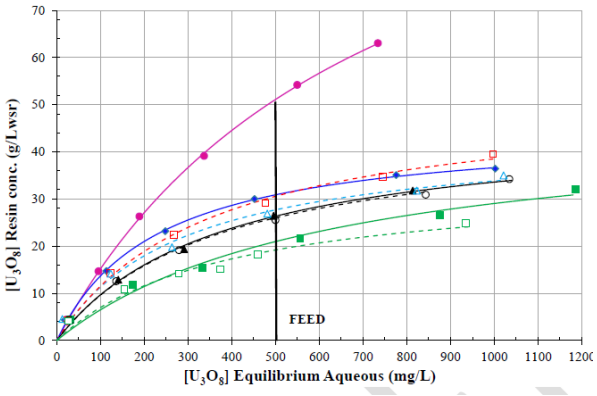
Hydrometallurgical Resin-in-Leach Test Results (Ambassador East beneficiated ore)

Process Control Targets						Head Grade	Uranium Grade of Leach Products			Uranium Extraction (%)	Net H_2SO_4 Consumption (kg/t)
Temp (°C)	% Solids	Leach Time (hrs)	H_2SO_4 Addition Rate (kg/t)	Fe^{3+} (g/L)	Cl^- (g/L)	Uranium (ppm)	Residue (ppm)	Liquor (mg/L)	Resin (%)		
60	40	12	30	2.0	9.0	1634	230	19	1.73	90	22
60	39	12	30	2.0	9.0	1786	212	20	1.72	89	23

- Further testwork has confirmed additional 2-3% increase in Uranium %Recovery with RIP after RIL
- U leach extractions consistently between 88% and 90% irrespective of the amount of acid added (in range from 25 kg/t to 40 kg/t)

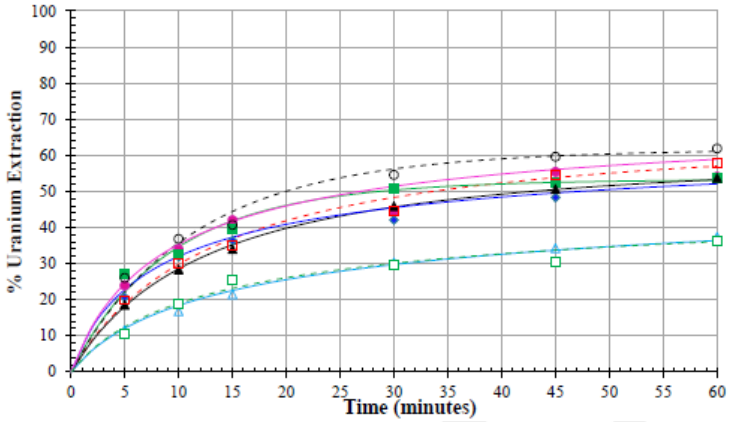
IX Resin Comparison Testwork – Loading Isotherms

- Uranium Loading Isotherms (pH 1.5, 50ºC, 10 g/L Cl)
- Expected loading from modelling is ~ 25-30 g/L
- Theoretical RIP stages: 5
- 7 stages required due to back mixing
- 8 stages allowed in design to allow 1 RIP tank to be offline

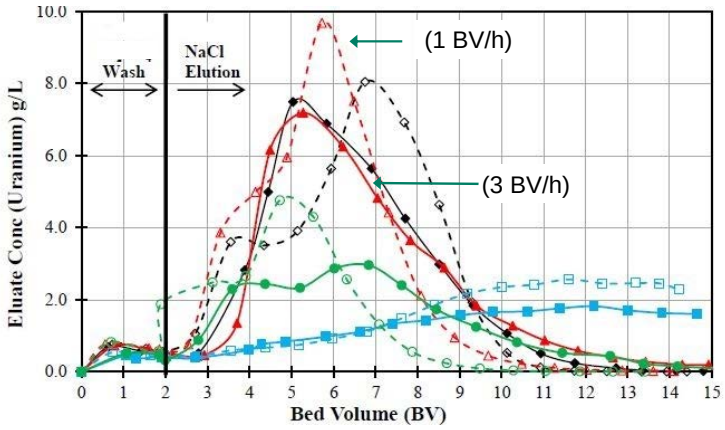


IX Resin Comparison Testwork – Loading Kinetics

Uranium Extraction Kinetics (pH 1.5, 50ºC, 10 g/L Cl)



IX Resin Comparison Testwork – Elution Profiles (NaCl eluent)



Hydrometallurgical Uranyl Peroxide Batch Precipitation Test (using eluate from IX test)

- Uranium grade (74-76%) exceeds Standard Specification for Uranium Ore Concentrate (ASTM C967-13)
- Product quality easily meets standard specifications with metallic impurity levels well below penalty limits
- Cl is only major metallic impurity – further removal to meet spec. achievable with optimised washing of precipitate filter cake
- Cu, Zn, Co all < 0.001%; Fe < 0.03%
- Low S (< 0.2%)

Summary - Mulga Rock Project – Western Australia

Australia's third largest undeveloped U deposit	75Mlb U_3O_8 Resource + 17 year mine life
Geology	Flat lying lignite-hosted; shallow open pit
Mining	Proven techniques; free-dig mining methods Strip mining allows "real time" rehab
Metallurgy	Beneficiation breakthrough; Low cost acid leach technology
Product	Yellowcake product shipping via Adelaide

Acknowledgements

- The metallurgical results presented are the outcome of testwork programs variously conducted at ANSTO Minerals (Lucas Heights, NSW), ALS Metallurgy (Balcatta, WA) and Allied Mineral Laboratories (Osborne Park, WA). The assistance and technical support provided by these laboratories, some for almost a decade, is thankfully acknowledged.

- The technical contributions of the geological, drilling, mining, metallurgical and environmental consultants (and contractors), and Study engineers that have provided input into the Mulga Rock Project, as well as the dedicated efforts of Vimy personnel are all duly acknowledged.

KVANEFJELD REFINERY PILOT PLANT OPERATIONS

By

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ABSTRACT

Greenland Minerals and Energy is a junior project development company which is listed on the Australian Stock Exchange (asx:GGG). It is developing the Kvanefjeld rare earth and uranium project located in the southern tip of Greenland. The project has completed a Feasibility Study and is currently in the permitting phase.

Last year was a busy time for the company as it completed a Feasibility Study, a mining licence application (draft submitted in December 2015) and pilot plant operations. Beneficiation pilot plant operations were completed at GTK in Finland in April 2015. This pilot plant treated approximately 30 tonnes of ore to producing almost 2 tonnes of rare earth mineral concentrate.

Later in the year a hydrometallurgical pilot plant was performed which mimicked the Refinery process. This pilot plant was performed at Outotec's Pori Research laboratories in Finland from September till October 2015. The pilot plant treated approximately 200 kilograms of concentrate over 4 split operating campaigns. Each campaign was performed to focus on the performance of a specific part of the refinery flowsheet. This allowed for full operating focus on a single unit operation to ensure that it was operating correctly.

The pilot plant operations were quite successful with no major issues with the flowsheet identified through continuous operation. Some fine tuning of conditions was required to ensure adequate removal of impurities was performed with recycle streams incorporated. Overall the leach extractions observed in the pilot plant exceeded the design assumptions in the Feasibility Study.

These programs were partially funded by the EURARE program. The EURARE program aims to encourage the sustainable development of European based rare earth projects. This has the goal of allowing Europe to become less reliant on importation of these key raw materials. The professionalism and performance of both GTK and Outotec contributed significantly to the success of the pilot plant operations.

Keywords: Kvanefjeld Project, rare earths, uranium, refinery, beneficiation, hydrometallurgical, pilot plant

GMEL's Vision

A Small Company with a Big Project

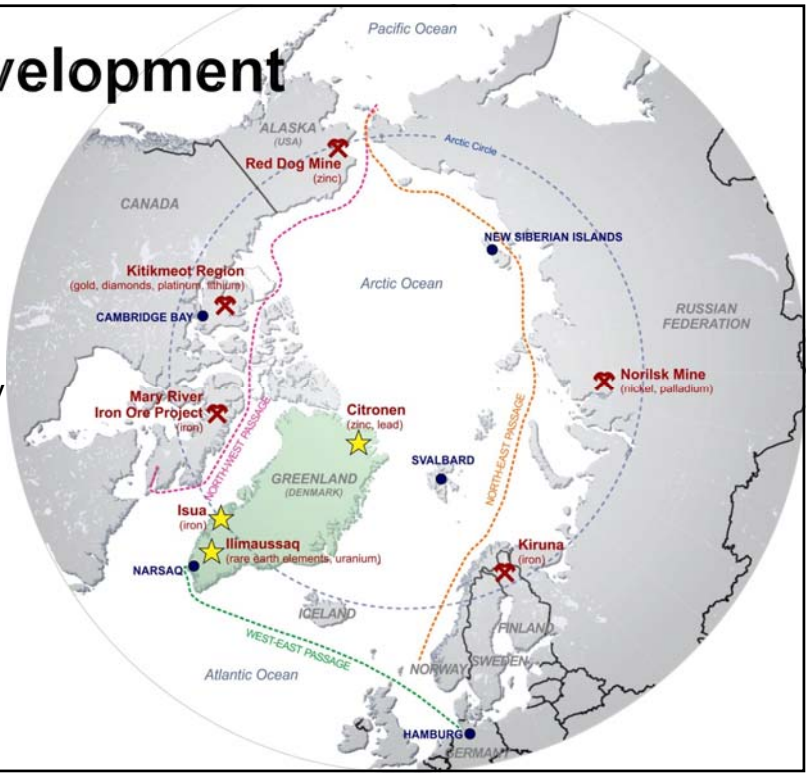
Globally Significant, Locally Important

- Listed on the Australian Stock Exchange – ASX: GGG
- Developing the Kvanefjeld Project
  - Rare Earths ~90% of Revenue
  - Uranium
  - Zinc and other minor by-products
- Immense resources of rare earths and uranium
- Located in the Southern Tip of Greenland
- Currently at the permitting Stage post Feasibility Study
- Will be a large, long life, expandable and low cost mine
- Will provide jobs, opportunities and tax for Greenland

Arctic Development

Greenland is increasingly the centre point of Arctic resource focus due to:

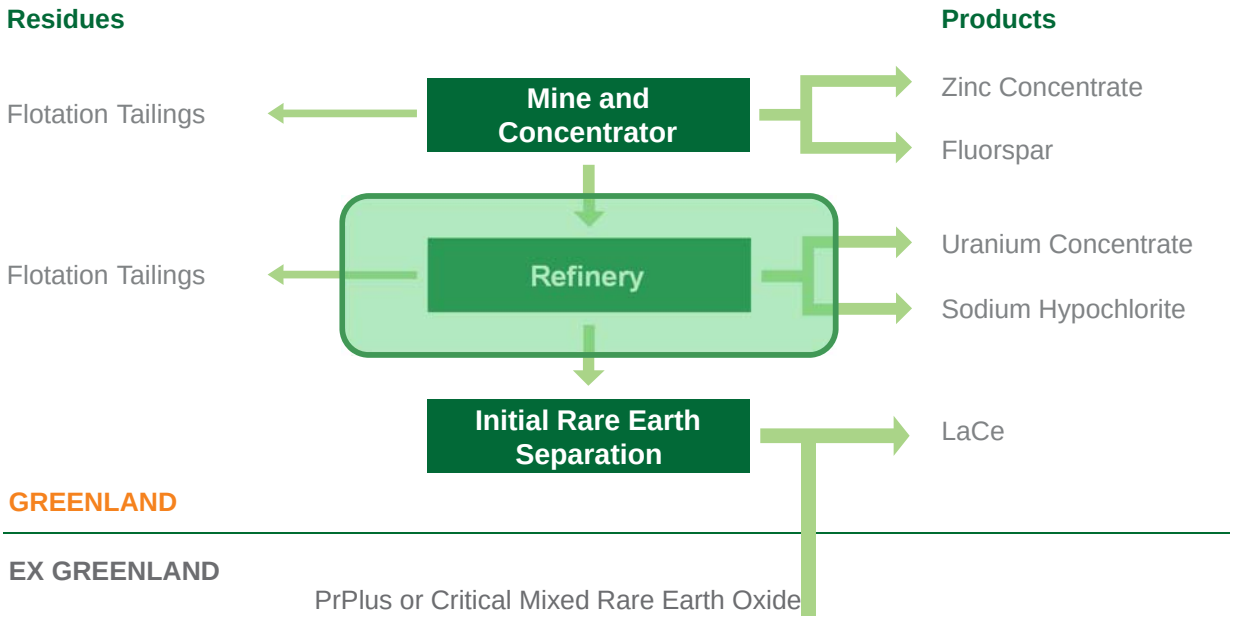
- Political stability with increasing independence
- Political push to move toward a natural resource-based economy
- Numerous mineral resource projects awaiting development
- Mining licenses being issued
- Opening of Arctic shipping lanes providing access to Asia-Pacific



European Union Funding

- The EU is encouraging the development of a rare earth for the EU region.
- The EURARE program aims to:
- ‘Safeguard supply of REE for the EU in a sustainable, economic and environmentally friendly way.’
- The program consists of a number of partner which each contribute expertise, services and knowledge
  - Mining companies, universities, technology, refiners, end users
- GMEL is the leader for the Mining Work Package
- The pilot plant was partially funded by Eurare

Kvanefjeld Overall Metallurgical Flowsheet

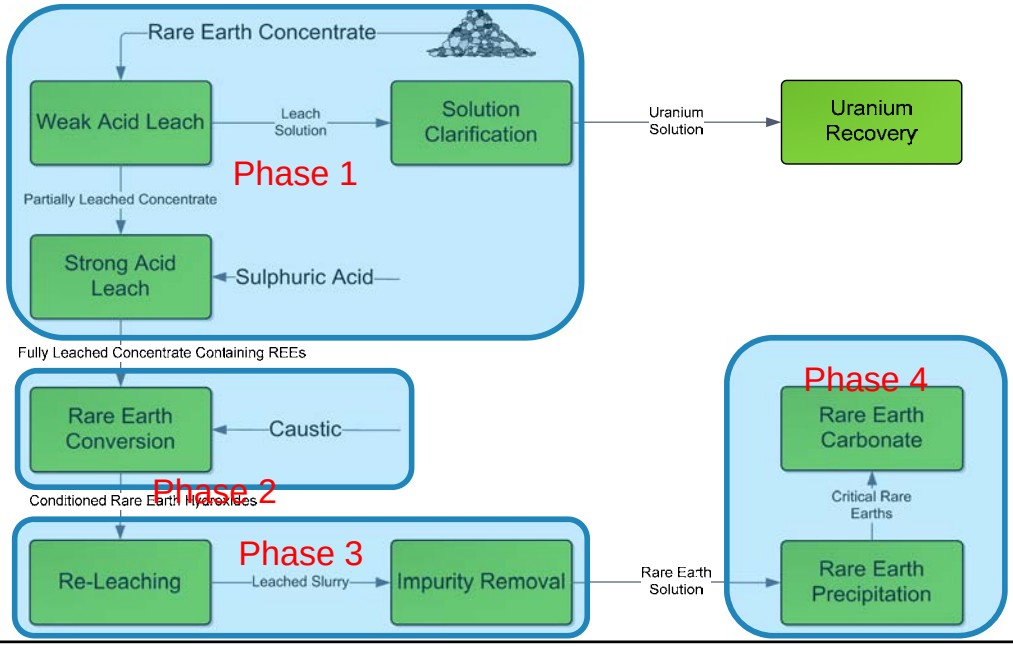


Piloting Performed at Outotec's Pori Laboratories

Pilot Plant Feed

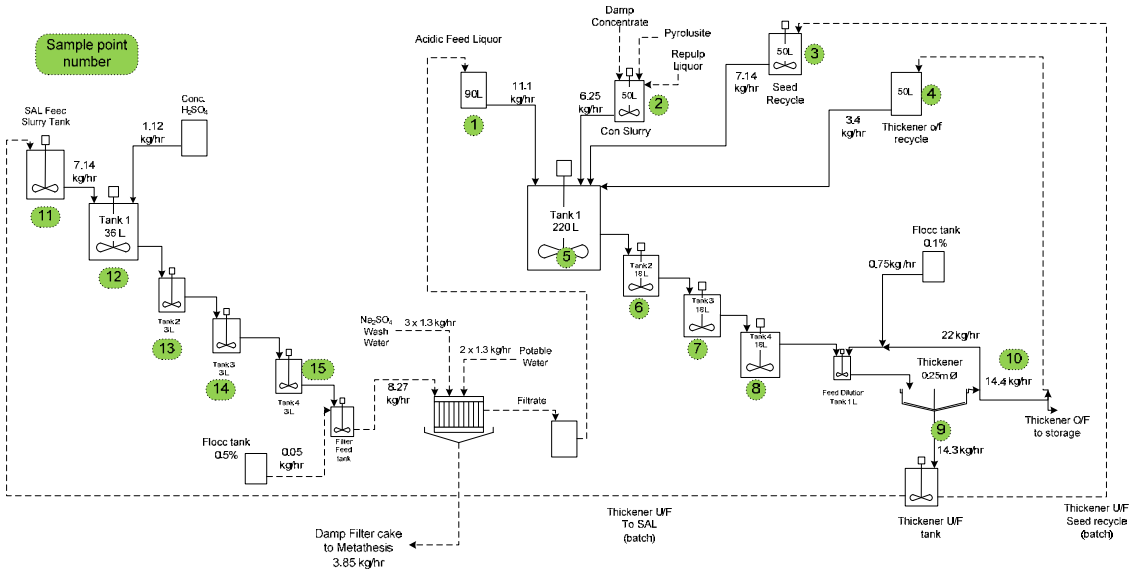
- 1st Kvanefjeld Refinery Pilot Plant Performed
  Previously completed 100 hour continuous leaches
- Concentrate from 26 tonne flotation pilot plant in May 2015
- Fully integrated two stage leach
- 250 kg of rare earth concentrated treated

Pilot Plant Overall Flowsheet
Performed in Four Phases

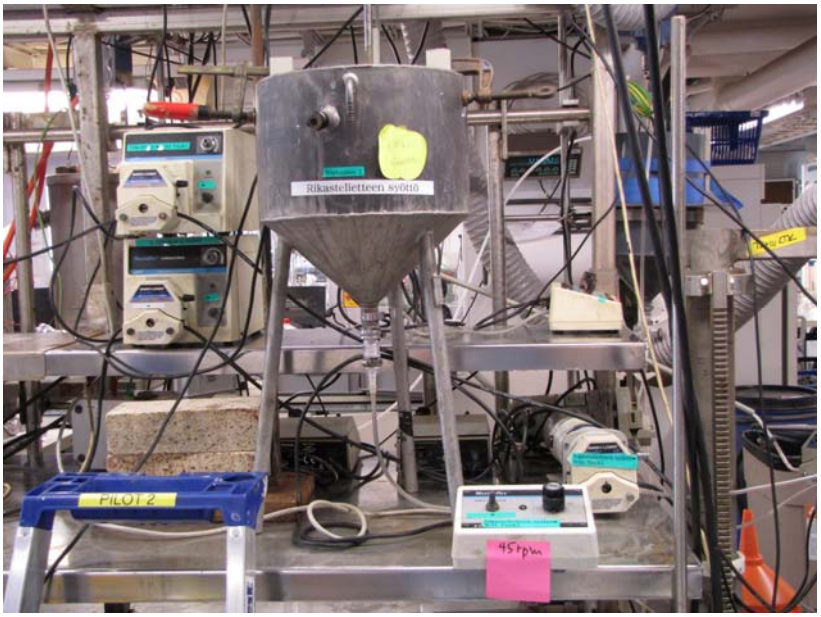


Pilot Plant Phase 1: Counter Current Leach

Two Stage Counter Current Leach Circuit



Phase 1: Concentrate Storage



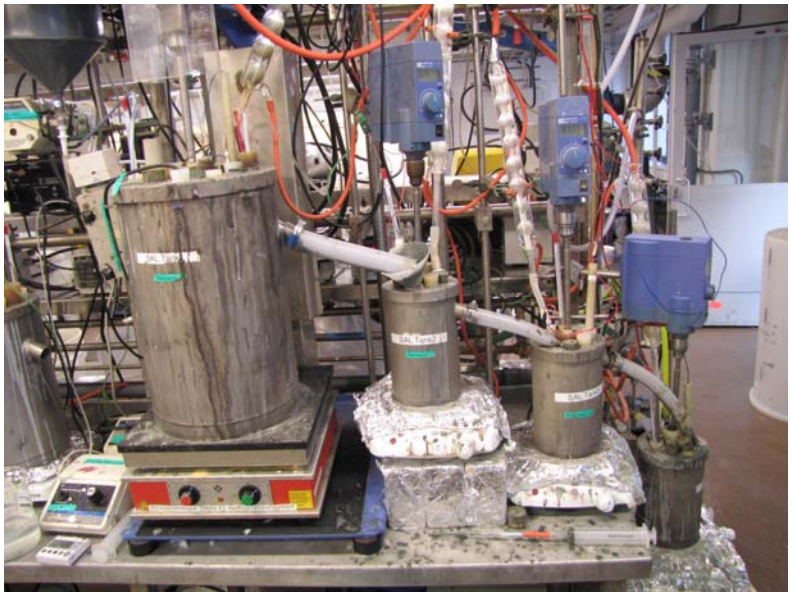
Weak Acid Leach Tank 1: *Large 1st Reactor to seed Silica Precipitation*

Weak Acid Leach: CSTRs

Weak Acid Leach Thickener: Clear Overflows Required for Uranium Solvent Extraction

Strong Acid Leach Circuit

- High Acid Strength required for >90% extraction
- Acid at ~80 g/L of free H_2SO_4



Strong Acid Leach Filtration

- Direct Filtration of SAL discharge needed to keep rare earths in the solid phase.
- Belt Filtration successfully tested
- Washing with sulphate solution and warm potable water

Strong Acid Leach Filtered Residue

- Contains ~14% REO with most U extracted
- This residue contains the rare earths for the next stage…metathesis

Weak Acid Leach Thickener Overflow

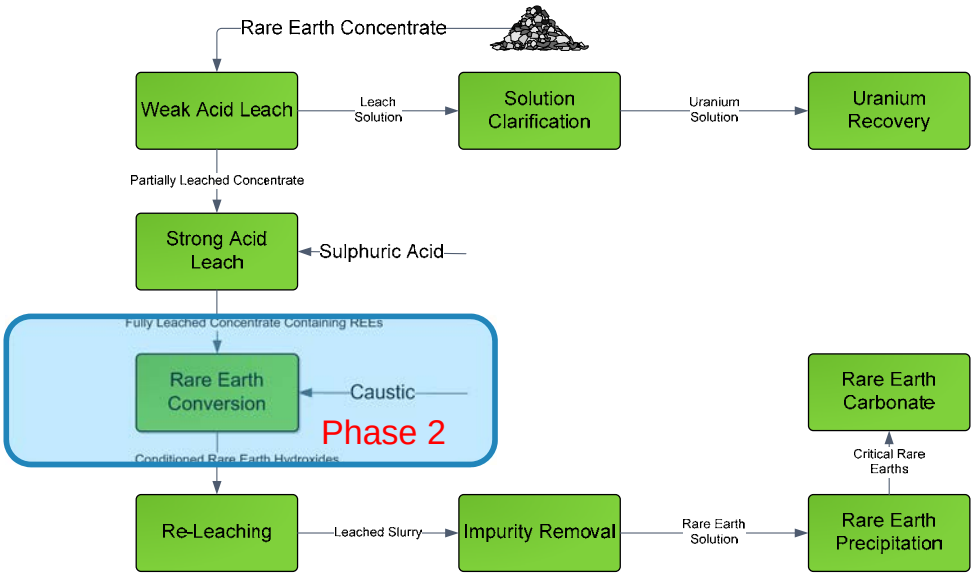
- Low grade uranium solution
- Contains ~250 ppm U with Al, Fe, Na, K, Mn in a sulphate solution.
- End point for Phase 1

Good Facilities including PC Control: Operation 31st Aug till 11th Sept

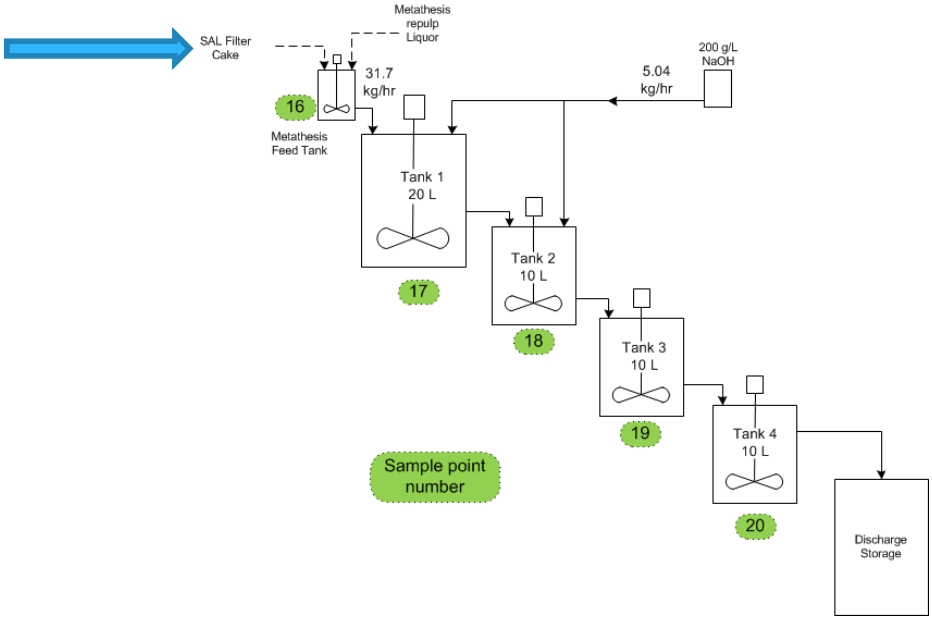
Phase 1 Performance = Very Good

- High availability with only 4 hours of downtime
- Rare earth leach extraction of ~95%
- Exceeding Feasibility Design of 77%
- Uranium leach extractions of ~85%
- Good circuit operability
- Silica control effective with no gelling
- Filtration and Thickening working well

Phase 2: Metathesis Pilot Plant



Rare Earth Double Sulphate Conversion

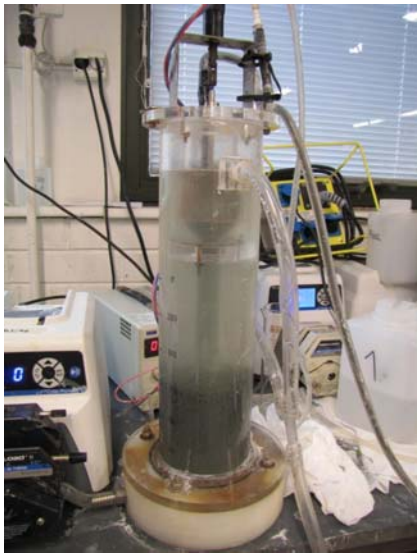


Repulped Strong Acid Leach Filter Cake

Metathesis CSTR Cascade

- $NaREE(SO_4)_2.xH_2O$ converted to $REE(OH)_3$
- Sodium sulphate solution produced

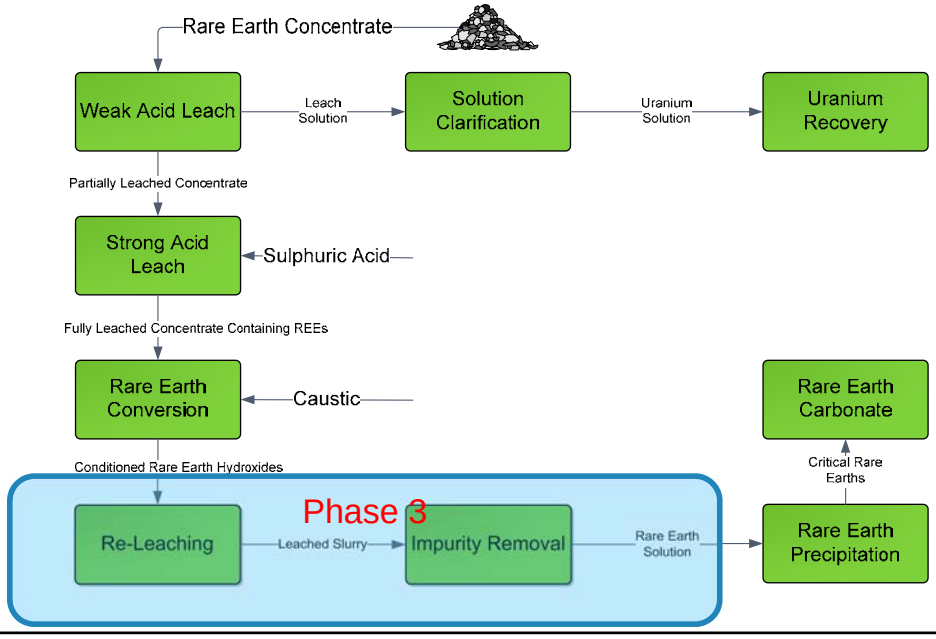
Dewatering of Metathesis Residues: Engineering data confirmation



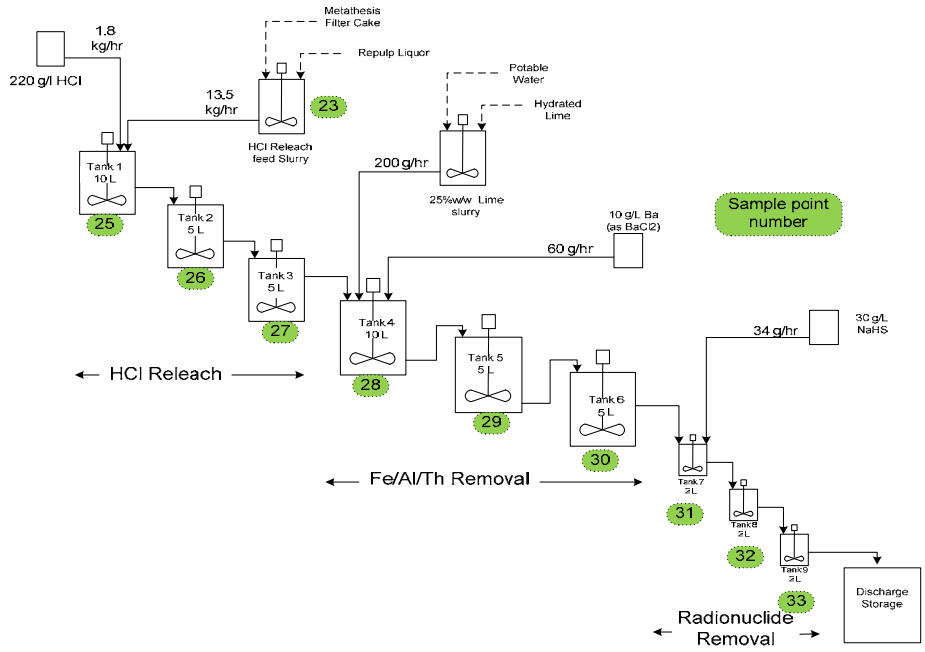
Metathesis Performance

- High availability, no downtime
- Extensive double salt conversion achieved
- Short residence time of ~1 hour
- No requirement to heat circuit confirmed
  - Room temperature and pressure
- Good circuit operability
- Thickening and filtration working well

Phase 3: Re-leaching and Impurity Removal



Phase 3: Flowsheet – *HCl mild leach then impurity precipitation*



Hydrochloric Acid Mild ReLeach

- Rare earths dissolved with HCl
- pH 1.8
- Room Temperature
- RT = 1.5 hours
- Three CSTRs

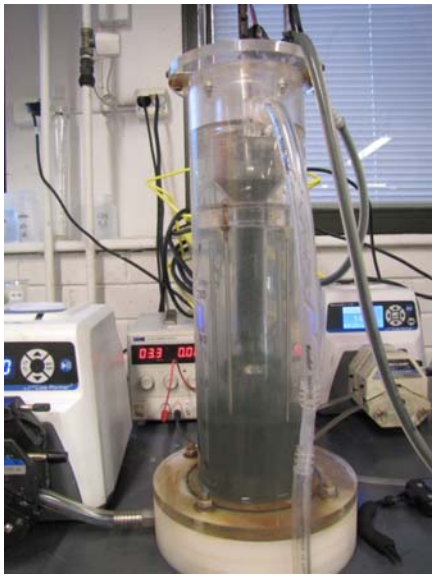
Phase 3: Impurity Precipitation

- Impurities removed via precipitation
- pH adjustment with hydrated lime slurry
- Room Temperature
- Fe/Al/Th precipitated with very low REE losses

Radionuclide Removal

- Hydrogen Sulphide Precipitation
- Precipitates Pb/Zn/Po/Bi
- Radium precipitated with Barium salts

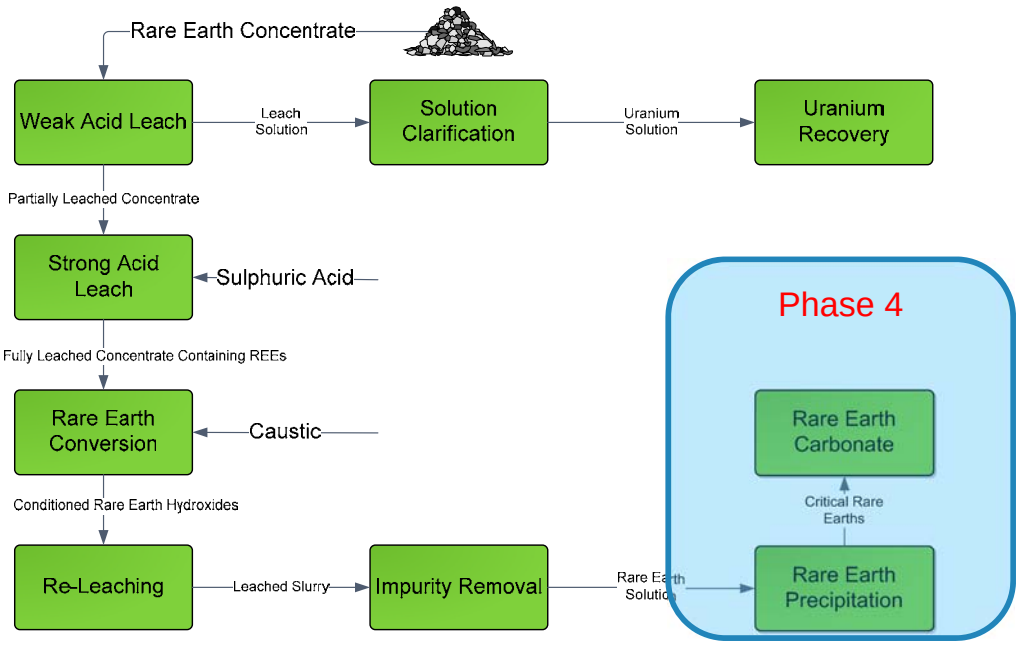
Solids Removed by Thickening and Filtration



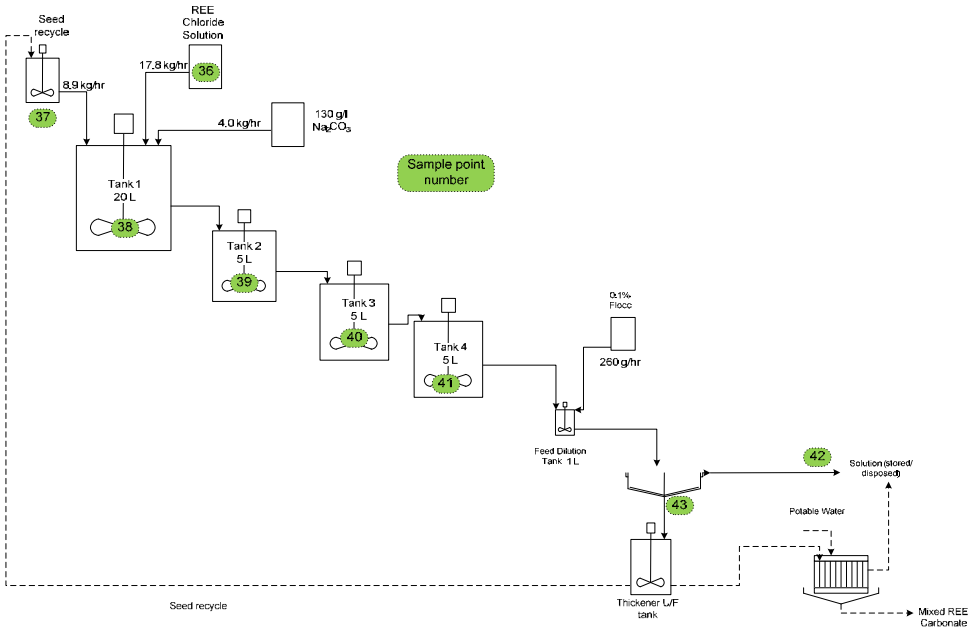
Phase 3 Performance

- Rare earth recovery from converted double salt >95%
- Low iron and aluminium dissolution in HCl releach
- High rejection of impurities.
- No requirement to heat circuit confirmed
- Good circuit operability
- Thickening achieved good underflow density and overflow clarity

Phase 4: Rare Earth Carbonate Precipitation



Phase 4: Mixed Rare Earth Carbonate Precipitation with Soda Ash



Phase 4: Carbonate Precipitation CSTRs

- Carbonate gradually dosed into tanks
- Rare earths precipitate fully at around pH 6.8
- All 15 are precipitated
- Seeding needed to improve S/L

Final Product: 50% REO washed cake – *Sent to MEAB for Solvent Extraction*

Phase 4 Overall Performance

- High availability, no downtime
- High rare earth recovery from solution
- Good selectivity against impurities (Ca)
- No requirement to heat circuit confirmed
- Simple circuit operability based on pH

Successful Pilot Plant Campaign yet…lessons learned.

- Check specification of all reagents used in the pilot plant
  - Including first fill synthetic solutions
- Have 24 hour monitoring by owners teams which know the chemistry
- Plan set point changes carefully
- Bring a wide range of coagulants and flocculants
  - Continuously produced residues are different to batch
- Fast assay turnaround for important assays
  - i.e. Silica

GMEL would like to thank

- The competent and experienced staff of Outotec's Pori Research facility for their patience and hard work
- Outotec for hosting the pilot plant
- EURARE for supporting the project
- Domenic Furfaro and Andrew Wydler who worked 12+ hour shifts during the pilot plant

Uranium-REE Proceedings

Process Development

THE EXTRACTION OF URANIUM FROM BRANNERITE

By

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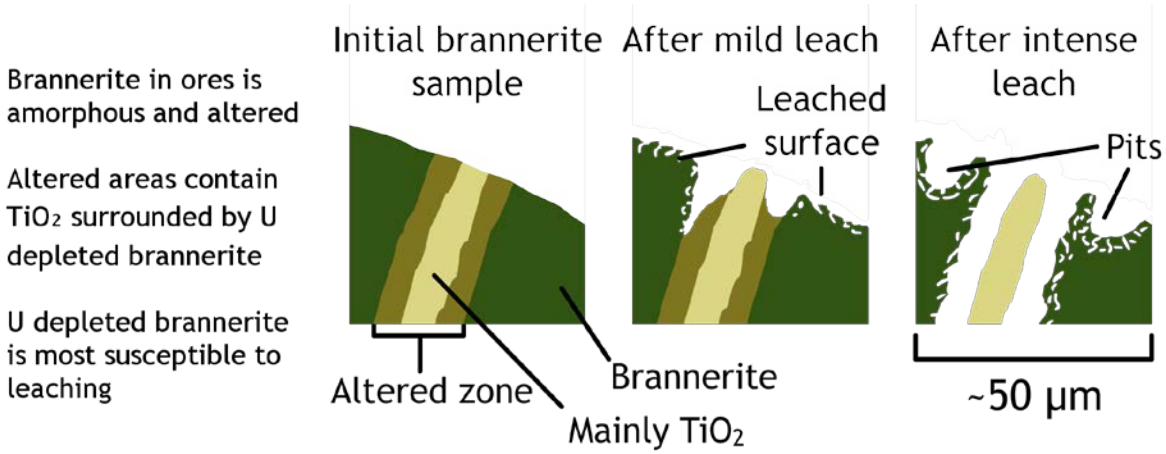
ABSTRACT

Brannerite, UTi_2O_6 is the most important uranium mineral after uraninite, UO_2 and coffinite, $U(SiO_4)_{1-x}(OH)_{4x}$. It is also the most common refractory uranium mineral. Ores containing brannerite typically require intense conditions (>50 g/L H_2SO_4, >75°C) compared to other uranium ores for effective uranium extraction to occur. To develop an effective process for the extraction of uranium from brannerite containing ores and improve the extraction from the ores currently being processed, it is necessary to understand the chemistry of the brannerite leaching process.

As this study has shown, brannerite is typically an altered and amorphous mineral, with an extent of alteration depending on the age of the sample and the geological history of the deposit. A sample of brannerite from Cordoba, Spain, was leached over a range of conditions in acidic ferric sulphate media. The sample was filled with cracks and altered zones containing anatase (TiO_2). Process parameters studied included temperature (25-96°C), acidity (10-200 g/L H_2SO_4) and the effect of adding selected gangue minerals (apatite, fluorite and ilmenite). The feed and the leached residues were characterised in detail by XRD and SEM-EDX techniques.

The results of this study showed that brannerite dissolution has a stronger dependence on temperature and lesser dependence on free acid concentration. Comparisons between the residues and the feed showed that the altered and amorphous areas of the brannerite sample are more readily leached than crystalline areas. The crystalline areas of the brannerite dissolved congruently, with titanium subsequently precipitating as anatase physically separated from the original brannerite grains.



Keywords: Uranium, Titanium, Brannerite, Leaching, Kinetics, Mineralogy

INTRODUCTION

Brannerite, UTi_2O_6 is the most important uranium mineral after uraninite, UO_2 and coffinite, $U(SiO_4)_{1-x}(OH)_{4x}$ (Finch and Murakami, 1999). It is also the most common refractory uranium mineral. It has been identified in many uranium and rare-earth element deposits around the world, including several in Australia.

Brannerite is typically metamict, rendered amorphous by self-irradiation. The degree of metamictisation varies with age (Lumpkin et al., 2012) and has been found to influence leachability (Charalambous et al., 2014).

Ores containing brannerite require relatively intense conditions for processing. The results of numerous laboratory and industrial studies were summarised in a literature review by Gilligan and Nikoloski (2015a). Lottering et al. (2008) leached three South African uranium ores at 60°C for 24 hours with reagent dosages of 16.3 kg/t H_2SO_4 and 4.0 kg/t MnO_2. Under these conditions nearly all of the uraninite and coffinite were dissolved while most of the brannerite remained intact.

The leaching of high-brannerite ores has required high temperatures (~75 °C), high free acid concentrations (60–75 g/L) and long leaching times (36–48 h) to achieve satisfactory uranium extraction (LaRocque and Pakkala, 1979; Hester, 1979; Ifill et al., 1996). Stanrock Uranium Mines, in the Elliot Lake district, have successfully leached brannerite and thucholite (U/Th oxides associated with organic matter) in 50 g/L H_2SO_4 for 60 h at 65–70 °C (Merritt, 1971). A few of these mines in the Elliot Lake area have also successfully extracted uranium through bioleaching (Mac Gregor, 1969; Wadden and Gallant, 1985).

Brannerite dissolves under oxidising conditions in the conventional acidic ferric sulphate system, releasing uranium into solution as uranyl sulphate complexes such as $UO_2(SO_4)_2^{2-}$ (1) and forming secondary titanium oxide through the reversible hydrolysis of titanyl ions and complexes(2) (Gilligan and Nikoloski, 2015b; Gogoleva, 2012; Smits, 1984). This process is driven by the presence of ferric ions in solution to oxidise uranium to the hexavalent state, sulphate ions to complex uranium, and acid to attack the titanium oxide.

$$UTi_2O_6 + 2\,FeSO_4^+ \rightarrow 2\,TiO_2 + UO_2(SO_4)_2^{2-} + 2Fe^{2+} \quad \text{(Reaction 1)}$$
$$E_a = 36\ kJ/mol$$

$$TiO_2 + 2H^+ + SO_4^{2-} \leftrightarrow TiOSO_4^0 + H_2O \quad \text{(Reaction 2)}$$
$$E_a = 48\ kJ/mol$$

The activation energy (E_a) values were derived from initial extraction rates measured previously by Gilligan and Nikoloski (2015b). At higher temperatures and under more strongly acidic conditions, the uranium and titanium in brannerite dissolve congruently through reaction(3) (Gilligan and Nikoloski, 2015b).

$$UTi_2O_6 + 2\,FeSO_4^+ + 4H^+ + 2SO_4^{2-} \rightarrow UO_2(SO_4)_2^{2-} + 2Fe^{2+} + 2TiOSO_4^0 + 2\,H_2O \quad \text{(Reaction 3)}$$
$$E_a = 23\ kJ/mol$$

The resulting Fe^{2+} ions are re-oxidised to Fe^{3+} with an oxidant, which is usually pyrolusite (MnO_2), sodium chlorate ($NaClO_3$) or oxygen gas depending on availability and process economics. The choice of oxidant has little to no effect on the rate of uranium extraction as long as the E_h is maintained constant (Ring et al., 1984).

MATERIALS AND METHODS

Brannerite was leached for five hours in an aqueous leach solution containing ferric sulphate and sulphuric acid over a range of temperatures (25-96°C) and acid concentrations (10-200 g/L H_2SO_4). The ferric sulphate concentration was kept constant at 2.8 g/L Fe^{3+}.

Both uranium and titanium extraction kinetics were studied, though the latter have been omitted from this paper for brevity. For the full explanation of titanium dissolution kinetics, see Gilligan and Nikoloski (2015b).

The brannerite and all leached residues were characterised by XRD, SEM and SEM-EDX methods. For details of the analyses, see Gilligan et al. (2016).

SAMPLE CHARACTERISATION

The brannerite used in this study originated in the Dieresis deposit near Cordoba in the Sierra Albarrana region of Spain. It is within typical range of brannerite compositions (Gilligan et al, 2016). The sample was obtained as a single crystal. The brannerite itself was translucent and dark green in colour. The crystal was coated with a thin layer of pale yellow/brown anatase and interlaced with cracks containing the same material, which is indicative of natural alteration.

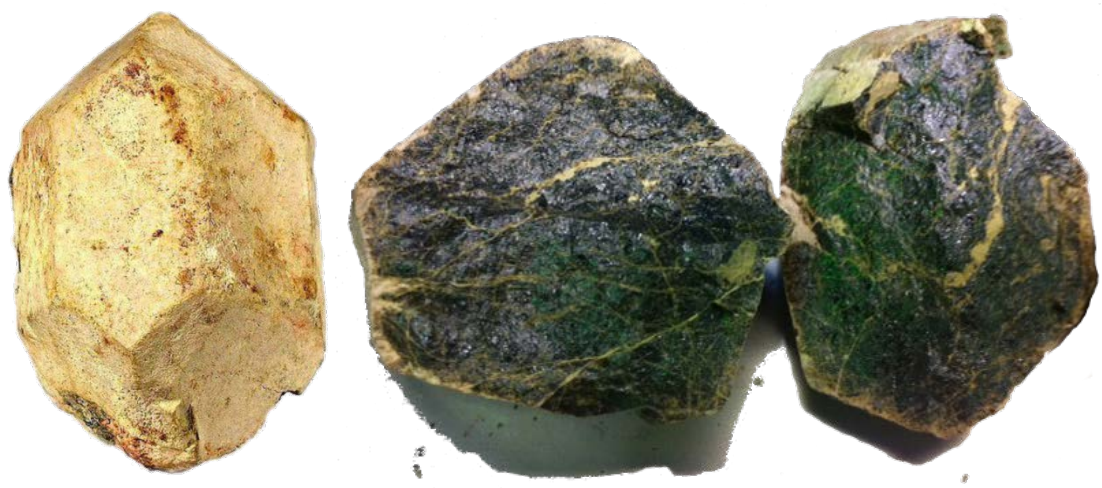


Figure 1: The brannerite specimen; left: outer surface; right: the inside of the crystal

The cracks in the brannerite were clearly visible in backscattered electron SEM images and element maps. These zones were enriched in titanium and depleted of uranium and calcium. The edges of these altered zones were enriched in silicon and lead (
Figure 2).

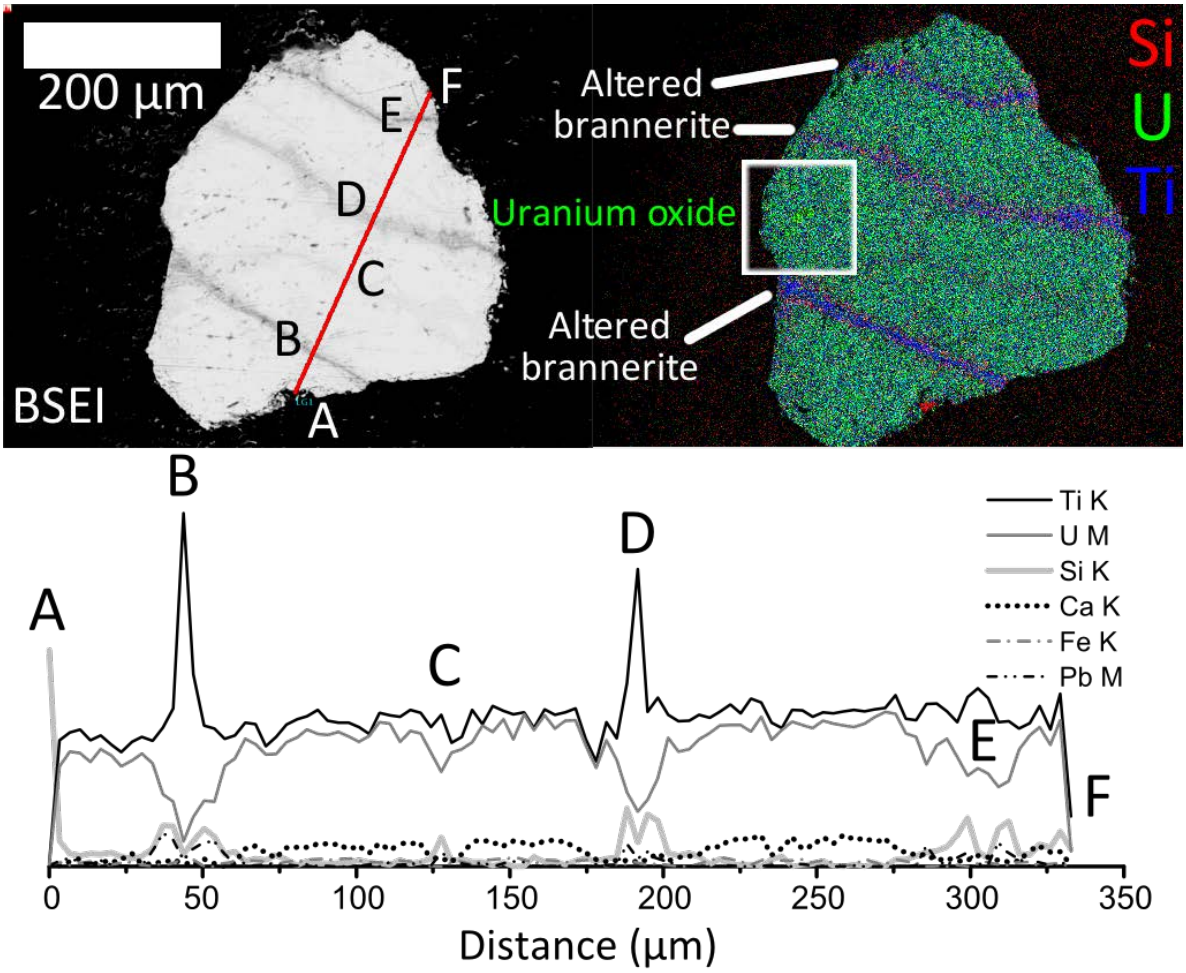


Figure 2: Backscattered electron image (top left), element map (top right) and EDX line analysis (bottom) of an unleached brannerite particle. The position of the line analysis is shown on the BSE image. Letters on the line analysis correspond to points on the BSE image.

X-ray diffraction analyses showed that the brannerite was metamict. Broad humps were identified on the XRD pattern of the feed material from 20-35° and from 40-65°, characteristic of metamict material. Microcrystalline anatase was present as a minor phase, along with small amounts of crystalline thorutite, $(Th,U,Ca)Ti_2O_6$. Calculations indicate that the size of the anatase crystallites was around 10-20 nm. The structure and crystal chemistry of the brannerite specimen are described in detail in a separate paper focusing on the mineralogical aspects of the study (Gilligan et al., 2016).

LEACHING KINETICS

Effect of Acid Concentration

Variations in solution acid concentration had a small effect on the rate of uranium extraction. Increasing the acid concentration beyond 25-50 g/L H_2SO_4 did not significantly improve the rate of uranium extraction. Higher acid dosages were shown to result in increased gangue dissolution, which in turn leads to higher acid consumption (Gilligan and Nikoloski, 2015a).

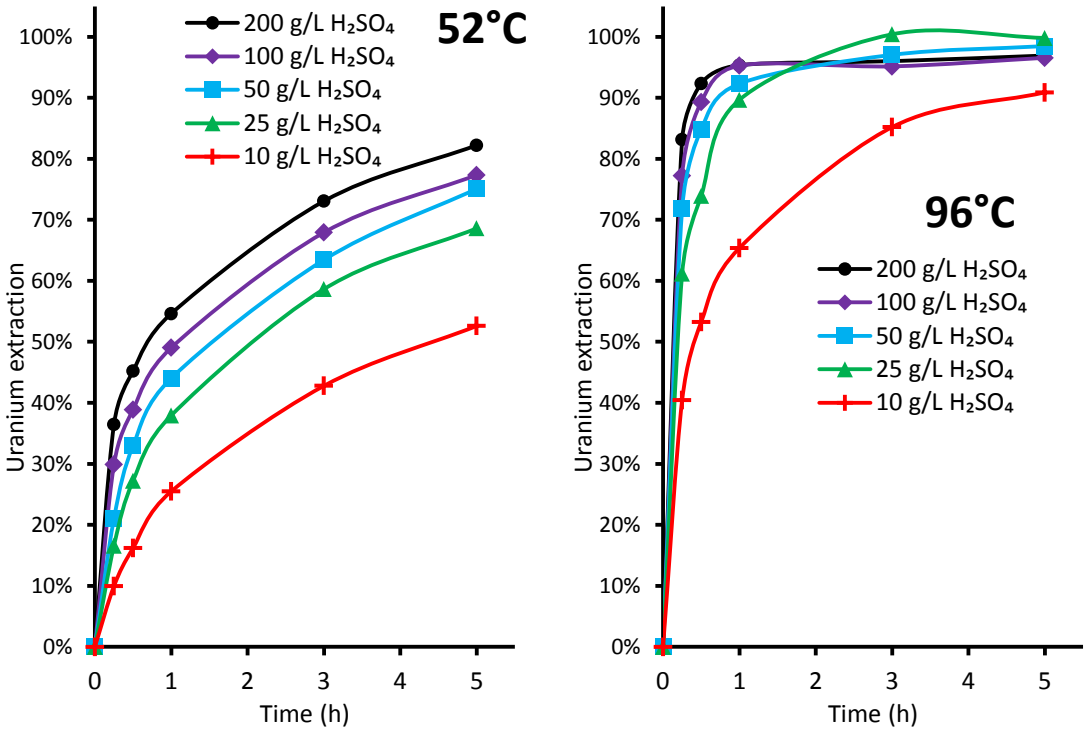


Figure 3: Uranium extraction at varied acid concentrations. Left: 52°C; right: 96°C.

Higher acid concentrations are known to suppress the dissolution of uranium. For uraninite, this concentration is >35 g/L H_2SO_4 (Merritt, 1971). There is some evidence for a limiting acid concentration when leaching brannerite. Gogoleva (2012) found that this was around 100 g/L H_2SO_4. The optimum acid dosage for brannerite leaching is higher than that for uraninite, but not excessively high.

The optimum acid dose is affected by the gangue mineralogy. When then ore contains phosphates, the optimum acid dosage will be higher. These observations will be reported in a forthcoming paper by Gilligan and Nikoloski (under review) and are briefly described under here the heading *Effects of gangue additives*.

Effect of Temperature

Temperature was shown to have a strong effect on the rate of uranium leaching as commonly reported. Raising the leaching temperature by 10°C had a similar effect to raising the sulphuric acid concentration by a factor of 4.

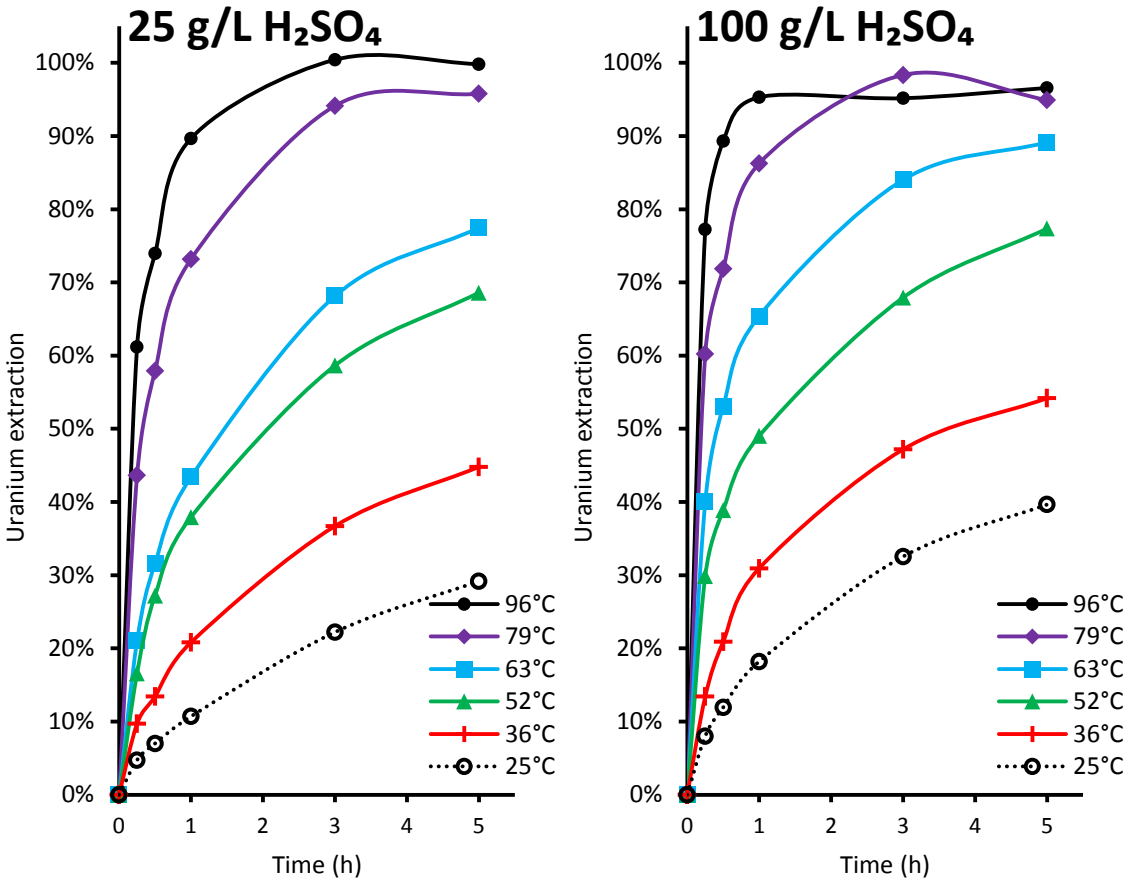


Figure 4: The effect of temperature on uranium extraction; left: 25 g/L H_2SO_4; right: 100 g/L H_2SO_4.

At higher temperatures and lower acid concentrations, titanium was observed to re-precipitate after initially dissolving. The solubility of titanium dioxide reaches a minimum around 115-130°C based on calculations with HSC Chemistry 7.1.1 (Roine, 2011).

For more details on the effect of temperature on the rate and extent of uranium leaching from brannerite, see Gilligan and Nikoloski (2015b).

Effects of Gangue Additives

Due to the geological processes involved in the formation of brannerite, apatite is often present with brannerite containing ores as a gangue mineral. It is therefore important to understand the indirect interaction between these two minerals during the leaching process. To this end some of the brannerite leaching tests reported above were repeated with the addition of fluorapatite. Tests were also carried out with other gangue minerals. Detailed results of this work will be published in a separate paper but a brief summary is provided here.

The results have shown that the addition of phosphate as apatite suppressed the dissolution of both uranium and titanium. When brannerite is leached in isolation, variations in temperature have a much greater effect on the rate of leaching than variations in acid concentration (
Figure 5).

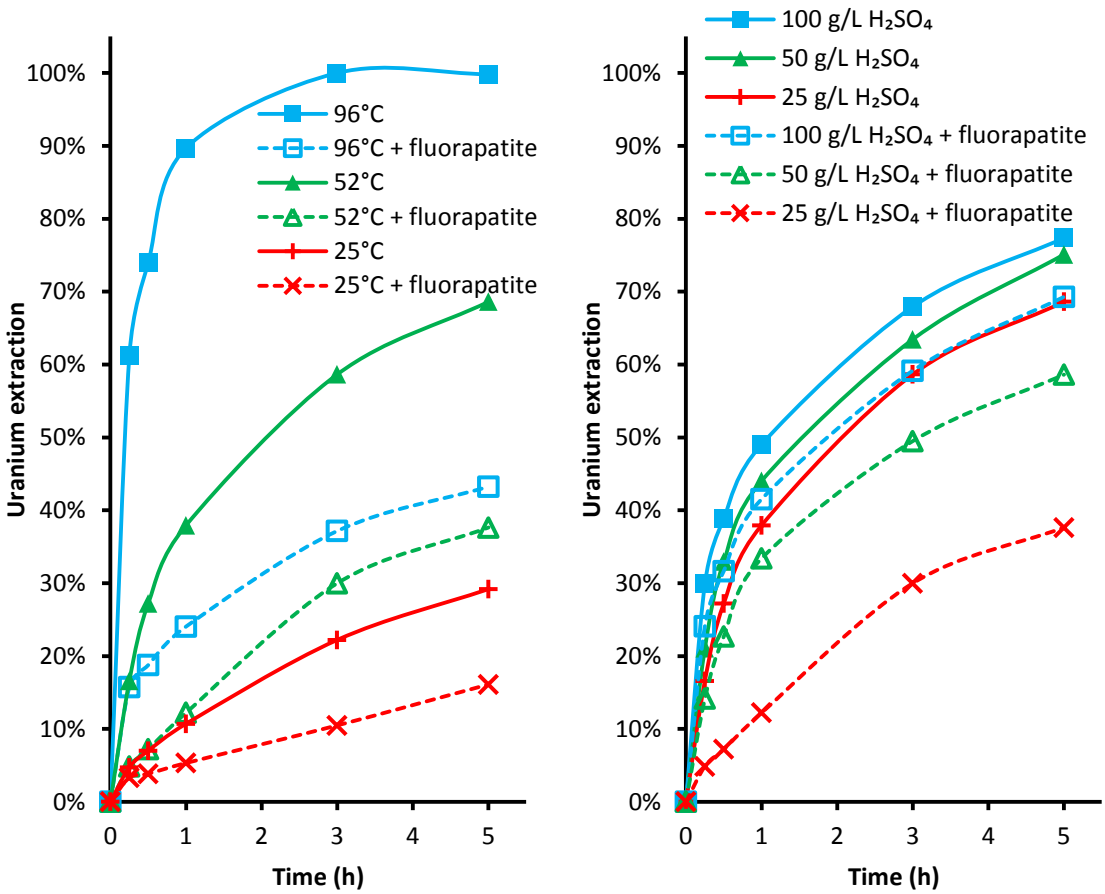


Figure 5: Effect of fluorapatite on the extraction of uranium from brannerite. Left: varied temperature, 25 g/L H_2SO_4; Right: varied acid concentration, 52°C

On the other hand, the addition of fluorite (also called fluorspar) (CaF_2) was shown to significantly increase the rate of brannerite dissolution, likely due to the formation of hydrofluoric acid in the leach solution after the dissolution of this additive.

RESIDUE CHARACTERISATION

Microscopy and EDX Analysis

Examination of a large number of brannerite particles leached over the full range of conditions showed that the leached material was covered in pits 10-20 µm deep. The fraction of the surface covered by these pits increased with the leaching temperature. Brannerite leached at 52°C and above was completely covered in pits. The reaction front at the base of the leach pits was cracked. EDX line analyses of several pits showed that the ratio of uranium to titanium was constant across the base of the leached pits (Gilligan et al., 2016).

Images of cross sections show that altered zones of the brannerite are more susceptible to corrosion, while the associated anatase is much less susceptible to corrosion. Two examples are shown in
Figure 6.

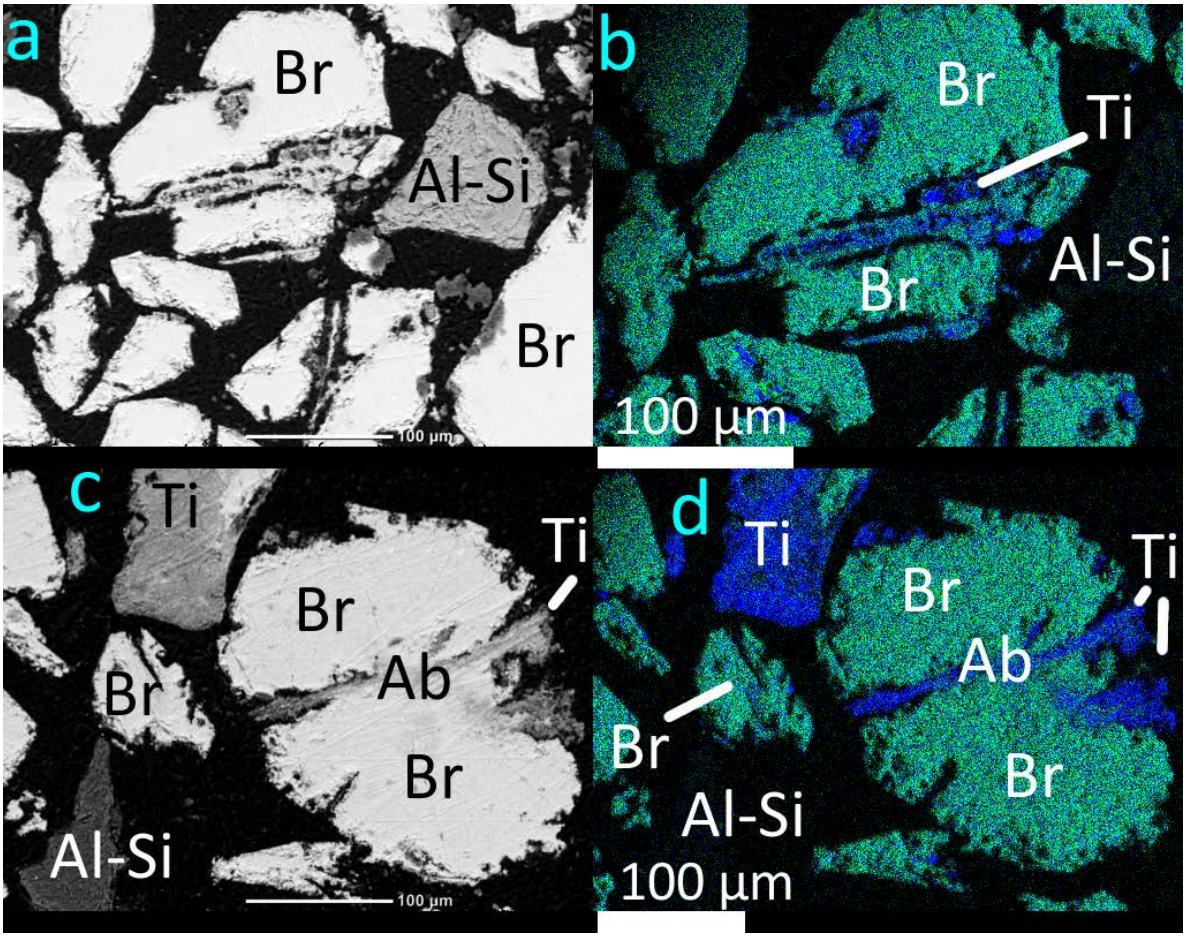


Figure 6: BSEI images (a, c) and element maps (b, d) of leached brannerite particles. Uranium is shown in green, titanium in blue. a/b: 0.50 mol/L H_2SO_4, 25°C; c/d: 0.10 mol/L H_2SO_4, 52°C. Phases: Ab: altered brannerite, Al–Si: aluminium silicate gangue, Br: brannerite, Ti: titanium oxide

One of the important findings of the mineralogical characterisation study (Gilligan et al., 2016) was a dependence of the leaching effectiveness on the texture of the brannerite grains. The results have shown that brannerite that has been altered naturally is more susceptible to leaching, with the extent of alteration having a strong influence on the leaching process. This introduces a new process performance parameter which will vary with age and geological history of a deposit.

It's often reported that a titanium oxide layer forms at the surface of brannerite during leaching. This was not observed in any of the experiments, with the exception of the leaches investigating the apatite interaction (
Figure 7). In some of these tests, titanium dioxide formed as a secondary product, separate from the brannerite. This side reaction occurred at higher temperatures and lower acid concentrations, when the titanium concentration in solution exceeded saturation.

This secondary titanium oxide phase was distinct from the titanium oxide in the original material. EDX analyses showed that it contained iron; while XRD analyses showed that it was anatase. The peaks were shifted slightly, indicating that the associated iron had been incorporated into the crystal structure. Unlike the anatase in the original material, this phase did not contain uranium (Gilligan et al., 2016).

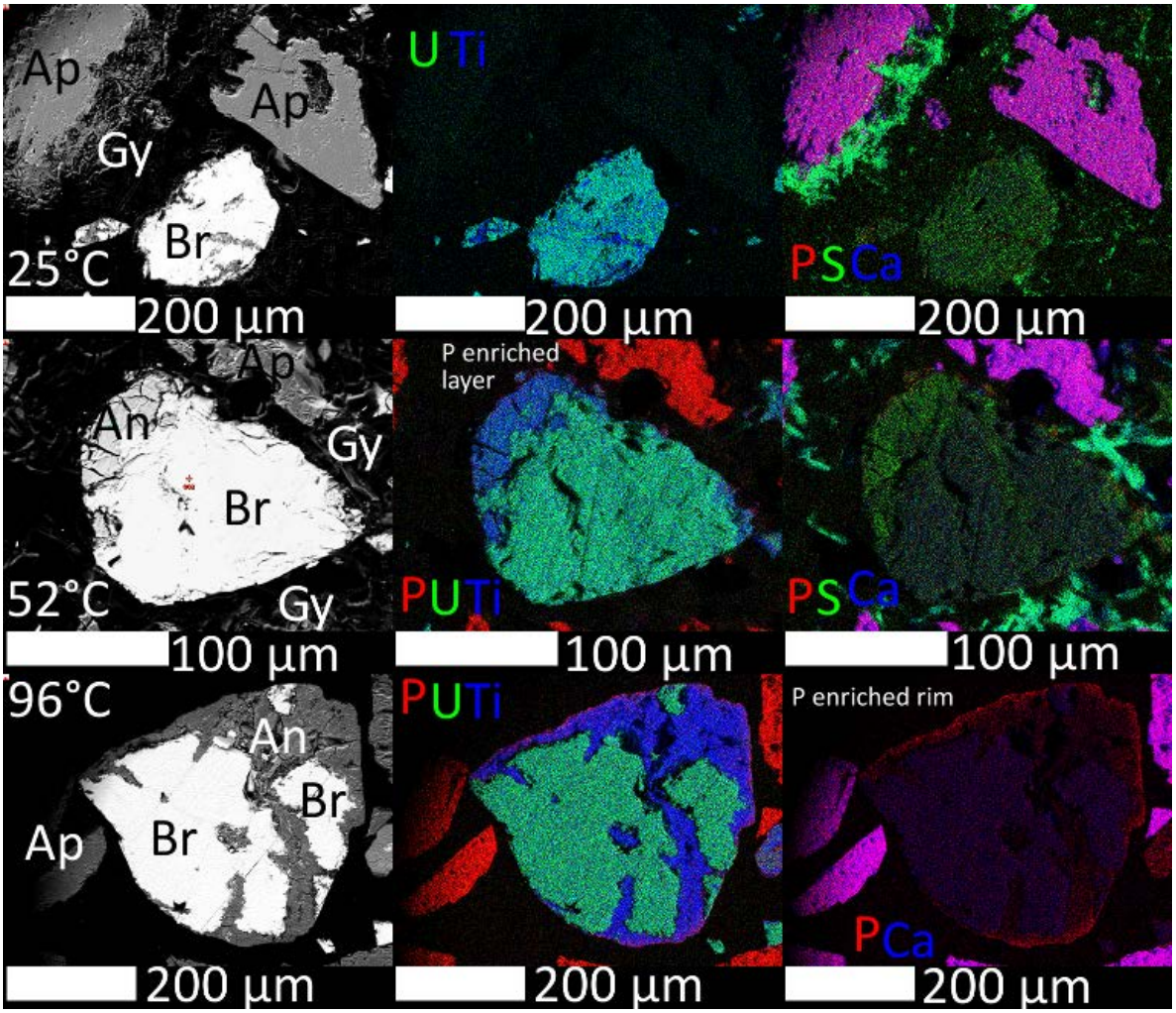


Figure 7: Backscattered electron images and elemental x-ray maps of corroded brannerite particles leached in25 g/L H_2SO_4 and 2.8 g/L Fe^{3+} at varied temperature in the presence of fluorapatite. An: anatase, Ap: fluorapatite, Br: brannerite, Gy: gypsum.

The influence of apatite and phosphates on the leaching of brannerite is complex. Phosphate was observed to interfere with the reactions between ferric ions and uranium, which is a well-documented effect. Phosphate also appeared to stabilise and promote the formation of a titanium oxide coating on leached brannerite, as is apparent from the association of titanium and phosphorus in
Figure 7. This effect was reduced at higher acid concentrations.

X-ray Diffraction Analyses

The broad humps from 20-35° and 40-65° were absent in the x-ray diffraction scans of the leached residues, suggesting that the majority of the amorphous material dissolved during leaching. Anatase was identified in all of the residues, with the anatase peaks being more prominent in the high temperature leach residues. Crystalline thorutite was identified in all of the residues by XRD, indicating that it was extremely resistant to leaching.

CONCLUSIONS

A specimen of brannerite was leached at different temperatures (25–96 °C) and acid concentrations (10–200 g/L H_2SO_4) to determine the effects of these parameters on the rates of uranium and titanium dissolution. Variations in temperature had a much larger effect on the rate of brannerite dissolution than variations in acid concentration.

Fluorapatite, a gangue mineral often associated with brannerite in uranium deposits was found to interfere with the leaching of brannerite in sulphuric acid media. If fluorapatite is present in a refractory uranium ore, higher concentrations of acid will be required, to counteract the effects of

phosphate on uranium and titanium leaching. Increasing the leaching temperature is not as effective for increasing uranium extraction when dealing with high-phosphate refractory uranium ores. When phosphates are present in refractory uranium ore, the preferred acid concentration is higher (>50 g/L H_2SO_4) and the preferred leaching temperature is likely to be lower (~60°C) compared to when low-phosphate refractory uranium ores are treated.

Examination of the brannerite specimen showed that it was altered and heterogeneous, consisting of more than two phases. Comparisons of the XRD analyses of the original material with those of the residues showed that the amorphous brannerite phase was much more susceptible to leaching than the anatase phase or the possible crystalline thorutite phase. While titanium dioxide has been reported to form at the surface of brannerite particles during leaching, no such layer was identified in the leaching experiments conducted as part of this study.

The extent of natural alteration appeared to affect the susceptibility of brannerite to leaching. There is a relationship between the texture of the brannerite grains and the leach recoveries, with heavily altered grains being more readily leached. The extent of alteration and texture of brannerite grains varies between deposits and has been found to affect the degree of leaching. It is shown that the texture of the brannerite minerals in an ore is an important process performance indicator along with the grade, liberation size and gangue mineralogy.

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DEVELOPMENTS IN URANIUM EXTRACTION AND RECOVERY TECHNOLOGY

By

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ABSTRACT

This presentation highlights a range of technologies at various stages of development and commercialisation.

Process technology for the extraction and recovery of uranium continues to develop driven by the need to reduce capital and operating costs, the move towards lower grade and more difficult ores, the need to improve the processing of saline leach solutions and the increasingly stringent environmental regulations.

Developing areas include preconcentration, solvent extraction/ion exchange and product recovery. Technologies highlighted in this presentation are Ablation, U-pgradeTM process, nonofiltration, strong acid strip SX/IX, strong acid strip/SX, basic aluminium sulphate strip, SX for high chloride solutions, alkaline SX, Wintray SX contactor, and fluid bed precipitation.

Some other developing areas, not included highlighted in this presentation include in-situ leaching, heap leaching, solid-liquid separation, IX resins and systems, and by-product uranium recovery. Process development is likely to accelerate as uranium demand increases to supply the projected expansion of nuclear power generation.

Keywords: Uranium, technology development, preconcentration, solvent extraction, ion exchange, product recovery

OUTLINE

- Introduction
- Preconcentration
- Nanofiltration
- Solvent Extraction/Ion Exchange
- Product Recovery
- Conclusions
- References

INTRODUCTION

- Drivers for developments in uranium extraction and recovery technology include the need to reduce capital and operating costs, the move towards lower grade and more difficult ores, the need to improve the processing of saline leach solutions and the increasingly stringent environmental regulations.

- This presentation highlights a range of technologies at various stages of development and commercialization.

PRECONCENTRATION

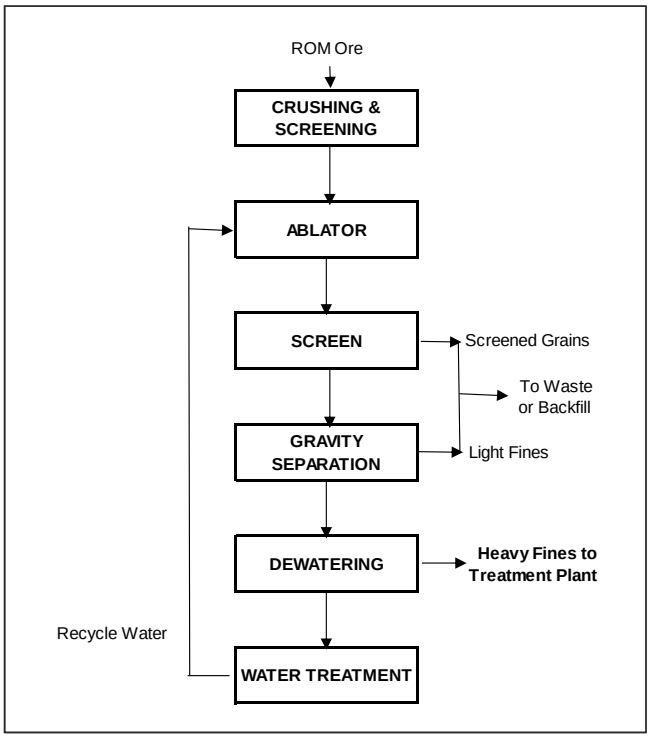
ABLATION

- Invented by Ablation Technologies, Casper, Wyoming, USA, initially for gold then patented for uranium in 2012.
- A JV, Mineral Ablation, was formed with Black Range Minerals, Australia, in 2012 to market the technology.
- Proposed for BRM's Hansen Uranium Project in Colorado, USA, along with hydraulic bore hole mining. Tested with a 5 t/h pilot ablation unit in 2013 which achieved 94.5 % uranium recovery into finest fractions.
- Black Range were taken over by Western Uranium, Toronto, Canada in 2015, who successfully tested the 5 t/h pilot plant on stockpiled ore at their Sunday Mine Complex in Colorado, and have constructed a 20 t/h commercial unit for operation in 2016.

ABLATION CONCEPT

- Uses kinetic energy and water to force grains against each other using opposing nozzles to remove uranium in coatings and interstitial deposits from barren sand grains typically found in sandstone ores.
- The resulting fine material commonly contains a high percentage of the uranium and can be separated by screening into a high grade, low volume, concentrate.
- The concentrate may be further upgraded by removal of light barren fines by gravity separation.
- The final concentrate is dewatered and the water treated as required for recycling and reuse.
- Extensive testwork shows typically more than 90% of the uranium mineralisation can be recovered into about 10% of the initial mass.

ABLATION FLOWSHEET



APPLICATION

- GoviEx Uranium, Vancouver, Canada have included Ablation in the base case flowsheet for their Madaouela Project in Niger.
- The proposed flowsheet involves primary crushing, radiometric ore sorting, and secondary crushing, ahead of ablation.
- After two-stage agitated tank leaching with sulphuric acid, Cyanex 600 SX extractant is used to extract both molybdenum and uranium which are recovered separately as saleable oxides by selective stripping.

U-PGRADE PROCESS™

- Developed and patented by Marenica Energy, Australia, initially for the Marenica low grade surficial deposit in Namibia.
- Beneficiation process targeting sequential removal of the gangue minerals using commonly used unit operations.
- Bench scale tests indicate concentration of uranium into <3% of the mass, upgrading by >30 times (without the use of leaching chemicals).

U-PGRADE FLOWSHEET

- A primary beneficiation stage comprising wet scrubbing of low grade ore to separate into fine and coarse fractions (possibly with a prescreening step to minimize scrubbing of liberated carnotite).
- Fine fraction is screened to provide an undersize fraction with most of the uranium and an oversize fraction.
- The undersize fraction is separated to produce an intermediate uranium concentrate.
- The intermediate uranium concentrate may be further processed in a secondary beneficiation stage to produce a high grade uranium concentrate – possible steps include desliming, gravity separation, flotation, reflux classification and magnetic separation.

POTENTIAL BENEFITS

Potential benefits include:

- Substantial rejection of mass prior to leach.
- Rejection of carbonates prior to leach.
- Rejection of interfering minerals in the separation processes.
- Allows acid leaching of concentrate from calcrete ore types.
- Processing of high sulphate ores, usually classified as waste.
- Significant reduction in opex and capex.
- Allows option of transport of concentrate to an existing treatment plant or to a new treatment plant located at a more favourable location.

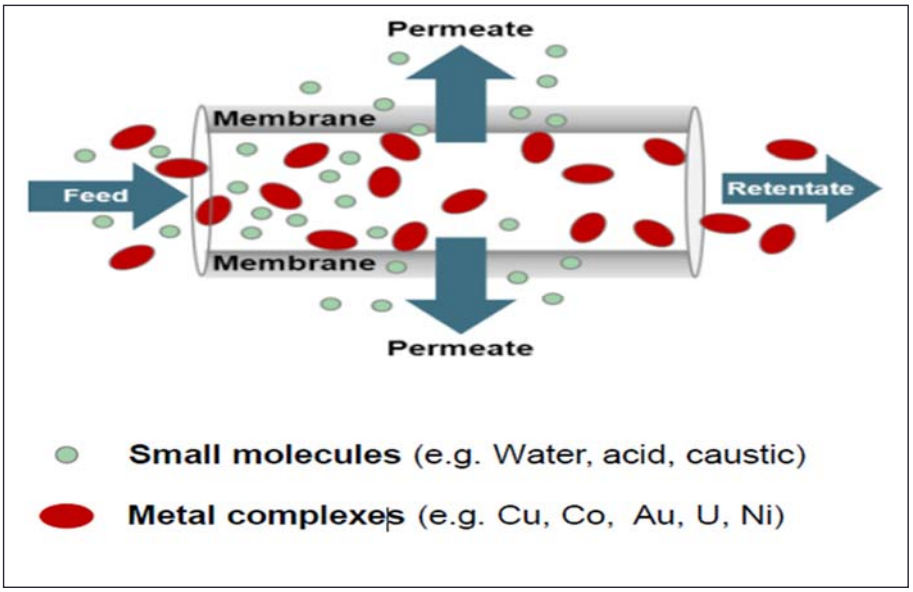
NANOFILTRATION

NANOFILTRATION

- Nanofiltration membranes have pore sizes from 1-10 Angstrom, which is smaller than for microfiltration and ultrafiltration, but just larger than for reverse osmosis.
- Used in water softening, waste water treatment, acid rock drainage, and oil & petroleum, food and phamaceutical industries.
- Small, monovalent ions pass through the membrane to the permeate, while larger ions are retained to the retentate.
- Advantages include low energy and no requirement for reagents, while disadvantages include cost and maintenance of membranes and risk of plugging or scaling.

NANOFIILTRATION CONCEPT

(Ref: AMS presentation, ALTA 2015)

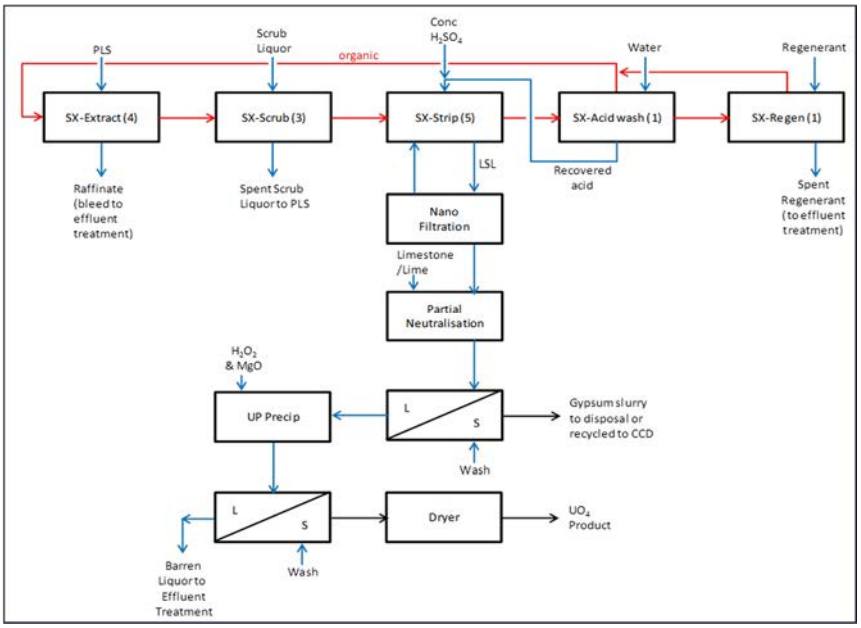


POTENTIAL APPLICATIONS

- Potential applications in uranium operations include:
  - concentration of SX strip solution or IX eluate with recovery of acid or other reagents.
  - concentration of SX or IX feed solution with recovery of acid or carbonate reagents.
  - treatment of waste or bleed streams.
  - treatment of acid rock drainage.
- Tested for a number of uranium projects including Letlhakane in Botswana for A-CAP; Michelin in Canada for Aurora Energy; Mkuju River in Tanzania for Uranium One; Kayelekera in Malawi and Langer Heinrich in Namibia for Paladin Energy (now installed at both sites).

STRONG ACID STRIP/NF FLOWSHEET

(Ref: AMEC paper, ALTA 2012)



COMMERCIALIZATION

- A world first nanofiltration system for recovering acid from IX eluate prior to precipitation, designed by BMS Engineers (Perth), was installed at Paladin Energy's Kayelekera uranium operation in Malawi in 2013. An average of 56% of the acid is recovered and the consumption of neutralizing agent reduced by over 55%.
- The acid recovery technology developed has been patented by Paladin Energy, with BMS personnel as co-inventors; and BMS Engineers and Paladin Energy have agreed to jointly develop and further this technology in the uranium industry.
- BMS have also installed the world's first system for recovering bicarbonate in a uranium operation at Paladin's Langer Heinrich plant in Namibia.

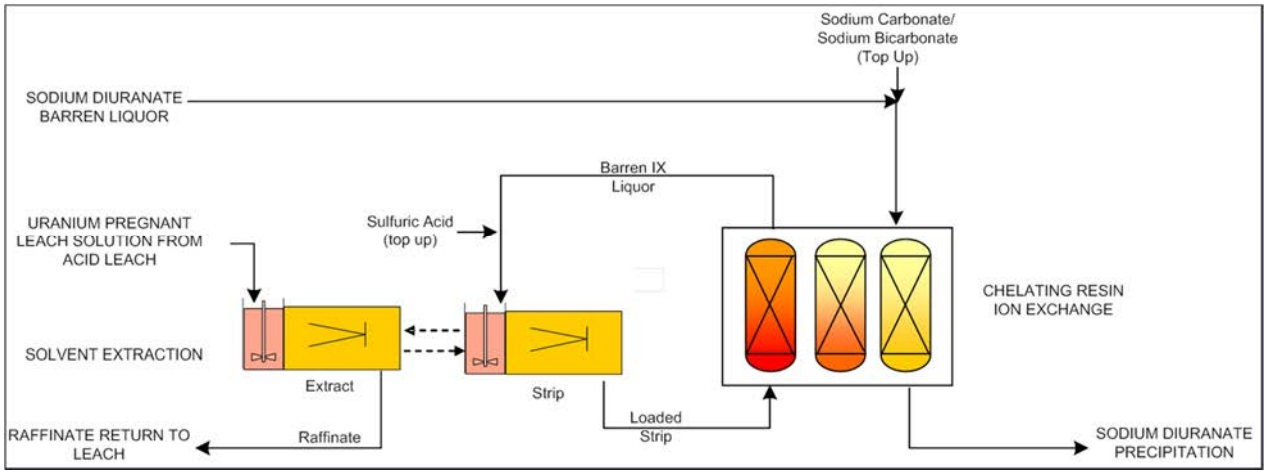
SOLVENT EXTRACTION AND ION EXCHANGE

APPLICATION OF IX TO STRONG ACID STRIP OR ELUATE SOLUTIONS

- Aimed at avoiding need for partial neutralization of strong acid SX strip or IX eluate solutions ahead of uranium oxide precipitation.
- Utilizes IX with chelating resin to extract uranium and allow the acid to be recycled and reused.
- The loaded chelating resin is stripped with sodium carbonate/sodium bicarbonate solution.
- Sodium hydroxide is added to precipitate sodium diuranate which is separated and redissolved in sulphuric acid, followed by uranium oxide precipitation and drying.
- Was developed and successfully tested to treating strong acid strip solution for A-CAP Resources' Letlhakane Project, Botswana.

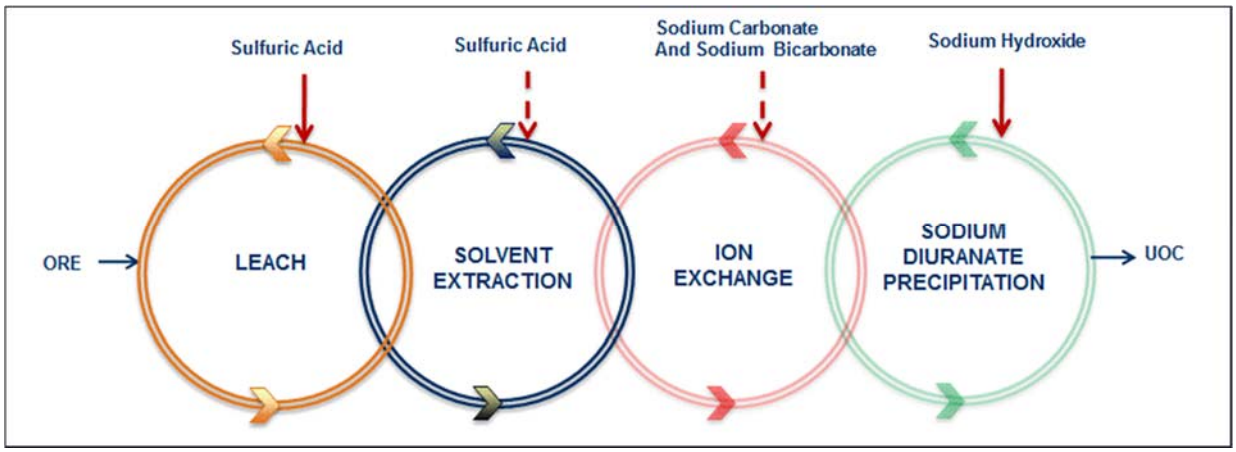
STRONG ACID STRIP/IX FLOWSHEET

(Ref: Orway paper, ALTA 2015)



STRONG ACID STRIP/IX REAGENT RECYCLE

(Ref: Orway paper, ALTA 2015)



POTENTIAL BENEFITS

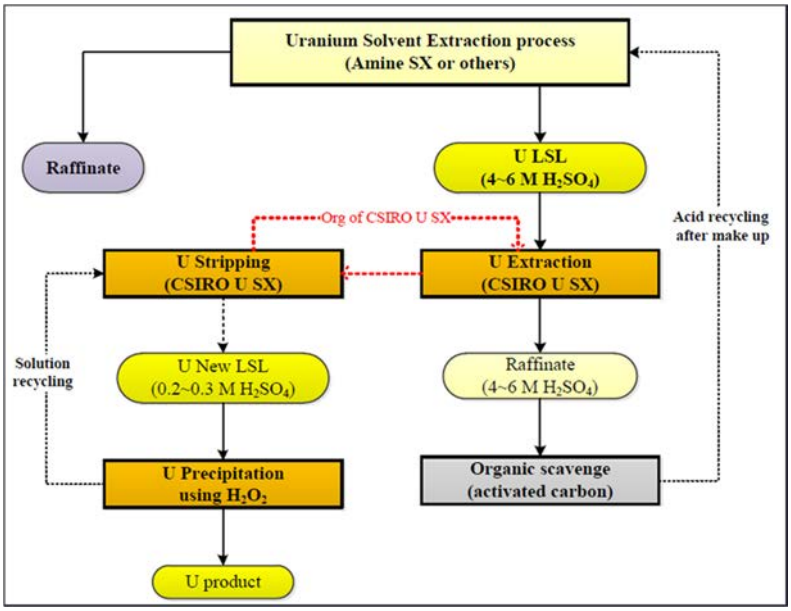
- Compared with partial neutralization method for strong acid strip application based on Letlhakane PFS testwork:
  - Saving of approx. 60% in overall recovery cost from leach PLS to UOC product due to recycle of acid and eluant.
  - Elimination of uranium loss in partial precipitation resulting in high overall uranium recovery of > 99% from leach PLS to product.
- Nano filtration was considered but there was concern over the stability of the membrane in the 4 M acid conditions and the perceived effect on the water balance (the commercial NF facility at Kayelekera operates on IX eluate at about 1 M acid strength).

APPLICATION OF CSIRO SSX SYSTEM TO STRONG ACID SX STRIP SOLUTION

- CSIRO (Perth) are developing a new synergistic SX (SSX) system to transfer uranium from strong acid (4-6 M) strip solution to a weaker acid strength (0.2–0.5 M) solution suitable for uranium precipitation with hydrogen peroxide.
- This avoids the need for partial neutralization as used at Rabbit Lake in Canada and allows the recycle and reuse of the acid.
- The SSX system is based on a blend of two stable commercially available extractants.
- Bench scale test results promising with high extraction and stripping efficiencies and fast kinetics in SSX.

CSIRO STRONG ACID STRIP/SSX FLOWSHEET

(Ref: CSIRO paper, ALTA 2015)

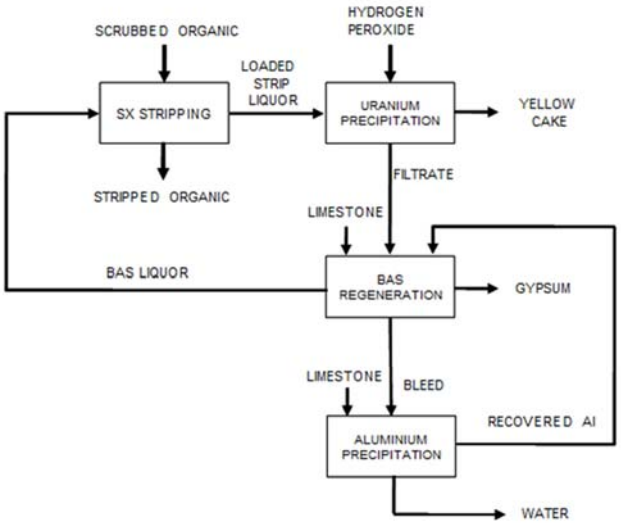


BASIC ALUMINIUM SULPHATE (BAS) STRIP PROCESS

- Strategic Metallurgy, Perth, are developing a new basic aluminium sulphate (BAS) strip process which avoids pH control and precipitation problems.
- Uses a solution containing basic aluminium sulfate (BAS) which allows uranium to be stripped from the organic via a de-protonation mechanism, and neutralizes the acid generated during uranyl peroxide precipitation with hydrogen peroxide.
- Uses inexpensive, non-hazardous reagents, aluminium sulfate (which is recoverable) and limestone (or lime).
- Testwork indicates the product contains about 0.33% Al.

BAS STRIP FLOWSHEET

(Ref: Strategic Metallurgy paper, ALTA 2014)

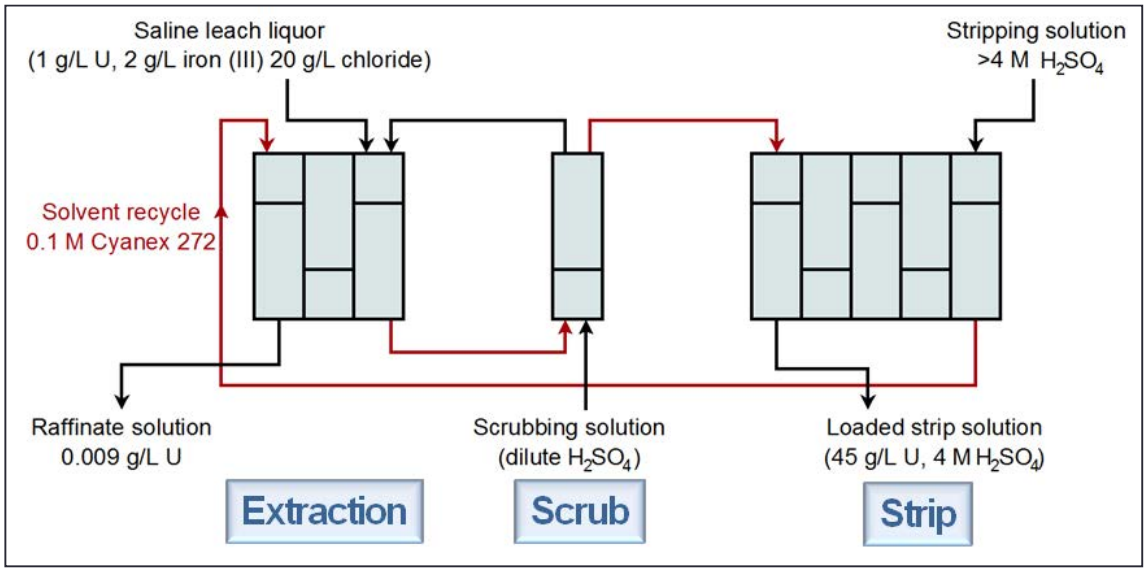


SX SYSTEMS FOR HIGH CHLORIDE SOLUTIONS

- D2EHPA / Amine synergistic mixture: improved performance, but ferric iron content must be low. Stripping with sodium carbonate. Commercially applied at Honeymoon ISL operation, South Australia. (Uranium One/PCMETS paper, ALTA 2014.)
- D2EHPA / Cyphos IL-101 (tetradecyl[trihexyl]phosphonium chloride) mixture: promising testwork results, but vanadium co-extraction is an issue. Stripping with strong sulphuric acid. (CSIRO, paper, ALTA 2014.)
- Trialkylphosphine oxides (TAPO) with or without Amine. Stripping with ammonium sulphate. (Patented by BHP Billiton Olympic Dam, 2014).
- Cyanex 272: promising testwork results. Stripping with strong sulphuric acid. (ANSTO presentation, ALTA 2015).

ANSTO PROPOSED CYANEX 272 FLOWSHEET

(Ref: ANSTO presentation, ALTA 2015)



ANSTO CYANEX 272 SYSTEM ADVANTAGES

Indications from bench scale batch testwork:

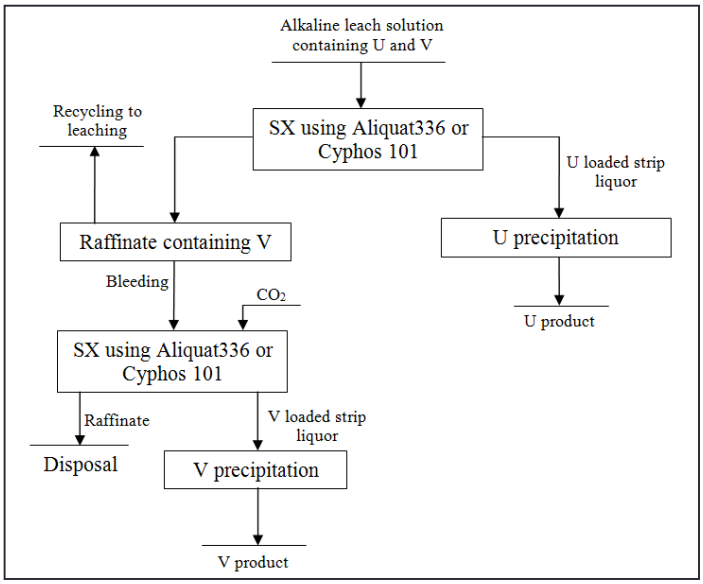
- Applicable to saline liquors 20 g/L Cl.
- High Uranium Loadings.
- Selectivity for uranium over Fe(III).
- Acceptable stripping at 4 M H_2SO_4.
- Avoids the use of ammonia.
- No requirement for phase modifier.
- Seamless integration with current conventional uranium recovery steps.

CSIRO SX SYSTEM FOR ALKALINE LEACH SOLUTIONS

- No current proven SX system for alkaline solutions.
- Cyphos 101, a tri-hexyl(tetradecyl)phosphonium salt and Aliquat 336, a quaternary amine, have been tested by CSIRO, Australia, for the recovery and separation of uranium and vanadium in alkaline leach solutions with promising results.
- Aromatic diluent or aliphatic diluent with isodecanol modifier effectively eliminate third phase formation.
- Cyphos 101 needs chloride to be < 1 and Aliquat 336 < 3.
- Uranium and vanadium can be separated at pH > 11.

PROPOSED CSIRO ALKALINE SX FLOWSHEET

(Ref: CSIRO paper, ALTA 2013)

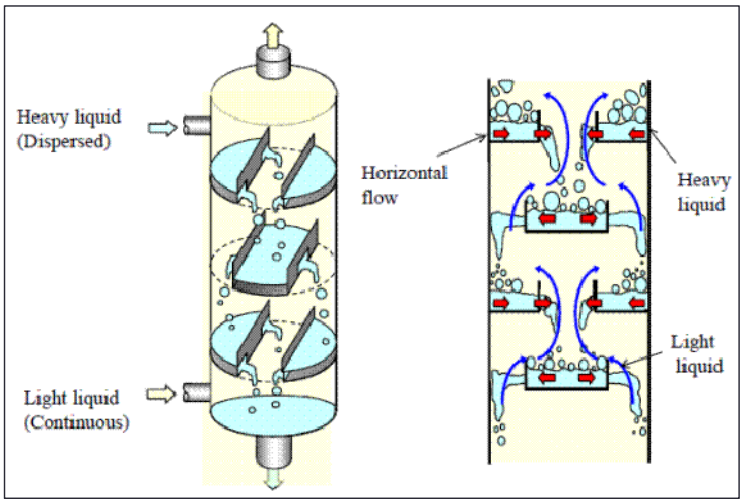


JGC WINTRAY SX COLUMN CONTACTOR

- Developed by JGC (Japan), and commercially applied in the petrochemical industry with 14 units operating in Japan and overseas by 2011, up to 2m diameter.
- Pilot scale test column program for uranium SX has been conducted at MINTEK South Africa. Also tested for cobalt SX.
- The column has multiple trays with two kinds of different shapes placed alternately, which have perpendicular plates (weir plates) with opening windows.
- Claimed advantages include large drop size, high extraction efficiency, and low plugging with crud.

WINTRAY COLUMN CONCEPT

(Ref: JGC paper, ALTA 2012)



The above is for organic continuous operation.
The plates would be inverted for aqueous continuous.

PRODUCT RECOVERY

AREVA FLUID BED PRECIPITATION PROCESS

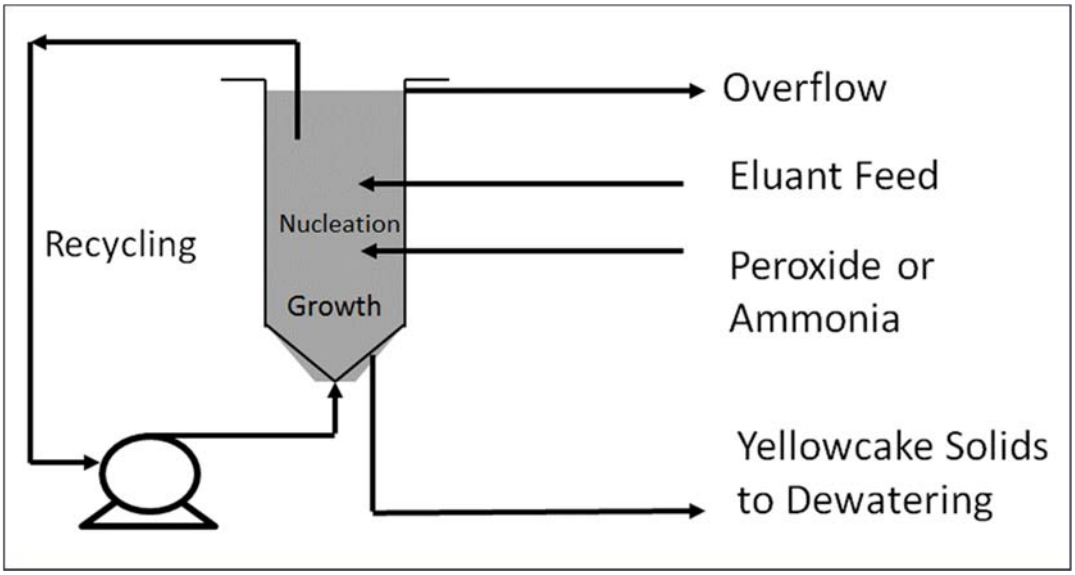
- Patented process developed and commercialized by Areva.
- Available from Adelaide Control Engineering (ACE), South Australia.
- Claimed advantages (by ACE):
  - Lower cost of production and maintenance.
  - Increased recovery of uranium.
  - Increased uranium content of calcined product.
  - Larger particle size.
  - Reduced fines, less dust and lower risks to operators.

AREVA FLUID BED PRECIPITATION PROCESS

- Improved dewatering reduces calcining costs or allows increased throughput.
- Increased calcined product bulk density - lower transport cost.
- Facilitates drying or calcining with horizontal kiln – previously, too much product was lost in off-gas and stuck inside the tube.
- Flexibility for peroxide or ammonia precipitation.
- Modular construction, smaller site footprint.

AREVA FLUID BED FLOWSHEET

(Ref: ACE presentation, ALTA 2013)



CONCLUSIONS

- Process technology for the extraction and recovery of uranium continues to develop driven by cost reduction, available resources, technical challenges and environmental issues.
- Developing areas include preconcentration, solvent extraction/ion exchange and product recovery.
- Some other areas not highlighted in this presentation include in-situ leaching, heap leaching, solid-liquid separation, IX resins and systems, and by-product uranium recovery.
- Process development is likely to accelerate as uranium demand increases to supply the projected expansion of nuclear power generation.

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EVOLUTION OF STRUCTURAL AND PHYSICAL PROPERTIES OF URANIUM-ORE AGGLOMERATES DURING HEAP LEACHING

By

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ABSTRACT

Heap leaching is commonly used to process low grade ores. However, ores containing fine particles and clays cause often clogging problems within heaps. To solve this problem, copper, nickel and uranium extractive industries use agglomeration. This process consists in gathering fine particles in order to adjust the ore particle size distribution. This allows improving the heap permeability and reducing fine migration during leaching. As agglomerates quality influences heap leaching efficiency, many quality tests have been performed. However they mostly focus on a column of agglomerates, and the influence of agglomerates structure on heap leaching remains poorly understood. The current study is an attempt to characterise the structure and the porosity of agglomerates and their evolution during leaching.

For this study, a low grade uranium ore from Niger has been used for agglomeration. The ore has been agglomerated using sulfuric acid as binder. Then, agglomerates have been leached during 10 days with sulfuric acid at 10g/L. Evolution of structural and physical properties of uranium-ore agglomerates during heap leaching has been investigated for different operating conditions: agglomerates size, flow rate or acid concentration.

Prior to heap leaching, X-ray tomography and SEM analysis highlighted that agglomerates are composed by the coalescence and layering of micro-agglomerates. These are composed by phyllosilicates (especially muscovite and kaolinite) coating a nucleus (mostly quartz or feldspar). One can also observe an aluminous silicate matrix phase around some nuclei. This might come from the reaction between phyllosilicates and the binder. Moreover, such a structure is the cause of the initial low connected porosity of the agglomerates (between 3 and 7%) which can be measured by mercury intrusion porosimetry (MIP). A positive correlation between the porosity and the agglomerate sizes has been exhibited.

A combined MIP–SEM analysis carried out on agglomerates after 10 days of leaching revealed that the process improved the connected porosity of agglomerates by creating new mesopores. These are mostly located around micro-agglomerates, as showed with SEM analyses and they may come from the leaching of the aluminous silicate matrix phase during the process. X-ray tomography corroborates these observations and the increase of connected porosity by about a factor 2. This allows a better diffusion of the leaching solution within the agglomerates.

Keywords: Heap leaching, uranium, agglomerates, SEM, X-ray tomography, mercury intrusion porosimetry

INTRODUCTION

Heap leaching allows processing low grade ores. Basically, this industrial mining process consists in percolating a leaching solution slowly down through an ore heap of 6 to 9 meters high to extract the metals of interest (uranium, copper or nickel). Physical and chemical factors (as temperature, reagent flow rates, particle size distribution and pores distribution) and the ore mineralogy influence this process. Fine particles and clays are indeed often the cause of clogging within heaps. This causes also permeability variability that may compromise the efficiency and homogeneity of the leaching process[1]. To solve this problem, the copper, nickel and uranium industry uses agglomeration of the ore particles. This process allows adjusting the particle size distribution by gathering fine particles, using mostly capillary forces, cohesion forces between particles and adhesion forces (e.g. hydrogen bonds, electrostatic and Van der Waals forces). This process is a way to improve the heap permeability and to reduce fine particle migration during leaching[2][3].

Agglomerates for heap leaching are formed by the adhesion of ore particles mixed at least with water within a rotation drum. In some cases, a binder can be added to the water, to make the agglomerates stronger[4]. Then agglomerates are stored for maturation in a time span from 14 to more than 300 hours. The storing time depends on the nature of the ore and the nature of the binder. During that time, the bonds between the particles of the agglomerates are hardened[2][4]. According to Bouffard (2005), four consecutive steps can be identified during the agglomeration process[3]:

(i) wetting of particles;

(ii) growth of the agglomerate by three phases (nucleation, coalescence of the nuclei in an agglomerate and organization of fines around the agglomerates);

(iii) consolidation and compaction of the agglomerate; and

(iv) fragmentation and abrasion.

As agglomerates quality influences heap leaching efficiency, numerous tests (as soaking, column permeability, particle size distribution analysis etc.) to control agglomerate quality have already been performed[2][5-8]. However, these tests mostly focus on a column or a batch of agglomerates. By this way the impact of the agglomerates structure on heap leaching remains poorly understood.

In this study we characterize the structural and petro physical properties of agglomerates from analytical techniques (e.g. X-ray tomography, SEM analyses, mercury intrusion porosimetry (MIP)) and its evolution during leaching. Since MIP and X-ray tomography reveal information about the pore distribution and connectivity and microscopy analysis gives an insight on pore geometry and mineralogy, a combination of these different techniques may help to obtain a more complete picture of the agglomerate structures.

MATERIAL AND METHODS

Ore

The agglomerates used in this study were produced from clay sandstone containing about 900 ppm of uranium and more than 10 % of clays (mainly kaolinites, chlorites and illites). Previous analyses showed that most of the uranium is hosted by clay minerals as chlorite. Crushed ore has been agglomerated for 3 minutes with an L/S ratio of 0.08. In addition, sulfuric acid at a ratio of 25 kg/t of ore has been used as binder. A second batch of agglomerates (water bound agglomerates) was made without using sulfuric acid for agglomeration. This batch has been used to understand the effects of sulfuric acid as a binder on the structure of agglomerates.

A particle size distribution (PSD) by image analysis (Figure 1) has been conducted to separate particles in the range between about 1 mm to 40 mm and determine characteristic diameters of the agglomerates. The analysis has been performed with the ImageJ software. This analysis shows that most of the agglomerates have a diameter upper than 3 mm, which confirms that fines particles have been gathered into bigger ones.

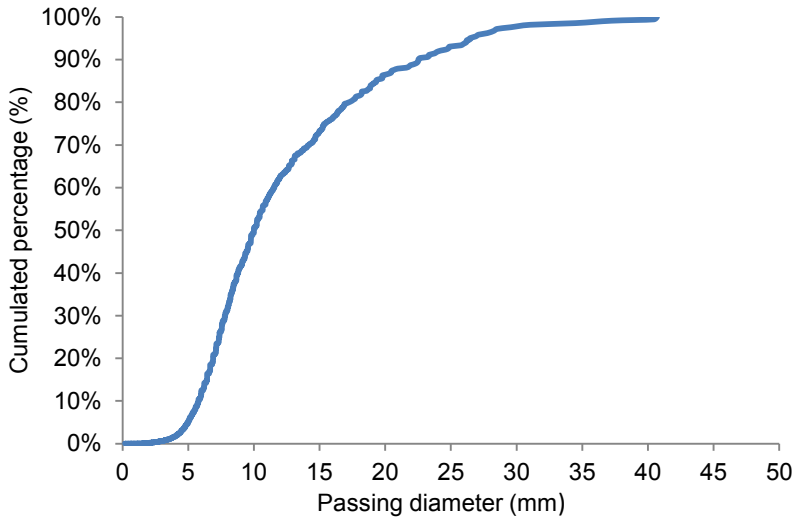


Figure 1: Cumulated particle size distribution of the agglomerates

A batch of agglomerates of a diameter of 10 mm has been leached within a decimetric column during 10 days with sulfuric acid at a ratio of 10 g/L at a flow of 7.2 mL/h. The leached solution has been sampled every day and analysed by ICP OES. At the end of the leaching process, agglomerates have been dried in the open air during 3 hours. Agglomerate analyses were post mortem analyses. In order to study the evolution of agglomerates structure at different stages of leaching, three other column leaching tests have been done, with leaching time of 2, 5 and 7 days respectively.

Analyses

Several analyses have been done to study agglomerates structure and porosity before and after leaching (Figure 2). Wet agglomerates have been analysed by X-ray tomography. Mercury intrusion porosimetry (MIP) and scanning electron microscope (SEM) analyses have also been performed on agglomerates which were previously freeze dried. This allowed removing the water contained in the agglomerates without disrupting their structure.

Table 1 summarizes all the tests performed for this study.

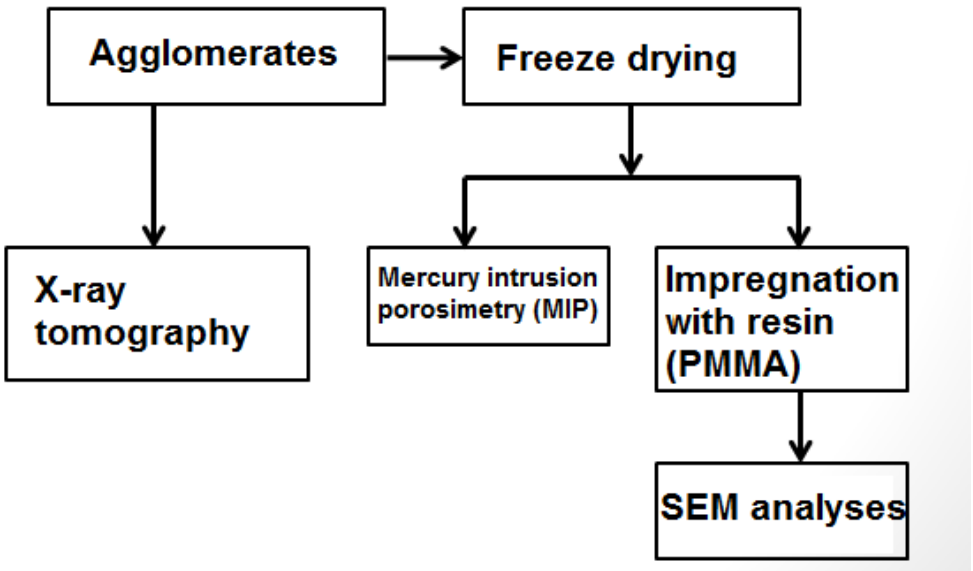


Figure 2: Agglomerates analyses flowsheet

Table 1: Summary of the tests and analyses performed

Test reference	Agglomerates binder	Agglomerate size	Leaching time	X ray tomography	SEM	MIP	PLS ICP OES analyses
#1	Sulfuric acid	5 – 10 and 20 mm	0 days	Yes	Yes (only on 10 mm agglomerates)	Yes	No
#2	Sulfuric acid	10 mm	2 days	No	Yes	Yes	No
#3	Sulfuric acid	10 mm	5 days	No	Yes	Yes	No
#4	Sulfuric acid	10 mm	7 days	No	Yes	Yes	No
#5	Sulfuric acid	10 mm	10 days	Yes	Yes	Yes	Yes
#6	Sulfuric acid	10 mm	3 days	No	No	No	Yes
#7	Water	10 mm	0 days	Yes	Yes	Yes	No
#8	Water	10 mm	10 days	Yes	Yes	Yes	Yes

AGGLOMERATES STRUCTURE AND POROSITY PRIOR TO LEACHING

X-ray Tomography and SEM Analyses:

Three acid bound agglomerates (one of a diameter of 5 mm, one of a diameter of 10 mm and one of a diameter of 20 mm) have been studied by X-ray tomography. This technique allows imaging the internal structure of the agglomerates without mechanical disturbance. In the three cases, we observed that most of the particles within the agglomerate have the same density. In this way, it was possible to observe several new structures inside the studied agglomerates as shown in Figure 3. The difference of porosity (which appears in black in the figure) between the middle and the edge of the agglomerate indicates the presence of a lithoclast at the centre of the particle. Moreover small ovoid structures at the edge of the agglomerate have also been noticed (e.g. at the top of Figure 3). These structures may have derived from the different stages of agglomerate growth.

In order to improve the comprehension of agglomerates structure, some 10 mm acid bound and water bound agglomerates have been impregnated with PMMA resin and studied with SEM. Some minerals as quartz, feldspars, pyrite, rutile and phyllosilicates (mostly muscovite and kaolinite) have been identified. This analysis also showed that some muscovites and kaolinites were coating bigger particles as quartz, feldspars or even lithoclasts (Figure 4). This formed micro agglomerates structures which could be related to the ovoid structures observed previously by X-ray tomography. Moreover an aluminous silicate matrix phase binding phyllosilicates to the nucleus of the micro agglomerate was noticed. One can suppose that this matrix comes from the dissolution of clay minerals as chlorite, smectites and illites (initially present within the ore but absent within the agglomerates) by the sulfuric acid added as binder during agglomeration.

Further SEM analyses showed kaolinite and muscovite coating adjacent micro agglomerates (Figure 5). This could explain growth mechanisms of agglomerates: after the coalescence of two micro agglomerates, the new particle act as a nucleus around which fines particles and the aluminous silicate matrix layered to form bigger micro agglomerate. Such growing mechanisms are consistent with those described by Iveson et al (2001)[9].

SEM analyses of water bound agglomerates highlighted the presence of chlorites, illites-smectites and uranium-titanium oxides in addition to the other minerals usually found in acid bound agglomerates. Moreover no aluminous silicate matrix phase was noticed within water bound agglomerates. This confirmed that sulfuric acid added during agglomeration caused the dissolution of most of the chlorites and illites-smectites, which formed aluminous silicate matrix phase.

However micro agglomerates structures were noticed on these agglomerates. This highlighted the effect of other bounding forces, allowing the formation of micro agglomerates, as capillary forces or adhesion forces between particles[6][10].

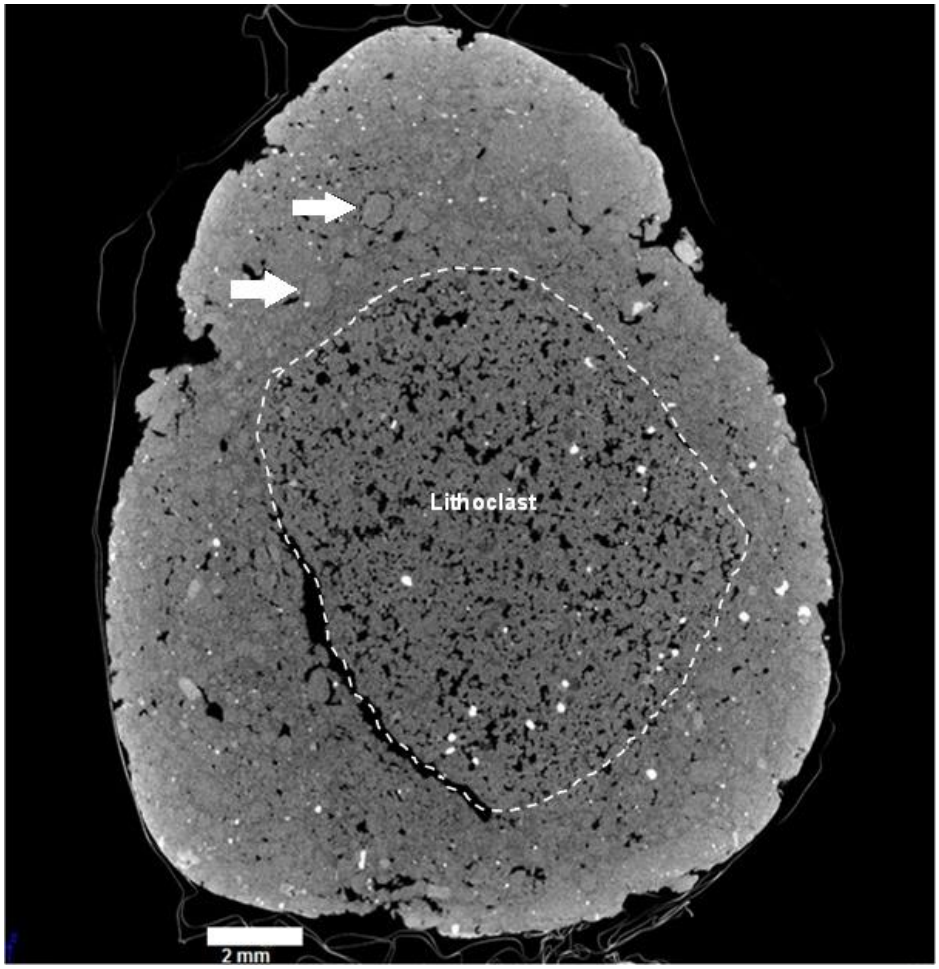


Figure 3: Acid bound agglomerate (diameter of 20 mm) observed by X-ray tomography. The white pointers and the black circle at the top of the figure highlight small pellets structures. The white circle highlights a lithoclast. The white points inside the agglomerates are high density particles as pyrites. As the studied ore is a low grade uranium ore, uranium oxides are not visible at this scale.

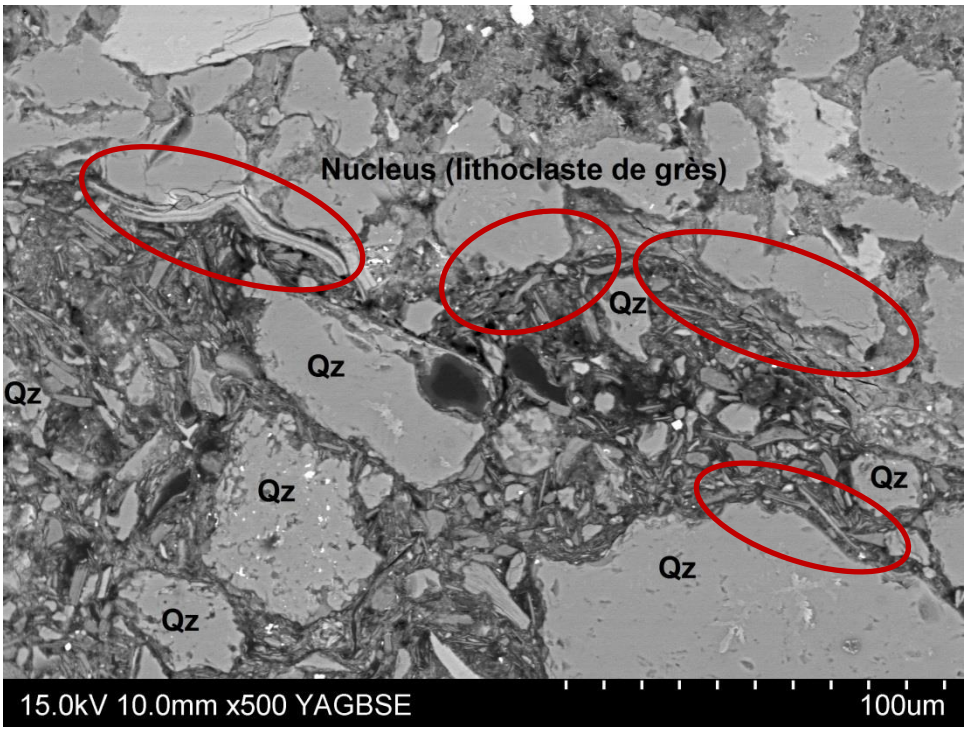
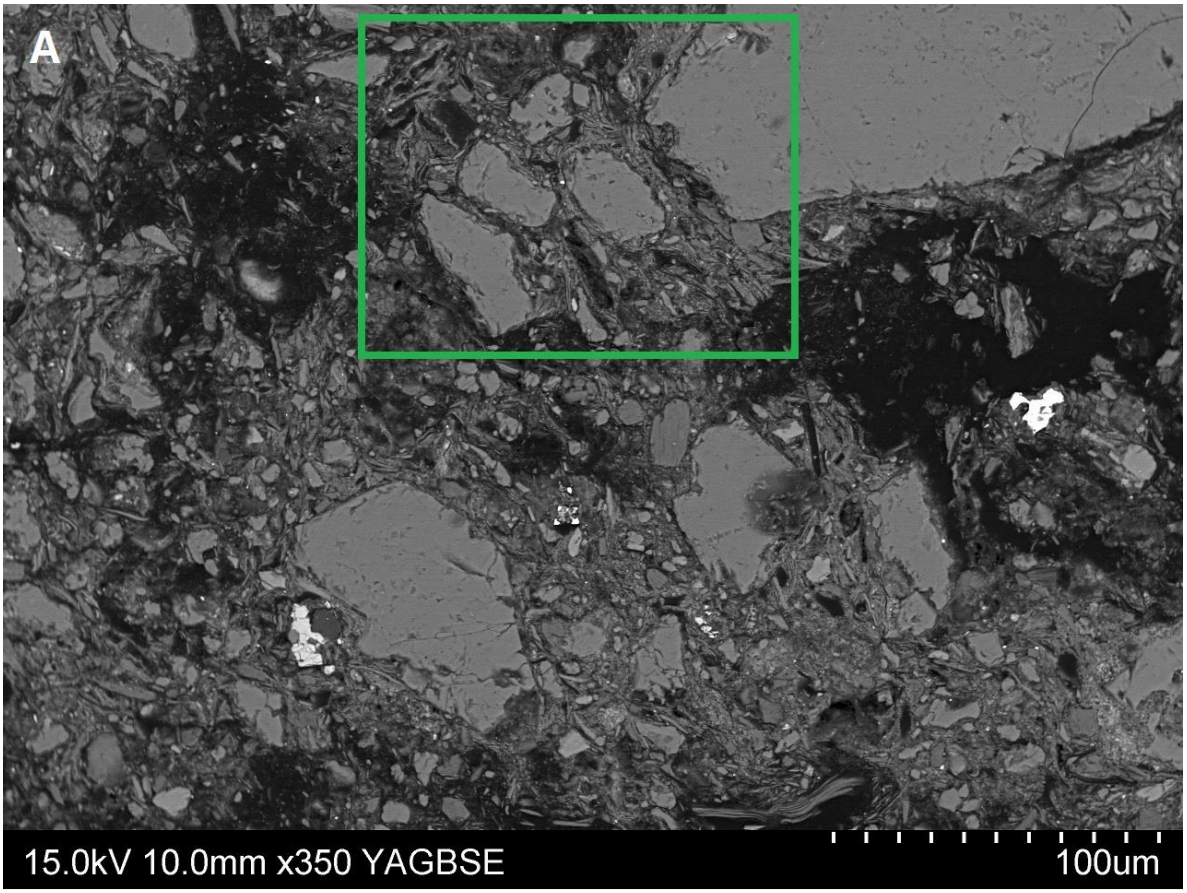


Figure 4: SEM analysis of a 10 mm acid bound agglomerate polished section. The circle show phyllosilicates minerals (especially muscovites and kaolinites) and the aluminous silicate matrix phase coating quartz minerals and a lithoclast.



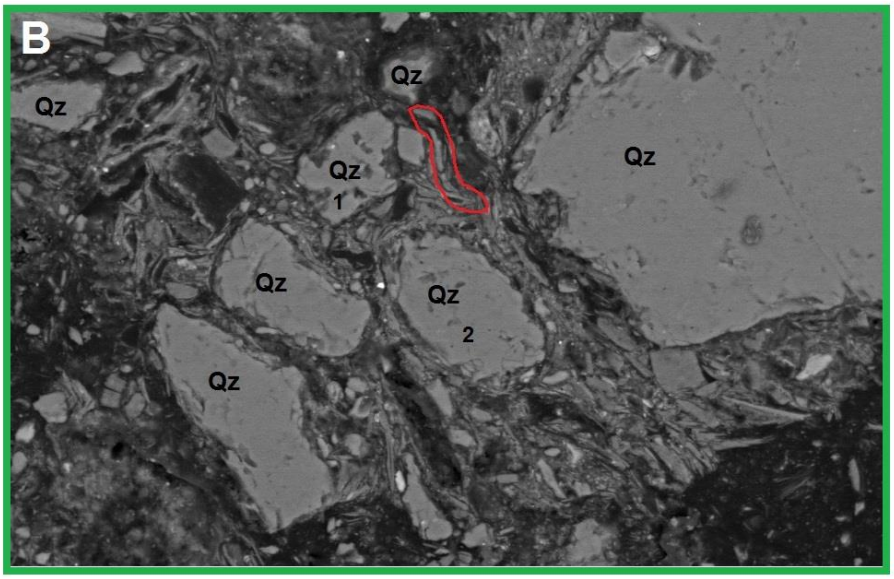


Figure 5: SEM analysis of a 10 mm acid bound agglomerate polished section. The red area show phyllosilicates minerals coating two coalesced micro agglomerates.

Agglomerates Porosity Before Leaching

Porosity influences heap leaching and agglomerates quality. The porosity properties have been studied by mercury porosimetry. Acid bound agglomerates have been previously freeze-dried in order to remove the water within the samples without damaging their structure.

Mercury porosimetry consists in injecting mercury within the sample pore network in vacuum conditions. The mercury injection pressure can be related to the pore size by the Laplace law. Moreover the injected fluid volume gives access to value of the porosity. Two mercury injections

have been done: the first one shows total porosity within the agglomerate and the second one is used to evaluate the percentage of connected porosity (in the sense of effective porosity). Results, presented in Tab. 2, suggest that the connected porosity decreases with increasing size of the agglomerate. Moreover this connected porosity value is quite low (between 2 and 7 %). These results are unexpected, compared to the value of total porosity (around 18 %).

Nevertheless, such porosity distribution is similar to the one of cluster materials described by Pellerin (1980)[11]. This is consistent with the structure of micro agglomerates highlighted with X ray tomography and SEM.

Moreover, we noticed that the trapped pores have a radius comprised between 0.01 µm and 5 µm (i.e. mesopores). Connected pores are either bigger or smaller and may correspond to fractures within the agglomerates or pores located at the periphery of the agglomerates. Note that these observations were similar between the three sizes of agglomerates.

Table 2: Porosity of acid bound agglomerates (results obtained by mercury porosimetry)

Diameter of the agglomerates	Total porosity	Connected porosity
5 mm	19.14%	7.12 %
10 mm	18.25%	3.43%
20 mm	17.55%	2.62%

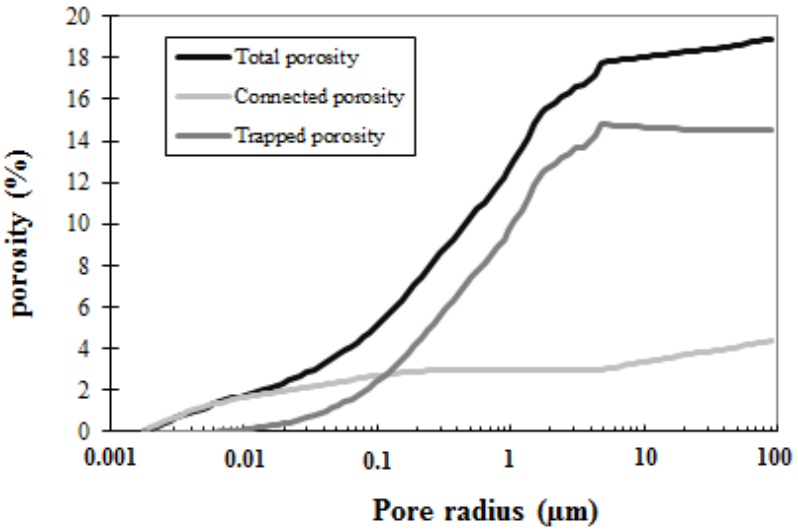


Figure 6: Porosity distribution within an agglomerate with a diameter of 10 mm. The black line is the total porosity, the dark grey one is the trapped porosity and the light grey line represents the connected porosity. Between 0.01 µm and 5 µm most of the porosity is not connected.

IMPACT OF LEACHING ON AGGLOMERATES STRUCTURE AND POROSITY

X-ray Tomography and SEM Analyses

Acid bound agglomerates after 10 days of leaching have been studied with X-ray tomography. These analyses highlighted that the micro agglomerates structure is more noticeable after leaching than before leaching (Figure 7). Moreover, many meso and macro pores have also been observed.

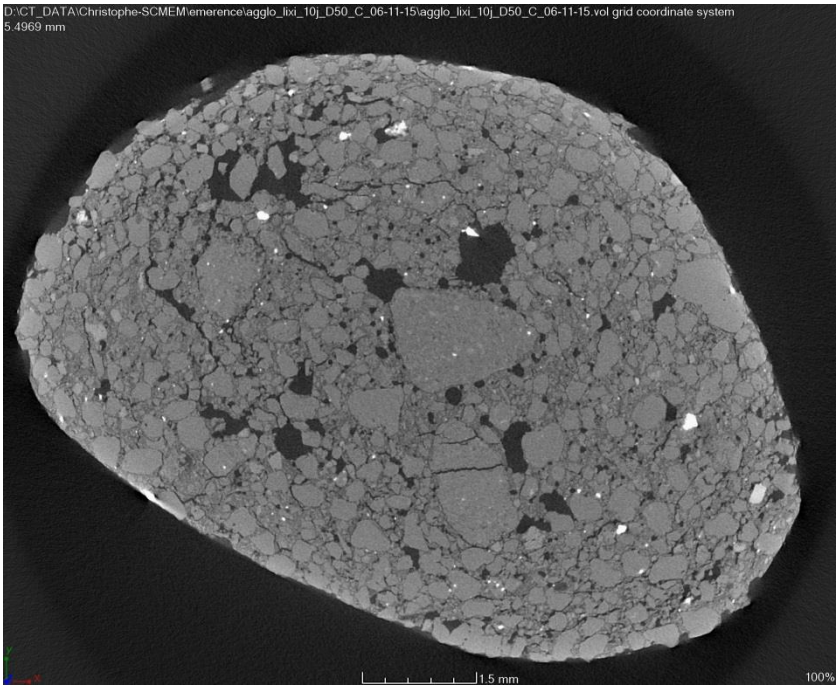


Figure 7: Acid bound agglomerate leached during 10 days (diameter of 10 mm) observed by X-ray tomography.

Polished sections of acid bound agglomerates leached during 2, 5, 7 and 10 days and of water bound agglomerates leached during 10 days have been made and analysed with SEM (Figure 8). This showed that the aluminous silicate matrix phase located around the micro agglomerates in the acid bound agglomerates was leached during the early stages of process, allowing the formation of new connected pores. This also explained the x-ray tomography observations about the micro agglomerate structure.

However, a secondary aluminous silicate matrix was also found within the studied agglomerates (Figure 9). The proportion of the neoformed matrix increases with leaching time. EDX analyses showed that most of the time, this matrix had a composition similar to kaolinites, muscovites to the blending of illites and smectites. We assume that this secondary matrix might come from the dissolution or the decomposition of kaolinite, muscovite and illites-smectites by the leaching solution. This secondary matrix was also found on water-bound agglomerates after 10 days of leaching.

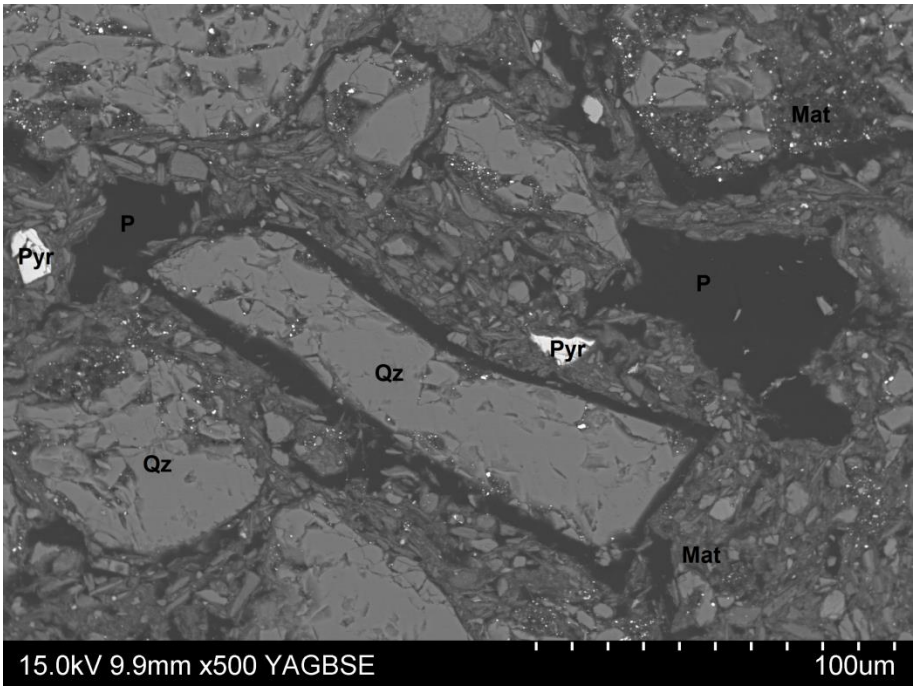


Figure 8: SEM analysis of an acid bound agglomerate leached during 10 days (diameter of 10 mm) polished section. One can notice the porosity around the central quartz crystal. Qz: quartz – Pyr: pyrite – P: porosity – Mat: aluminous silicate matrix phase.

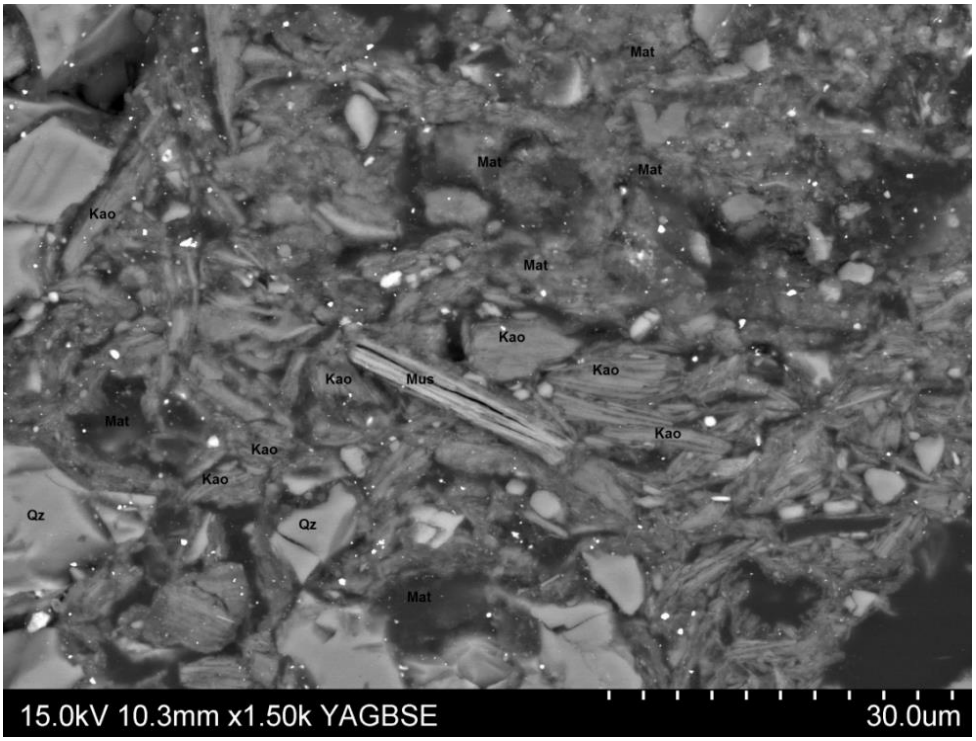


Figure 9: SEM analyses of an acid bound agglomerate leached during 10 days. Mat: aluminous silicate matrix phase – Kao: kaolinite – Mus: muscovite – Qz: quartz. The limit between the matrix and phyllosilicates is vague, which let suppose that this matrix comes from the degradation of these minerals during leaching.

Leached Solution Analyses

ICP OES analyses on the leached solution have been performed. Results, gathered in Table 3 and in figure 10, highlighted two different stages during leaching:

(i) The two first days, the leached solution is enriched aluminium, calcium, iron, sodium, magnesium and uranium (more than 60% of the total uranium contained within the column is leached out during the first day). We suppose this came from the leaching of

the aluminous silicate matrix phase formed during agglomeration (which we assume to be formed by the dissolution of chlorites and illites-smectites holding the uranium of the ore). This hypothesis could indeed explain this enrichment and would be consistent with the structural observations.

(ii) During the others days of leaching, the concentrations were quite similar and displayed another reaction between the agglomerate and the leaching solution. This could signal the formation of the secondary matrix as observed by SEM.

Table 3: ICP OES analyses of the leached solution

Leaching time (h)	Al (ppm)	Ca (ppm)	Fe (ppm)	K (ppm)	Mg (ppm)	Na (ppm)	Si (ppm)	U (ppm)
24	1376,8	502,2	3388,5	15,5	702,0	44,0	49,4	304,1
48	77,9	193,8	302,3	14,3	35,6	11,9	59,8	14,0
72	51,2	80,6	209,8	14,9	22,6	7,3	61,0	9,5
96	59,0	46,7	214,1	15,3	26,1	8,8	72,1	11,2
120	57,4	31,1	202,5	14,6	26,6	7,7	73,2	10,7
168	58,4	25,8	192,1	15,0	27,1	8,7	78,7	11,1
192	41,4	16,3	125,7	10,7	19,1	6,5	59,4	8,1
216	40,8	16,7	120,6	11,1	19,1	6,5	61,2	8,0
240	37,4	19,0	107,4	10,9	17,7	6,3	59,8	7,6

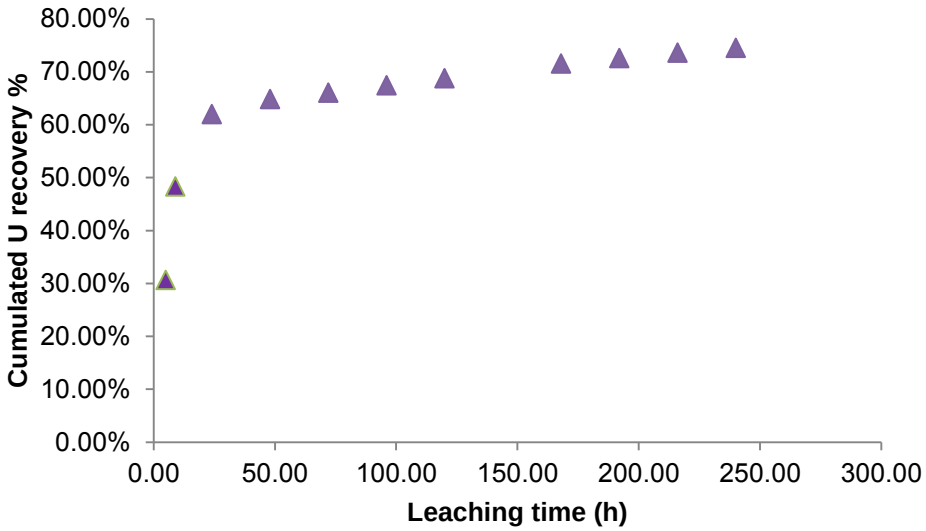


Figure 10: Cumulated Uranium recovery in function of leaching time (h).

Porosity Analyses

Considering the structural evolution of agglomerates due to leaching, an increase of porosity was expected. MIP analyses on acid bound agglomerates leached during 2, 5, 7 and 10 days confirmed this tendency (Table 3). Total and connected porosity increased, compared to non-leached agglomerates. This increase is due to the modification of the connected pores size distribution during leaching: we can especially notice an increase of the number of mesopores (and the creation of new ones) and a decrease of the number of free micropores (Figure 10). This can be related to the leaching of the aluminous silicate matrix phase located around the micro agglomerates before leaching: the matrix is indeed located within these pores, as showed on SEM and X-ray tomography analyses. Moreover, leaching conducts to the dissolution of new minerals and to the conversion of smaller pores to bigger ones.

Table1: Evolution of agglomerates porosity during leaching (MIP analyses)

Leaching time (days)	Total porosity (%)	Connected porosity (%)	Trapped porosity (%)
0	18.09	3.27	14.83
2	23.4	9.91	13.49
5	23.37	9.21	14.16
7	25.24	9.09	16.15
10	23.8	7.85	15.95

However, one can also notice that connected porosity decreases slightly after 2 days of leaching. We assume that this comes from the clogging of some mesopores with the secondary matrix.

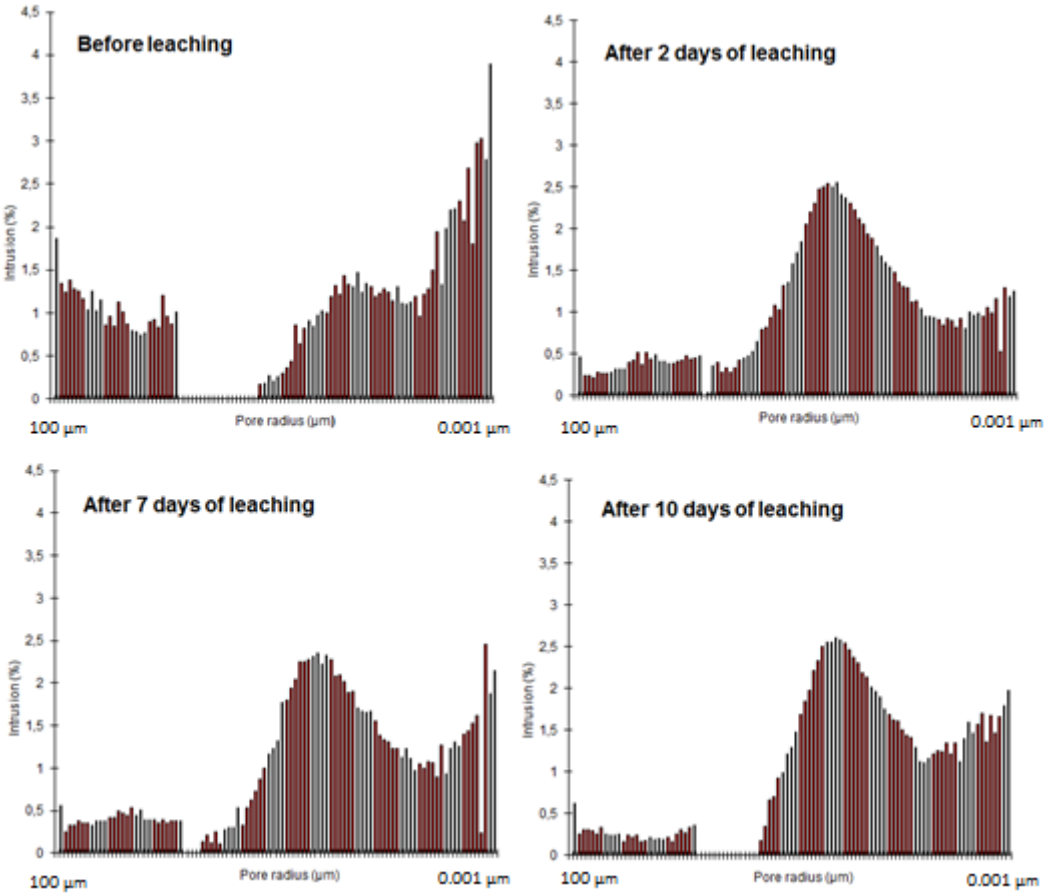


Figure 11: Evolution of connected porosity repartition during leaching. Bigger pores are on the left side.

DISCUSSION

Agglomerates Formation and Growth

The previous tests allowed us to improve our understanding of agglomerates formation and growth. Our main conclusions were the following:

During agglomeration, sulfuric acid reacts with chlorites and with illites-smectites. According to Lowson et al (2007) the proton attack allows removing the interfolded cations of these clay minerals[12] (especially chlorites, which dissolve rapidly[13]) and then attacking the aluminium contained within the TOT folders. This causes the breaking of the silicate structure of the minerals and its incongruent dissolution. We suppose these reactions leaded to the formation of a primary aluminous silicate matrix phase containing most of the uranium of the ore.

The agglomerate structure allows proposing a chronology for agglomerates growth:

(i) During the early stages of agglomeration, the primary matrix and remaining phyllosilicates as muscovite and kaolinites coat bigger particles as quartz, feldspars or even lithoclasts, forming micro agglomerates.

(ii) With the rotation of the agglomeration drum, micro agglomerates grow, by coalescence or layering, depending of their size. We assume that the primary matrix acts as a viscous binder allowing micro agglomerates to assemble to each other's. Moreover, given that the primary matrix is located around micro agglomerates, we assume that it filled the mesopores, causing low connected porosity of non-leached agglomerates.

(iii) When the size of the agglomerate is too high, it breaks into smaller agglomerates.

This chronology is consistent with the agglomeration processes described by Bouffard (2005) and Iveson et al (2001)[3][9].

Evolution of Agglomerates Structure During Leaching

Two leaching stages were highlighted by the presented tests.

— An early stage from the beginning to around the second day of leaching in which the primary matrix is leached. This is especially underlined by the leaching of more than 60 % of the uranium of the agglomerates and the appearance of new meso pores around micro agglomerates. During this stage, we suppose that sulfuric acid from the leaching solution reacts with the remaining phyllosilicates of the agglomerates (muscovites and kaolinites). Due to their structure and the low concentration of the acid, the dissolution of these minerals is not complete but we suppose it causes the formation of a secondary matrix.

— A secondary stage after the second day of leaching. During this step, the secondary matrix is leached but it also continues to be formed. This causes pore clogging and agglomerates deterioration. Given these observations, we suppose that after a given time of leaching, agglomerates would collapse, due to the structural reorganization highlighted by the previous tests.

CONCLUSION AND PERSPECTIVES

X-ray tomography, SEM and MIP analyses allowed us to improve agglomerates structure as a cluster structure composed by the gathering of micro agglomerates which are bound by an aluminous silicate matrix phase coming from the dissolution of clay minerals. During leaching this primary matrix is removed and another one is formed by the partial dissolution of remaining phyllosilicates by the leaching solution. This increased agglomerates connected porosity compared to the one before leaching. However the secondary matrix formation also causes agglomerates deterioration. In order to complete the understanding of the reactions causing the formation of the aluminous silicate matrix phase, dissolution modelling will be done.

Moreover as understanding agglomerates evolution during leaching is a good way to understand the process involved during column leaching, the impact of other agglomeration and leaching parameters will be studied to understand their influence on agglomerates evolution during process.

ACKNOWLEDGMENTS

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DEVELOPMENT OF ROASTING PLANT CONFIGURATIONS TO IMPROVE ECONOMICS AND OPERABILITY OF RARE EARTH ROASTING CIRCUITS

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ABSTRACT

Rare earth minerals are often not leachable at atmospheric conditions without first having to crack the mineral matrix at elevated temperatures with or without the presence of strong acids. Leachability of Rare Earth minerals normally require laboratory test work to determine optimum conditions of temperature, acid type and addition rate and residence time for a particular mineral. Laboratory test work generally starts in small scale muffle furnaces and progresses to larger scale muffle furnace test work, laboratory scale rotary kilns before possibly demonstrating on small scale kilns that are available in commercial metallurgical laboratories. Feasibility studies and even commercial plant designs then copy not only the process conditions but also the piloting or demonstration plant equipment designs.

Paying more attention to the configuration of commercial roasting equipment and the physical properties of the roasting chemicals and minerals by comparing alternate equipment types and configurations can significantly improve the operating and capital costs, operability and the overall financial viability of the finally selected flow sheet.

The effect of different flow sheet configurations on costs have been investigated by process modeling and consideration of the physical and thermodynamic properties of the minerals, chemicals and roasting products for the case of sulphation roasting of a rare earth concentrate.

Comparison of a conventional directly fired rotary kiln process with alternate flow sheets are used to demonstrate the improvements that are possible in the capital and operating costs leading to an improved and more robust flow sheet.

Keywords: Rare Earth Minerals, Roasting, Sulphation, Leaching, Process Development, Rotary Kiln

BACKGROUND

Rare earth minerals are often not leachable at atmospheric conditions without cracking the mineral matrix at elevated temperatures, with or without the presence of strong acids or alkalis[1,18]. Rare earth minerals requiring cracking by acid or alkali include; xenotime, monazite, fluoroapatite, allanite and bastnasite[2,3,4,5,19].

Each ore requires specific conditions of temperature, residence time and acid or alkali addition to obtain a leachable product at minimum cost. These conditions are obtained by a range of laboratory tests that generally start as small scale batch, unmixed samples in muffle furnaces. Once successful conditions are identified in small scale tests then larger batches in muffle furnaces, small scale batch rotary kilns are used to produce larger quantities for hydrometallurgical test work. Pilot and demonstration scale rotary kilns in commercial metallurgical laboratories have also been used for proving processes on a larger scale before final project approvals.

Feasibility studies and even commercial plant designs then duplicate - not only the process conditions - but also the piloting or demonstration plant equipment designs.

This paper considers the configuration of commercial roasting equipment and the physical properties of the roasting chemicals and minerals by comparing alternate equipment types and configurations, and their influence on the operating and capital costs, operability and the overall financial viability of the finally selected flow sheet.

PROCESS EXAMPLE

The effect of different flow sheet configurations on costs have been investigated by process modelling and consideration of the physical and thermodynamic properties of the minerals, chemicals and roasting products for the case of sulphation roasting of a rare earth concentrate.

Ore containing xenotime was chosen as the source rare earth mineral for this paper in order to illustrate how process plant configurations can affect capital and operating costs. The example is not based on a specific ore exiting ore data and test work conditions, instead it is based on assumptions on the chemical species present including; xenotime, inert material and impurities that generate off gases that have to be treated.

The process data has been generated by an HSC Chemistry simulation that calculates heat and material balances using thermodynamic data. All data is from literature sources and does not refer to any specific ore or project. The size of the plant in the process simulation was based to match the size of several rare earth commercial projects that are either in operation or in study phase.

The following basic modelling assumptions have been made of the material to be processed:

- Feed is a concentrate from an ore beneficiation process that includes grinding to a particle size p90 of 100 micron
- Concentrate contains 25% xenotime
- Ore can be cracked by sulphuric acid baking at 200 ^{o}C
- Ore contains impurities with reactive Cl and F species
- Feed rate is 2 tph of concentrate containing 40% moisture

The costs are reported to an order of magnitude accuracy that is sufficient to compare different process options. The costs only cover the scope of a drier, calciner and associated gas cleaning and waste treatment plants.

The paper therefore describes an approach to evaluating process options for a roasting process rather than recommendations for any specific project where the physical and chemical properties of the ore, the process conditions and the behaviour of the ore during processing will dictate the viable process options.

The high temperature reaction of sulphuric acid with the ore is referred to as a sulphation bake, acid bake, acid cracking, acid roasting or calcination but for this paper will be referred to as calcination and the equipment as a calciner, which could be a rotary kiln or some other device.

Chemistry

The mass and heat balances have been based on the following chemistry:

$$2\,YPO_4 + 3\,H_2SO_4 \rightarrow Y_2(SO_4)_3 + 2\,H_3PO_4$$
$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\,HF$$
$$CaCl_2 + H_2SO_4 \rightarrow CaSO_4 + 2HCl$$

Process Flow Sheets

Two process flow sheets have been considered for this duty. Firstly where the dryer and calciner are heated internally by fuel combustion as shown in Figure 1. Combustion gases are combined with process gases. The two units may be combined into a single kiln.

The second variation considered has an indirectly heated dryer and calciner as shown in Figure 2. In this case heat is transferred though the walls of the kiln and the process gases and combustion gases are kept separate.

There are various combinations of the flow sheet but these two extremes have been considered to show the influence of the different flow sheets on the process sizing and costing.

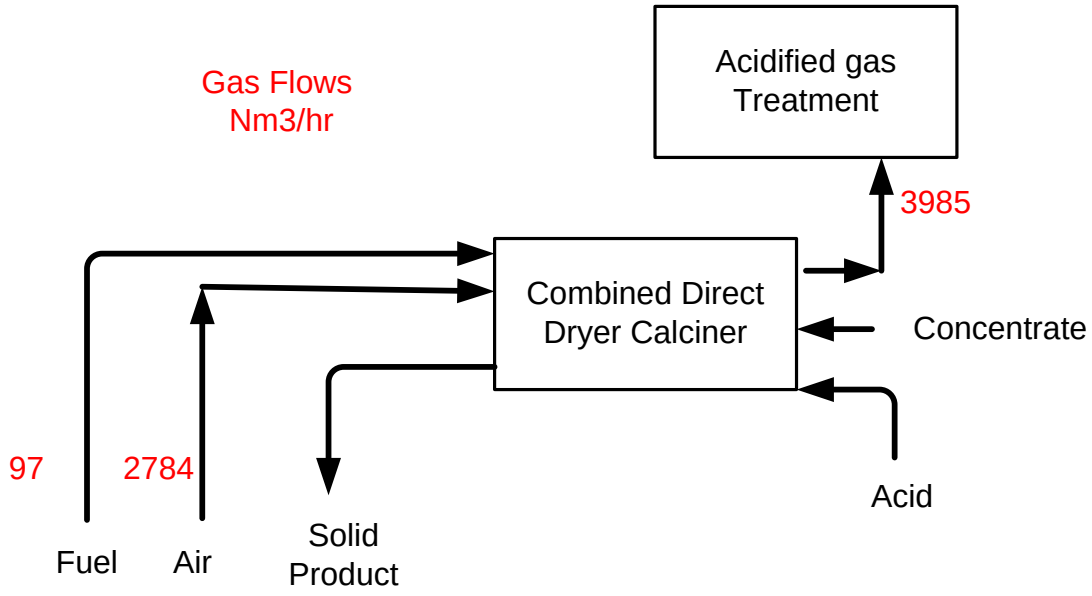


Figure 1: Directly Heated Combined Unit Flow Sheet

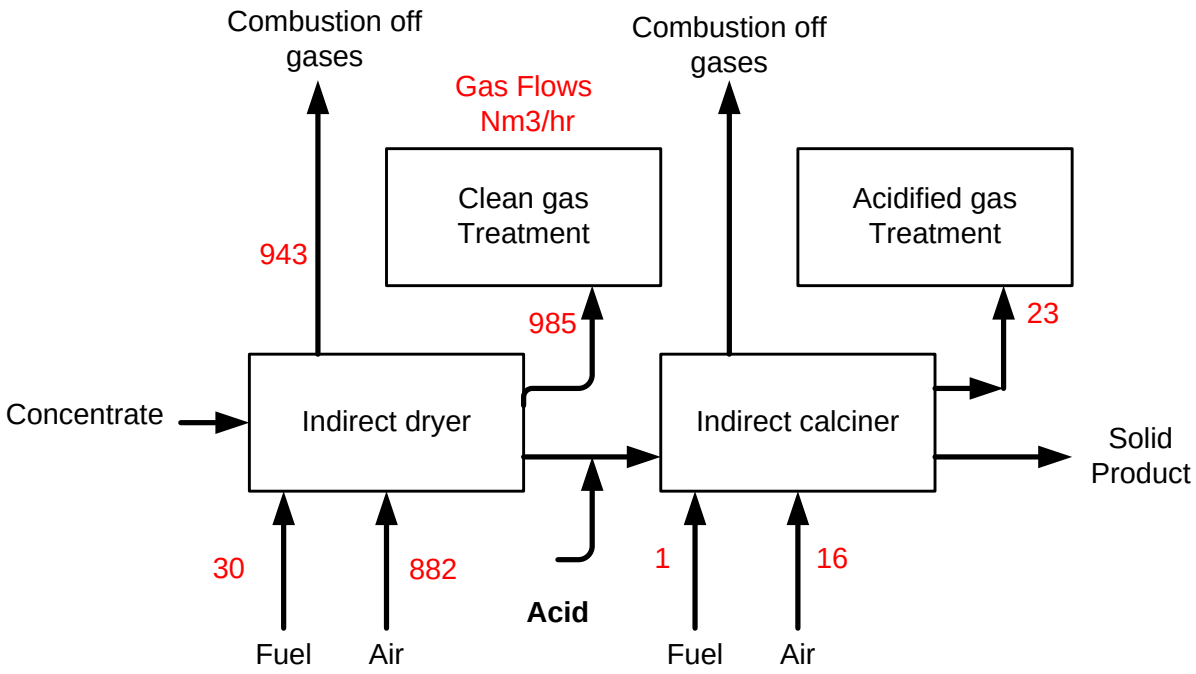


Figure 2: Indirectly Heated Separate Drier and Calciner Flow Sheet

Indirectly Heated Kilns (Ansac 9m x 1.5m ϕ)

Physical Properties of Acids

Sulphuric acid has been used to treat xenotime. During processing the contact of concentrated sulphuric acid with chlorine and fluorine containing minerals generates hydrochloric and hydrofluoric acids. The acid physical properties play an important part in the selection of the process flow sheet.

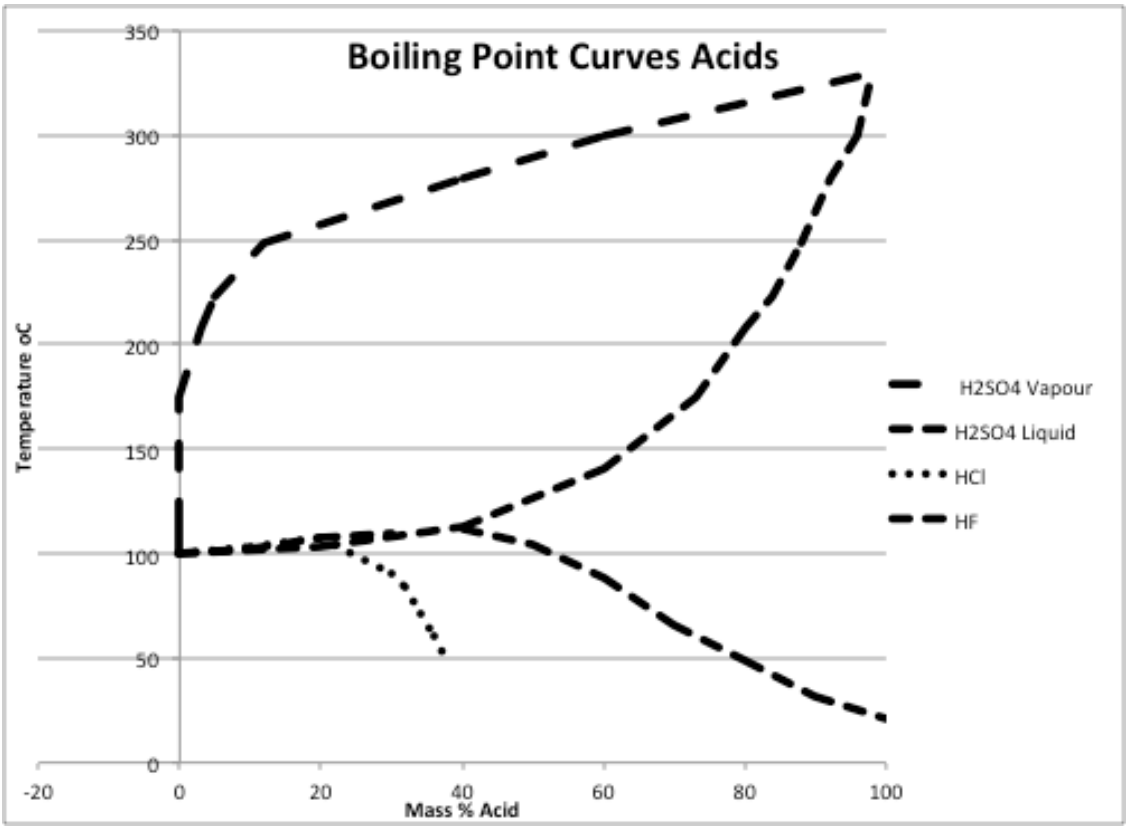


Figure 3: Acid Boiling Point Curves

Figure 3 shows a phase diagram for aqueous solutions of acids based on boiling point[6,7,8]. For sulfuric acid, in addition to the boiling point curve the vapour acid composition is also shown. All three of the acids shown have a maximum boing point azeotrope but concentrated sulfuric acid boils at a much higher temperature than the other acids. At the process conditions expected in the roasting process both the initial drying and the sulphation occurs above the boiling points of HCl and HF while depending on the concentration of sulfuric acid the process conditions may be below or above the boiling point for sulfuric acid.

Figure 4 shows the same boiling point curve but with the addition of the path the acid in the process will follow for two process options:

- a separate drier and calciner
- a single combined drier and calciner

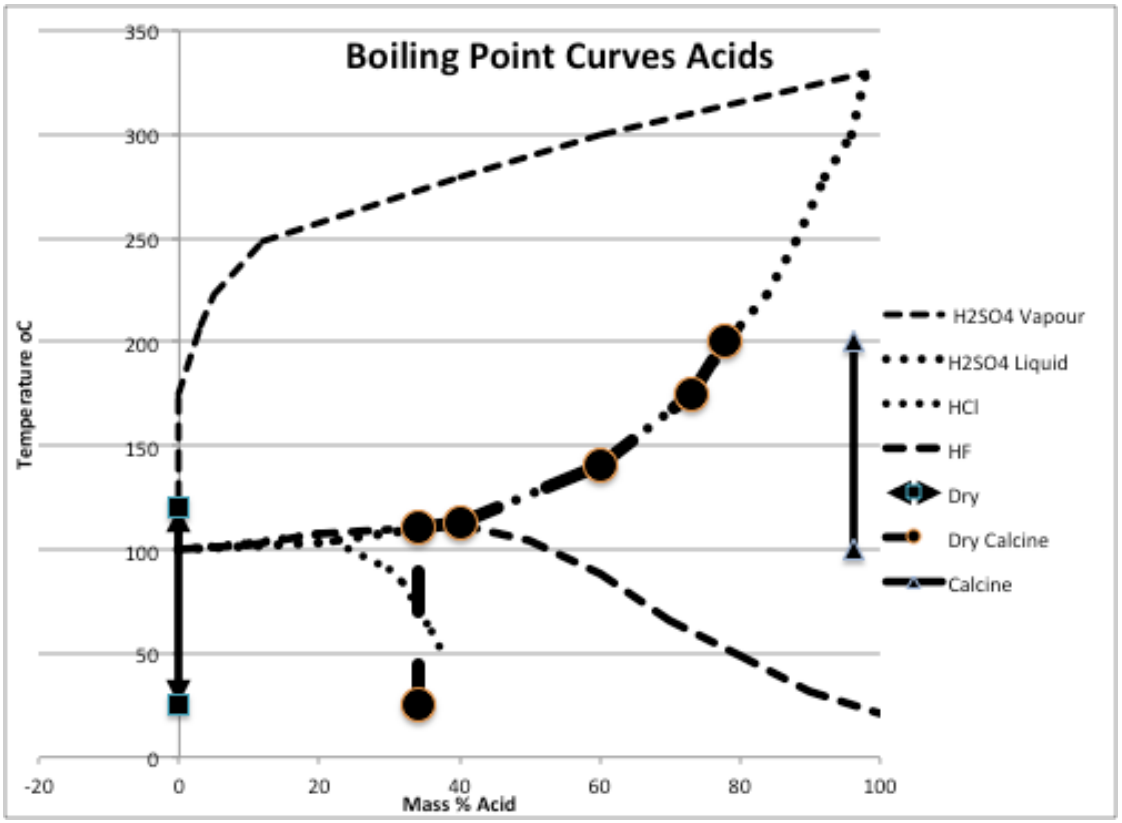


Figure 4: Process Path on Acid Boiling Point Curves

If we first consider the case of a separate dryer and sulphation roaster, the drying takes place before acid addition and therefore there is no sulfuric acid and also no HCl or HF which both form after the acid addition. If most of the water is removed during drying, here shown as 99% removal by heating to 120 ^{o}C, the process in the calciner remains below the sulfuric acid boiling point for the heating to 200 ^{o}C, but is always above the boiling point of HCl and HF. One would therefore expect most of the HCl and HF to be in the vapour phase and most of the sulphuric acid to remain in the liquid phase.

For a single piece of equipment for drying and roasting the process will follow the dry-calcine curve shown in Figure 4. The wet ore after sulfuric acid addition has approximately 34% acid content. As the ore is heated, firstly HCl is driven off then the heating curve follows the sulfuric acid boing point curve. HF is then driven off and sulfuric acid continues to boil until the final temperature of 200 ^{o}C is reached. The overhead vapours can therefore expect to contain all the water driven off, all the HF and HCl and a substantial amount of sulfuric acid. The amount of sulfuric acid boiled off is expected to be 8% of the feed acid forming a 4% acid content in the vapour.

The gas/vapour flows for the two cases based on indirectly heated process equipment is 985 Nm^3/hr for the drier and 21 Nm^3/hr for the calciner, for the two separate processes and 1006 Nm^3/hr for the combined process. The separate processes need two different gas handling steps, a large clean dust and vapor stream and a small acid contaminated stream. The single step leads to a large contaminated stream that needs materials of construction to handle the corrosive acid mix.

In the case of directly fired equipment the drier produces 1915 Nm^3/hr and the calciner 25 Nm^3/hr If these two duties are combined in a single unit can expect to produce 2094 Nm^3/hr of gases for treatment that have been contaminated by acids compared to the 25 Nm^3/hr for separate processes.

Heat Requirements

The heat requirements for the process can be visualised as a heating curve that plots the heat rate required at each temperature. The two graphs Figure 3 and 4 show the heating curves for the drying and the calcining separately and then as a composite curve considering only the heat requirements based on the chemistry and allowing for no losses[9,10]. This is the minimum amount of heat required for the process without heat recovery systems. The latent heat of drying is the

major heat required whilst the heat required for calcining is low as the heat to bring reagents to temperature is almost balanced by the exothermic heat of reaction.

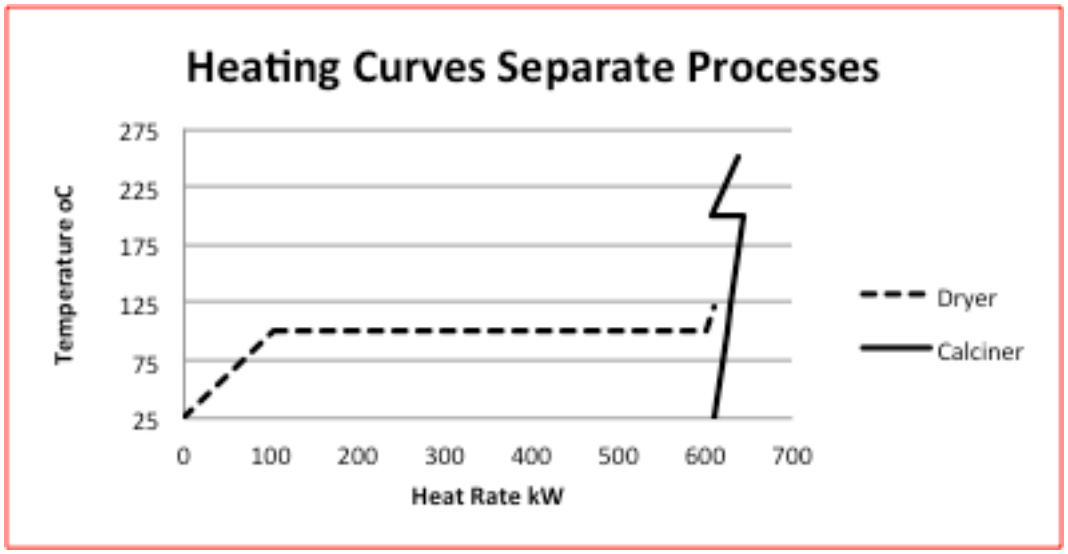


Figure 5: Heating Curves for Separate Processes

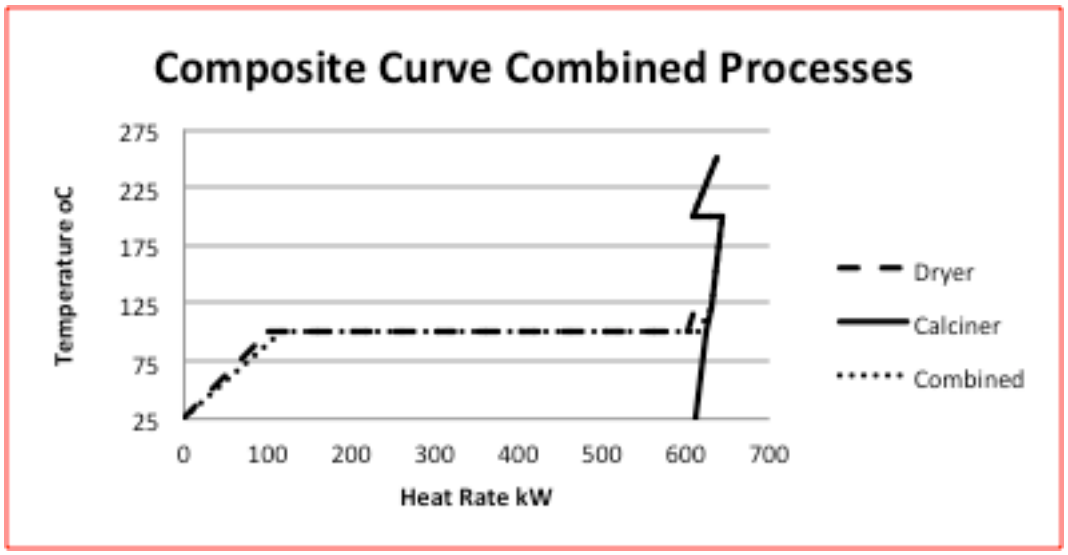


Figure 6: Heating Curve Combined Processes

If indirectly heated equipment is used, and heat losses are allowed for, the heating required increases as shown in Figure 7.

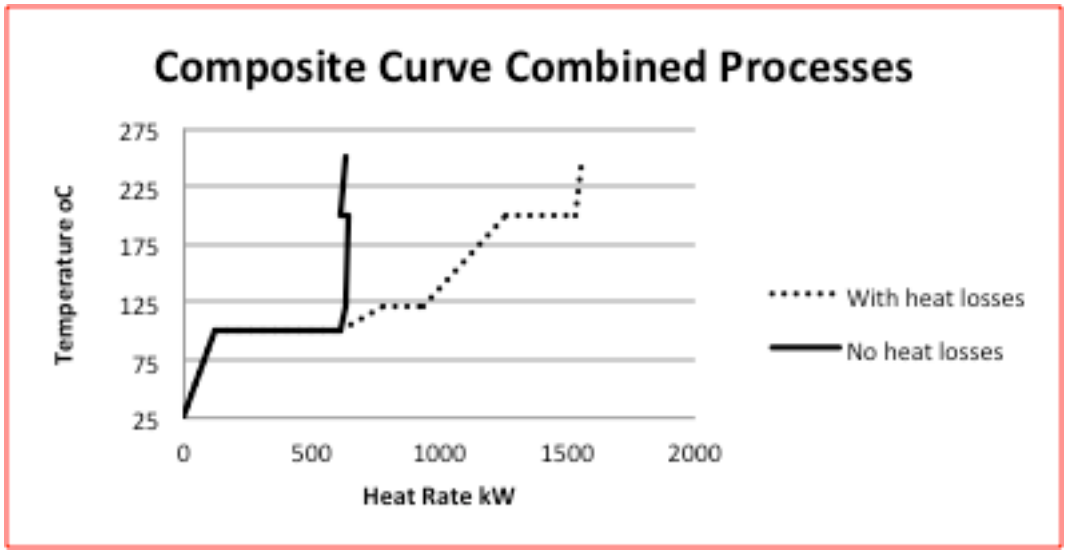


Figure 7: Heating Curves With-And-Without Heat Losses Combined Processes

In addition to heat losses, the way that heat is introduced to the process affects the heat curves as shown in Figure 8. With direct heating, the combustion gases join the process gases, and in a single processing unit all gases have to leave at the calciner outlet temperature. The major effect is that a larger gas volume leaves the kiln at high temperature, and in the case of a fine powder, this requires a larger diameter kiln, with larger heat losses.

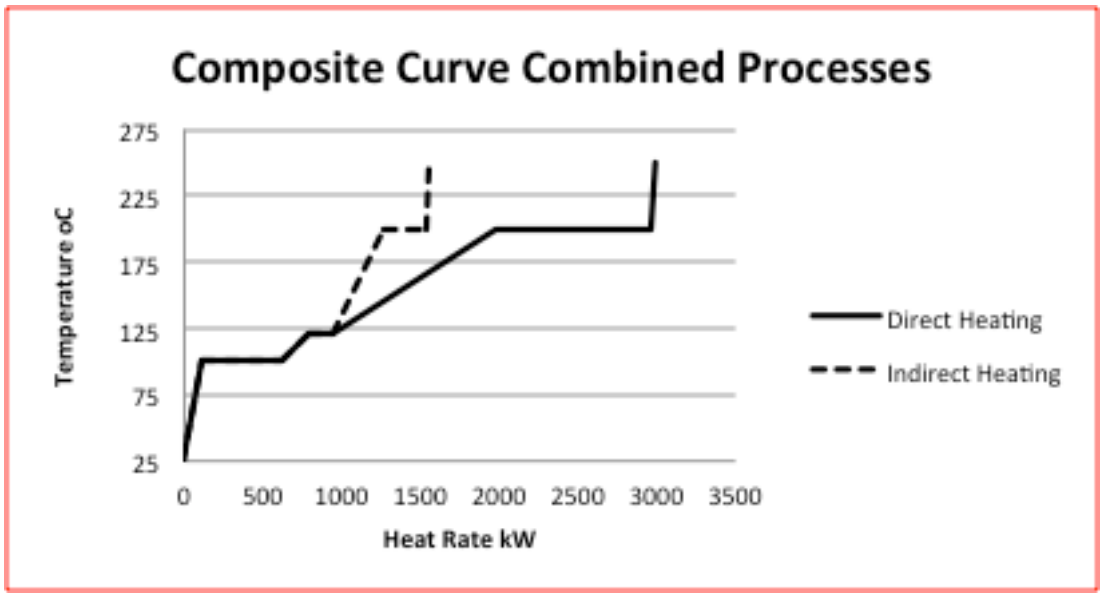


Figure 8: Heating Curves for Directly and Indirectly Heated Combined Processes

Heat Recovery

Just as the heat rate for heating the streams to temperature can be plotted, the cooling of hot streams can also be plotted against temperature and this shows how much heat can potentially be recovered.

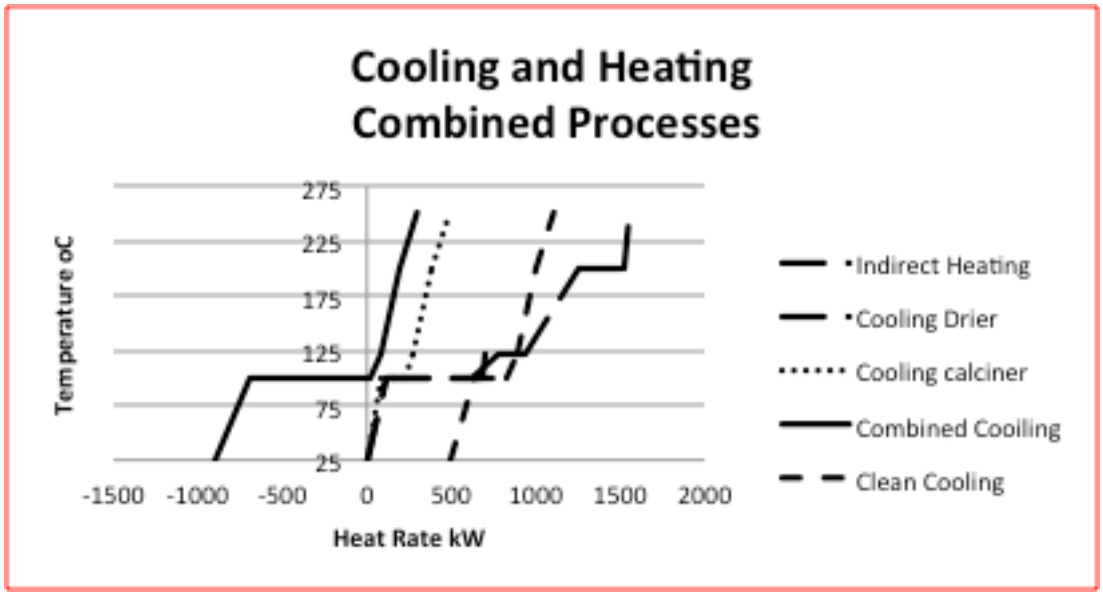


Figure 9: Cooling and Heating Curves for Indirectly Heated Combined Processes

Figure 9 shows the Indirect heating curve but also shows curves for cooling down the hot drier streams, the hot calciner streams and the cooling of the combined hot streams. These curves have been shifted on the x axis so that they don't overlap and are easier to identify. A curve considering the cooling of only clean (non acidified) streams is also shown as this is the most likely source for heat recovery.

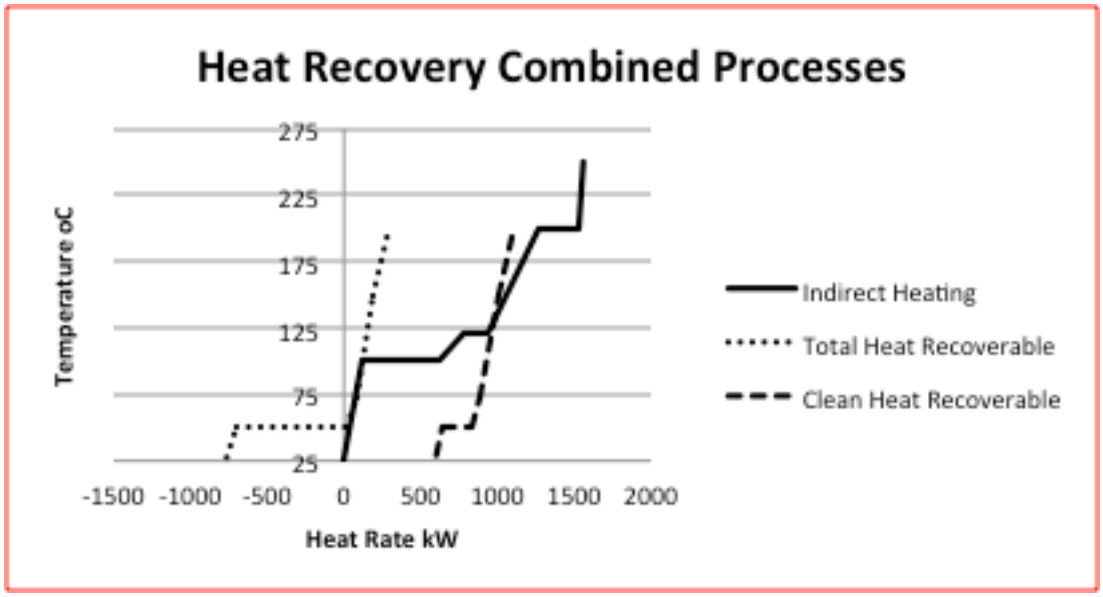


Figure 10: Heat Recovery Combined Processes

Figure 10 shows the potential heat recovery from clean heat and in total, and this has been plotted at a temperature 50^{o}C lower than the stream temperature. This allows a temperature difference for heat transfer so that if one of the heat recoverable curves lies on or above the heating curve this heat will be recoverable. These curves show that heat is available for preheating the calciner and the drier.

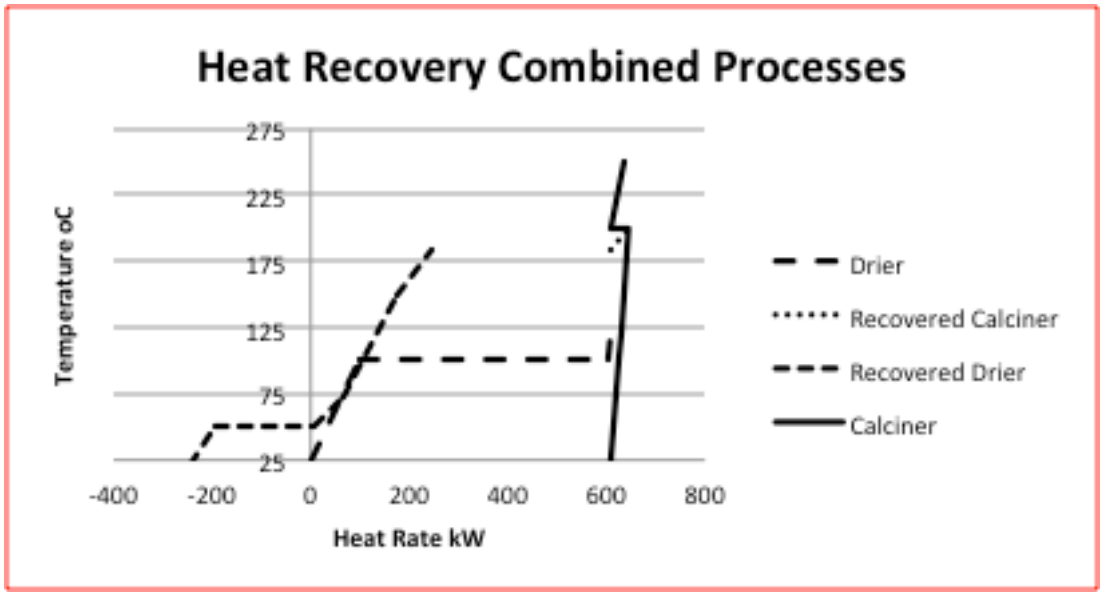


Figure 11: Heat Recovery Drier and Calciner

Figure 11 shows the recoverable heat available for the drier and for the calciner. Most of the calciner heat preheating can be supplied by recoverable heat and approximately 50% of the drier heat from clean gas cooling. There is also heat available to heat process streams up to 50^{o}C which may be useful for a upstream or downstream hydromet plant.

Solids Flow

Solids flow in the drier and particularly in the calciner has proved to be difficult for a range of projects that heat minerals with sulphuric acid, and problems generally occur with solid material sticking to hot surfaces forming a crusty buildup. This material may not leave the kiln and forms an insulating layer on heat transfer surfaces. The insulating layer may be patchy with resulting hot and cold areas on the heat transfer surfaces. Hot areas will tend to attract further build up of material.

The material flow behaviour and build up is dependent on the individual ore properties and can only be determined by piloting. A range of options that have been successful in preventing build up include:

- mechanical devices such as chains, scrapers and more complex rotating devices
- pre-mixing and agglomeration to produce a feed that flows freely
- recycle of product to the calciner to promote better flow properties

Free flowing material in a kiln takes up only a small part of the kiln volume (~5-10%), so if a large residence time is required the residence time sets the kiln sizing. For other indirectly heated types of equipment, the available space for solids holdup is larger and a smaller overall unit may be able to be used.

Without a firm understanding of the issues affecting solid build up and how to overcome these, the resultant commercial design will not operate robustly, and expended downtime periods are likely for periodic cleaning.

The options discussed here will have to be piloted to prove that solids flows are achievable for extended periods.

Gas Treatment

There are three sources of gas that have to be treated in this flow sheet

- clean hot gases from indirect burners
- dusty vapour containing gases from the drier
- dusty acid contaminated gases from the calciner

The clean hot gases require little treatment and are suitable for use in heat recovery to preheat burner air or feed solids.

The dusty vapour from the driers will have to have the solids removed before the gases are cooled, to avoid sludge forming with the solids and condensing water vapour. The vapours and sludge should not be acidic and the clean wet gases may be able to be used to provide low temperature energy.

The dusty acidic gases provide a challenge in removing dust before condensation occurs as the high dew point sulphuric acid vapour will start condensing soon after leaving the kiln. Until the temperature is reduced to levels where plastics are can be used expensive materials of construction will be required. The changing composition of sulphuric acid condensate from very concentrated to dilute will make material selection difficult. The captured acidic sludge will have to be treated to be able to recycle it and some may have to be treated as waste. Early flash cooling to drop temperature makes material selection easier but will limit useful energy recovery.

The costs of treating the acid contaminated gases will be much higher than that for dusty clean gas.

Kiln Sizing

There are many factors to consider in kiln sizing but for this analysis the only factors considered were:

- Solids residence time
- Gas superficial velocity
- Heat transfer rate for the indirectly heated options

The following sizing factors were limiting for the kiln sizing

Table 1: Kiln Sizing Factors

Equipment	Direct Fired	Indirectly Fired
Drier	Gas Superficial Velocity	Heat Transfer Area
Calciner	Gas Superficial Velocity	Solids Residence time

The solids residence time has been assumed to be 1 hour for the calciner. A kiln has a relatively low volume of solids feed, so this becomes the limiting factor in the indirectly heated calciner that has low gas flows and a low heating requirement with the exothermic reaction. The directly fired units combine the combustion gases with the process gases and as the feed is fine, the limiting velocity is estimated as 0.5m/s, and this results in the larger sizing of the indirectly fired calciner. The major heat requirement is the evaporative heat load for the drier and for the indirectly heated drier this heat transfer through the kiln wall limits the kiln size.

Overall Costs

The capital costs for the direct and indirectly fired options have been costed to an order of magnitude accuracy (±40%). Mechanical equipment costs were based on historical budget quotations from vendors and scaled to the capacity required. Other direct costs such as civil, structural, piping electrical and instrumentation were factored based on the mechanical equipment cost. Indirect costs were factored based on the direct costs. The mechanical equipment cost was split into areas for the drier, clean hot gas treatment, calciner and the acidic contaminated hot gas treatment. The costs for these areas were based on the estimated sizes of each of these areas.

The estimate accuracy is low, so rather than take these values as absolute costs, they should rather be considered as showing a significant difference the two process options.

Table 2: Capital Costs (million AUD)

Cost Item	Direct Fired	Indirectly Fired
Direct Costs		
Drier	0.7	0.7
Drier Gas Treatment	0.0	0.1
Calciner	1.1	0.8
Calciner Gas Treatment	1.2	0.2
Platework	0.1	0.1
Piping	0.4	0.3
Electrical And Instrumentation	0.4	0.3
Concrete	0.3	0.2
Structural	0.4	0.3
Sub-Total Directs	**4.7**	2.7
Indirect Costs		
EPCM @ 18% of Directs	0.8	0.5
Temporary Works @ 3% of Directs	0.1	0.1
Insurances @0.1% of Directs	0.0	0.0
Reagents and First Fills @ 2% of Directs	0.1	0.1
Spares @ 2.5% of Directs	0.1	0.1
Contingency @ 20% of Directs	0.9	0.5
Sub-Total Indirects	**2.1**	**1.2**
TOTAL	**6.8**	**3.9**

The operating costs have not been quantified, as these are dependant on the plant location where labour costs, power costs and reagents costs may differ substantially. The main differences between the operating costs are likely to be:

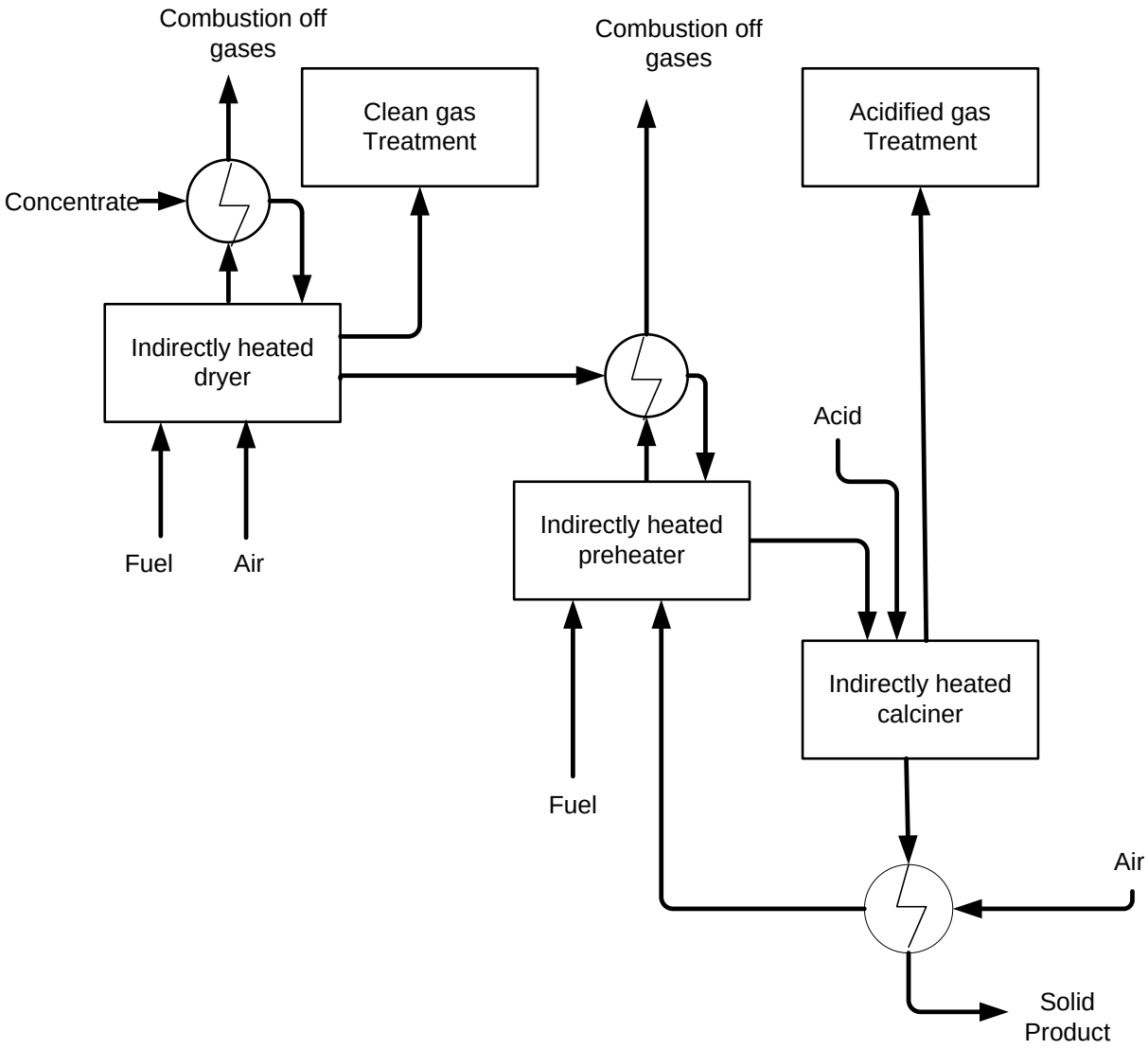
- Increased acid reagent costs for the directly fired calciner as an expected 8% of the feed acid is expected to boil off
- Increased neutralisation reagent costs for the directly fired calciner as neutralisation is required for 8% of the feed acid
- Increased fuel requirements for the directly fired option as the kilns are larger and therefore will have larger areas for heat loss and the larger volumes of hot off-gases also result in heat loss
- Increased power requirements for the directly fired option particularly in the larger gas volumes to be handled by the induced draught fan

Alternate Flow Sheet

The analysis above has shown that several factors limit the kiln sizing and costing. The major opportunities to improve the process include separating clean and contaminated gas streams, heat recovery and consideration of alternate equipment.

The amount of heat required for the indirectly heated calciner is quite limited and most of the heat required is to make up for heat losses. If an indirectly heated paddle type mixer is used, the solids take up a larger amount of the internal volume, and a smaller sized unit with less heat losses can be used. By preheating the solid feed, the calciner will require little external heat input, which may improve the solids flow behaviour as many of solids flow problems originate on the hot surfaces.

Heat can be recovered from cooling the hot product solids (34kW), the combustion gases from the drier and the calciner, and can be used to preheat combustion air (34kW) and preheat the solids fed to the kiln (103 kW).



CONCLUSIONS

Comparison of various options for drying and calcining of an acid bake flow sheet show that significant differences are possible in the capital and operating costs leading to an improved and more robust flow sheet. This type of analysis should be performed during pre-feasibility studies so that at the stage of piloting it is clear what information has to be determined to allow alternate flow sheets and equipment to be considered for commercial flow sheets.

This type of analysis is valid for many flow sheets where acidified off-gases and energy intensive steps are required.

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Uranium-REE Proceedings

Scandium Recovery

RECOVERY OF RARE EARTH ELEMENTS AND SCANDIUM FROM EUROPEAN DEPOSITS BY SOLVENT EXTRACTION

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ABSTRACT

Solvent extraction methods are being developed for the separation and purification of Rare Earth elements (REE) as part of the EC funded EURARE project. Following initial laboratory batch test work, the mission was to construct and operate a flexible solvent extraction purification and separation mini-pilot plant capable of testing the process developed and producing high purity REE products and scandium of high purity. So far, the work performed has resulted in the separation of heavy (HREE), medium (MREE) and light (LREE) Rare Earths elements, and the separation of yttrium from the HREE fraction and Nd from the LREE fraction. Scandium purification will follow using a separate flowsheet.

Keywords: EURARE, Rare Earths, Scandium, Solvent Extraction

INTRODUCTION

The Rare Earth Elements are 17 chemically similar metallic elements, including the 15 lanthanides, scandium and yttrium. They occur in a wide range of REE bearing minerals and are mined collectively. Due to their chemical similarities and high chemical activities, REE recovery and separation are technically complicated. REE are usually divided into light REE (LREE; La, Ce, Pr, Nd), medium REE (MREE; Pm, Sm, Eu, Gd, Tb and Dy) and heavy REE (HREE; Ho, Er, Tm, Yb, Lu, and Y). HREE are usually present at lower concentrations than MREE or LREE in REE bearing minerals and are hence more expensive.

Fractional crystallization, ion-exchange techniques and chromatographic methods are used to separate the REE in small amounts. Industrial scale separation is generally achieved using solvent extraction. Solvent extraction is a selective separation procedure for isolating and concentrating substances from aqueous solutions with the aid of an immiscible organic solvent. The procedure has a rapidly growing industrial importance and has been widely adopted for the recovery and separation of base metals and REE. Specific REE compounds (usually oxides) with purities in excess of 99.99% can be produced.

Europe has significant REE resources. Historically, REE were discovered in Scandinavia and today REE deposits in Greenland and Sweden are listed among the most interesting deposits in the world, resources that aim to undermine the Chinese REE monopoly in the coming years. Additionally, REE presence has been reported in by-products from the metallurgical industries. One example is the recovery of the Scandium content in bauxite residues (red mud), emanating from primary aluminium production in Greece.

The EC funded EURARE project therefore aims to set the technological basis for the development of a European REE industry. The reason is to safeguard an uninterrupted supply of REE raw materials and products at a crucial moment for the EU economy industrial sectors in a sustainable, economically viable and environmentally friendly way. Twenty three academic and industrial partners from 10 European countries participate in this 5 year project.

The MEAB Group has been active in the hydrometallurgical field for more than 50 years. The work has, to a great extent, been focused on the development of processes for the recovery of metals from metal containing solid or liquid waste. However, the recovery of REE from phosphate minerals also has been investigated. MEAB is therefore responsible for developing solvent extraction methods for the RE carbonates produced in the EURARE project.

In this study, MEAB's experimental work for the EURARE project is presented, with a focus on optimising a continuous solvent extraction separation and purification operation for the laboratory demonstration plant design.

Sources of the Rare Earth Carbonates

In this study, laboratory-scale experiments have been carried out using intermediate Rare Earth carbonates prepared in downstream EURARE operations. The project involves ores from four different European Rare Earth resources:

- Steenstripine from Kvanefjeld deposit in Greenland,
- Eudialyte from Norra Kärr deposit in Sweden,
- Eudialyte from TANBREEZ project (TANBREEZ is an abbreviation of the metals which are planned to be extracted from Eudialyte) in Greenland, and
- Bastnasite from Rødberg ore in Norway.

In addition, the recovery of scandium, yttrium and other REE is also being investigated from a Greek bauxite residue (Red Mud).

Conversion of REE Containing Ores to REE Carbonates

Due to the unique nature of the Kvanefjeld deposit in Greenland, a customised metallurgical flowsheet was developed by the Greenland Minerals and Energy Limited (GMEL) in-house metallurgical team. This selected flowsheet was then tested during the EURARE work program at GTK Mineral Processing in Outokumpu, Finland. The ore was beneficiated using flotation, which

increased the total REE concentration to more than 15 % Total Rare Earth Oxides. The following multi-stage circuit consisted of sulfuric acid leaching, uranium solvent extraction, caustic conversion, hydrochloric acid REE re-leaching and production of a mixed high value REE intermediate carbonate using sodium carbonate[1].

A hydrometallurgical flowsheet was developed for the Eudialyte deposits at IME Process Metallurgy and Metal Recycling RWTH Aachen University, Germany in cooperation with MEAB. After beneficiation using magnetic separation techniques, the resulting REE concentrate was treated with concentrated hydrochloric acid in order to stabilize silicon. After dilution with water, the resulting slurry was fed to a two stage neutralisation circuit to remove impurities (mainly Al, Fe, Mn, and Zr). Finally, a mixed high value RE intermediate carbonate was achieved.

Rødberg bastnasite ore of high iron content (78 % Fe_2O_3) underwent a reductive iron smelting procedure in a small electric arc furnace, with carbon added as a reducing agent. REE and impurities transferred to the slag and the REE were recovered with good recovery yields by adding sulfuric acid after milling. A direct leaching process was also developed for Rødberg bastnasite ore with a lower Fe content. After grinding and milling, the resulting fine fraction was leached using hydrochloric acid, followed by removal of dissolved iron by solvent extraction. The REE were precipitated from the raffinate using sodium carbonate[2].

Ionic liquids (ILs) have been identified as greener alternatives to conventional solvents as they are capable of enhancing the yield and selectivity of reactions. Research from National Technical University of Athens (NTUA) in the EURARE project showed that ILs can selectively leach critical metal including REE and scandium from bauxite residue. The functionalized hydrophobic ionic liquid betainium bis(trifluoromethylsulfonyl)imide (HbetTf2N) can selectively dissolve a range of metal oxides including REE against iron, aluminum and silicon oxides. REE dissolved in the ionic liquid were then stripped with an acid solution, and the ionic liquid was regenerated for reuse. The stripping process can be performed with any acidic solution; therefore this process can be easily adapted to any technology that is currently available for REE/Sc purification. A scandium-oriented process developed in EURARE resulted in Sc leaching efficiencies of around 45 % and produced acid strip liquor for further treatment of 40 mg/L Sc[3].

METHODS

Solvent Extraction - Separation and Purification of REE

MEAB's development of a continuous solvent extraction separation and purification method for a laboratory scale demonstration plant has proceeded as follows:

- Selection of reagents,
- Investigation of solvent extraction parameters (e g distribution coefficient, extraction rate, extraction selectivity),
- Determination of scrubbing and stripping liquors and conditions,
- Equilibrium curves for extraction and stripping,
- Flowsheet development,
- Set up of a mixer settler demonstration plant (MSU-0.5), and
- Demonstration plant operation.

Figure 1 shows a general flow sheet of the integrated REE dissolving and solvent extraction process.

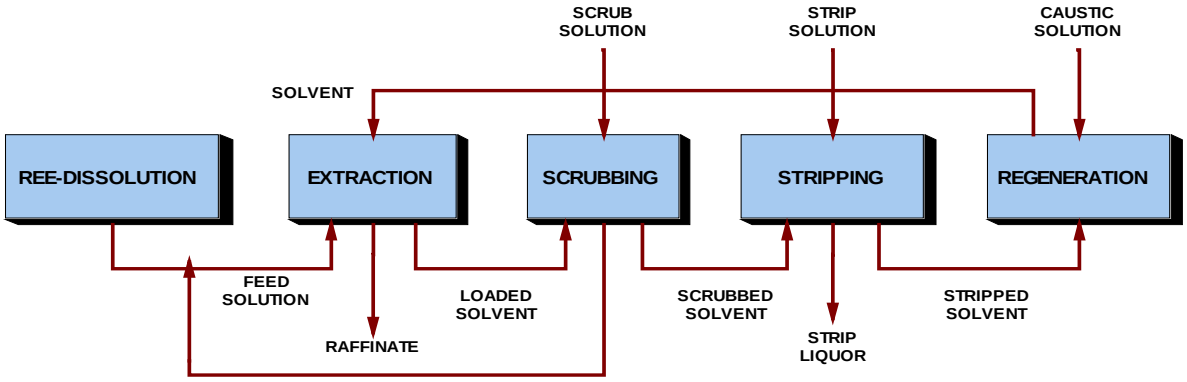

Figure 1: General Process Flow Sheet – REE Separation and Purification by Solvent Extraction

Definition of Solvent Extraction Parameters

Distribution coefficient D: The distribution coefficient D is defined as the concentration ratio C_o/C_a, where C_o represents the concentration of the extracted substance in the organic phase and C_a represents the concentration in the aqueous phase, at equilibrium. Distribution curves are commonly represented as D (%) versus pH plots or as log D versus pH plots.

Percentage of Extraction P (%): The percentage extraction P (%) states the percentage of extracted species in relation to its total quantity $m_o + m_a$.

$$\mathbf{P}\ (\%) = 100 * m_o / (m_o+m_a)$$

The variable m_o and m_a represent the quantities of the species under consideration in the organic and aqueous phases, respectively, after reaching equilibrium. m_o is only equal to the amount of extracted substance if fresh unloaded reagent has been used in extraction.

Selectivity S: The selectivity of a reagent for different groups of REE (REE_1 and REE_2) is represented by the separation factors S. This is calculated as quotient of the distribution coefficients D of the groups of REE.

Laboratory Batch Experiments

Laboratory batch experiments first were carried out using bench-scale laboratory equipment. To investigate the extraction efficiency of heavy REE over medium and light REE, equilibrium tests were carried out at different pH values using the intermediate product from Kvanefjeld. The dissolved RE carbonates contained 32 g/l La, 56 g/l Ce, 6.4g/l Pr, 19 g/l Nd, 2.7 g/l Sm, 0.2 g/l Eu, 1.6 g/l Gd, 1.7 g/l Dy, 0.2 g/l Ho, 0.5 g/l Er, 0.2 g/l Yb and 8.7 g/l Y. Hydrochloric acid and ammonia solutions were used to adjust the feed solution pH as required. Removal of co-extracted REE from a loaded organic solution was performed using dilute HCl. Finally, REE stripping from the loaded organic solution was investigated using concentrated HCl.

In all experiments, the organic solutions were mixed with the aqueous solution for about 15 minutes in stirred beakers under fairly high speed mixing conditions and at different organic to aqueous (org/aq) ratios. After phase separation, the resulting aqueous and organic phases were saved and analysed.

Advanced Research Equipment – The AKUFVE System

AKUFVE is a worldwide-recognised instrument for rapid and accurate measurement of partition factors in solvent extraction. The instrument is characterised as an idealised, one-stage mixer-(centrifugal) settler unit. It was developed about 40 years ago to improve accuracy and rapidity in the measuring technique of solvent extraction distribution data.

In applied research the AKUFVE instrument considerably reduces the time and labour in the evaluation and optimisation of solvent extraction processes. Its application to basic research has

included the determination of distribution and stability constants for various metal complexes, together with enthalpy and entropy values, obtained from temperature dependency measurements and the determination of reaction rates and activation energies. In general, the AKUFVE instrument offers great advantages over more conventional techniques[4]. General equipment set up is shown in the Figure 2 below.

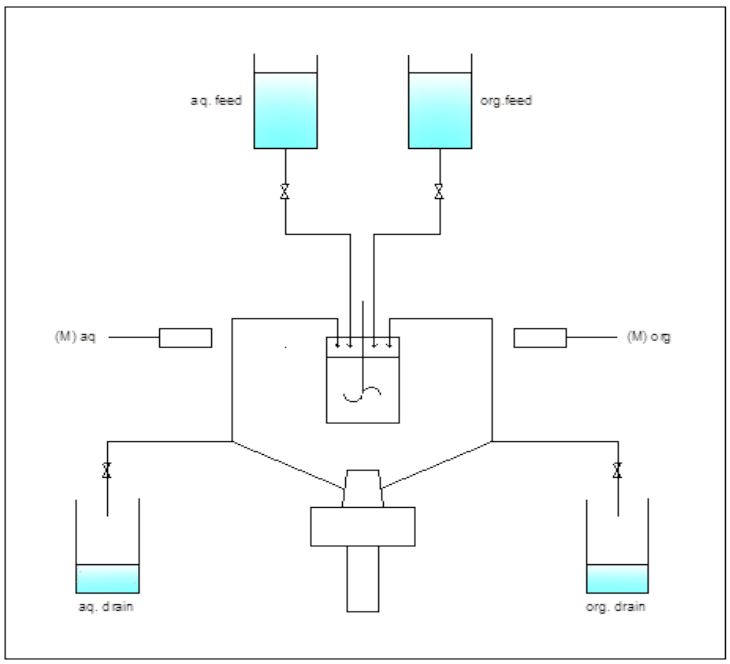

FIGURE 9

Figure 2: The AKUFVE instrument – Principal of operation

Mixer-Settler MSU-0.5 Laboratory Equipment

Figure 3: MSU-0.5 multi stage laboratory unit for REE separation and purification

The MSU-0.5 units shown in Figure 3 are compactly designed, self-contained mixer-settler units, built in blocks, one for each function – extraction, scrubbing, stripping, regeneration etc. The blocks include built-in heavier and lighter liquid flow transfers. The mixer includes a top-mounted, variable speed motor with mixing impeller. The stirrer also acts as a pump for the heavier liquid. The settler is equipped with a picket fence for distribution of the mixture and an adjustable interface controller (a jack-leg). The heavier liquid can be recycled. Altogether, the construction eliminates the need for

excessive pipelines, bulky framework and unnecessary bench space. The equipment possesses the inherent flexibility needed for rapid evaluation of solvent extraction data. In addition, the experience shows that the mixer-settlers are large enough to provide reliable chemical data and sufficient product solutions for further evaluation. At the same time, the units are small enough to minimize consumption of chemicals, maintenance and operation attendance[5]. The picture shows the mixer-settler (MSU-0.5) set-up used in the experiments.

The construction material in contact with process solutions is PVDF (polyvinylidene fluoride). The complete experimental set-up of the MSU-0.5 equipment includes:

- An flexible number of mixer-settler units arranged in functional blocks with the end supports containing inlets and outlets,
- Mixer motor speed control units one for each mixer, and
- Adjustable flow pumps and support tanks.

BATCH SOLVENT EXTRACTION LABORATORY TESTS

Reagent Selection

A literature review was conducted[6,7,8,9]. Acidic extractants of organo-phosphorus, carboxylic and sulphonic acids include functional groups. The most commonly used acid organo-phosphorus extractants are divided into phosphoric, phosphonic and phosphinic acids. Generally the extraction of metallic ions followed the cationic-exchange reaction:

$$REE^{3+} + 3\ HR \longrightarrow [REE * R_3] + 3\ H^+ \qquad \text{[Equation 1]}$$

Commercially, REE have been extracted from a weak acid solution by di(ethylhexyl)phosphonic acid (Ionquest 801), di(ethylhexyl)phosphoric acid (DEHPA) or blended extractants. The pH isotherms of REE obtained in laboratory experiments carried out for Orbite Aluminae Inc., Canada are shown in Figure 4 [10].

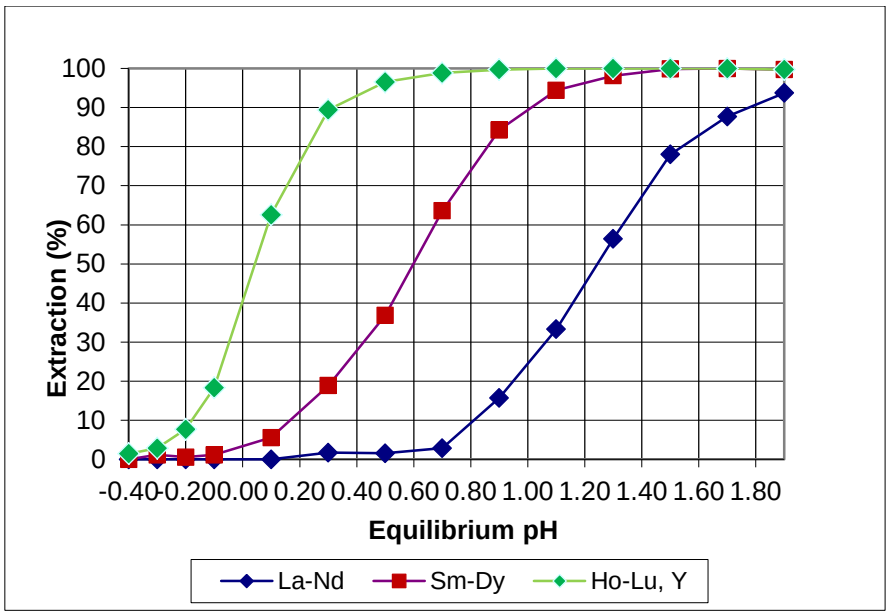

Figure 4: Extraction of REE in chloride solution with di(ethylhexyl)phosphonic acid (Ionquest 801)

Based on the literature, MEABs experience and previous experimental test work, di(ethylhexyl)phosphonic acid (Ionquest 801) was chosen as the organic reagent with aliphatic kerosene (Ketrul D85) as the diluent. No modifier was used in these experiments.

Feed solution (PLS) Preparation

The raw material provided from the EURARE test work program was a RE intermediate carbonate with the general composition given in Table 1. The feed stock material did not contain elevated concentrations of naturally occurring uranium and thorium or their daughter products.

Table 1: Kvanefjeld REE Carbonate, REE composition in g/kg (100 % solids)

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
133	230	22	74	11	0.8	6.2	<0.1	5.0	0.7	1.8	0.1	0.7	<0.1	34

The material was dissolved using concentrated HCl (30 to 32 wt.-%) at room temperature. The feed solution composition (PLS) is given in Table 2.

Table 2: Feed solution (PLS), Rare Earths composition in g/l

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
32	56	6.4	19	2.7	0.2	1.6	<0.1	1.7	0.2	0.5	<0.1	0.2	0.02	8.7

Optimisation of the pH

As shown by Equation 1, the extraction of REE is dependent on the hydrogen ion concentration, i.e. the distribution of a species between aqueous and organic phases depends on the pH in the system. The measurement of pH dependency is usually conducted using an organic to aqueous phase (O/A) ratio of 1.

From the literature review, it was found that the pH for the separation of HREE from MREE and LREE should be between pH 0.1 to pH 0.4. The extraction pH for the separation of MREE from LREE should be around 0.7. The extraction of the REE from chloride media using 40 vol.-% di(ethylhexyl)phosphonic acid was therefore investigated between pH 0.1 to pH 1.0, and the results are shown in Table 3.

Table 3: Extraction yields P (%)

pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
0.1	0.1	0.4	0.7	1.1	4.3	7.3	11	19	36	73	68	75	32	88	52
0.4	0.2	0.4	1.0	1.5	6.0	11	15	20	40	88	75	79	49	95	72
1.0	0.9	6.4	15	20	51	66	66	40	51	89	84	98	98	98	79

The extraction of a narrower range of REE from chloride media using 40 vol.-% di(ethylhexyl)phosphonic acid was investigated further between pH 0.6 to pH 1.1 and the results are shown in the Table 4.

Table 4: Extraction yields P (%)

pH	La	Ce	Pr	Nd	Sm	Eu	Gd
0.6	1.5	8.0	8.1	17	53	50	49
0.8	2.7	15	16	31	64	56	53
1.1	3.7	22	22	41	69	57	54

Finally, the extraction of the neodymium from chloride media was investigated using the AKUFVE instrument, shown in Figure 2.

Separation of Neodymium from the LREE Fraction

Batch extraction equilibrium tests were conducted to investigate the separation of neodymium from the LREE fraction. A synthetic RE chloride solution was prepared containing 23 g/l La, 21 g/l Ce, 2.6 g/l Pr and 9.0 g/l Nd. The extractant concentration was 40 vol.-% di(ethylhexyl)phosphonic acid (Ionquest 801) in aliphatic kerosene (Ketrul D85). No modifier was used in these experiments.

During the neodymium extraction the pH was adjusted using HCl and ammonia solution. The results are shown in Table 5.

Table 5: Neodymium extraction yield P (%)

pH	Aq/Org	Org.-Nd	Aq.-Nd	D	P
-	-	g/l	g/l	Co/Ca	%
1.3	2.15	6.89	8.20	0.840	9
1.3	1.20	5.24	5.78	0.907	36
1.4	0.68	4.29	2.09	2.053	77
1.2	0.45	2.68	2.48	1.081	72
1.2	0.34	2.02	2.47	0.818	73
1.2	0.28	1.81	1.61	1.124	82

Table 6 below shows the co-extraction of other LREE during the neodymium recovery tests, performed at pH 1.3 and carried out at an O/A ratio of 1.

Table 6: Composition of the aqueous feed and raffinate during neodymium extraction. Organic solution (40 vol.-% 801 in Kerosene)

Metal	Aqueous feed	Raffinate	Co-Extraction efficiency
	g/l	g/l	%
Lanthanum	23	19.7	14
Cerium	21	16.3	22
Praseodymium	2.6	1.9	27

Table 7: Selectivity data for Neodymium over light REE using 40 vol.-% 801 in Kerosene at pH 1.3

Nd/La	Nd/Ce	Nd/Pr	Nd/(La-Pr)
20	3.3	1.5	1.0

Therefore, to separate the light Rare Earth elements in a faction containing La-Pr and Nd the extraction pH should be adjusted to around 1.3.

Separation of Scandium from Hydrochloric Acid Solution

Organo-phosphorus acids are the most investigated cationic exchange extractants and they form a complex with scandium in the cationic-exchange reaction shown in equation 2.

$$Sc^{3+} + 3\ HR \longrightarrow [Sc * R_3] + 3\ H^+ \qquad \text{[Equation 2]}$$

A synthetic Sc chloride solution was prepared containing 100 mg/l Sc. Three different extractants were investigated at a concentration of 5 vol.-% diluted in aliphatic kerosene (D85). No modifier was used in these experiments. As shown in Figure 5, scandium was extracted efficiently almost irrespective of the HCl concentration or extractant used.

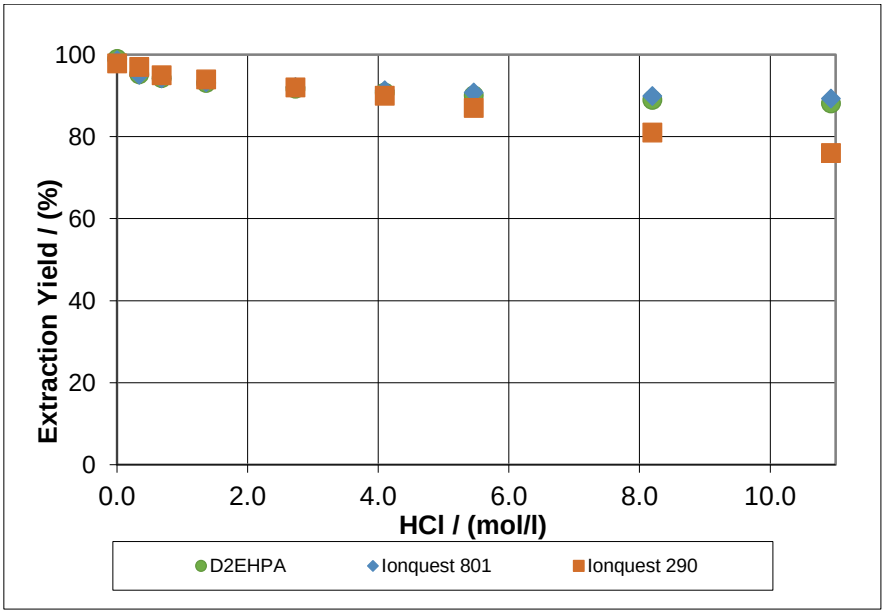

Figure 5: Extraction of Sc in chloride solution with di(ethylhexyl)phosphoric acid (DEHPA), di(ethylhexyl)phosphonic acid (Ionquest 801) and di(ethylhexyl)phosphinic acid (Ionquest 290)

DEMONSTRATION SCALE

Heavy Rare Earth Separation

To confirm the laboratory batch results, a mixer-settler demonstration plant was operated in a continuous mode. The equipment used for the tests are MSU-0.5 mixer-settler units in PVDF for all other functions. The mixer motor is regulated by frequency inverter and the dimensions are:

- Active mixer volume: 0.12 l
- Active settler volume: 0.48 l
- Active settler loading surface: 0.006 m^2
- Total capacity (aq+org+rec) at 1.5 m/h surface loading: 10 l/h

A modified McCabe-Thiele construction based on the batch experiment equilibrium data (Figure 6) was used to determinate the number of mixer settler stages required in the demonstration plant.

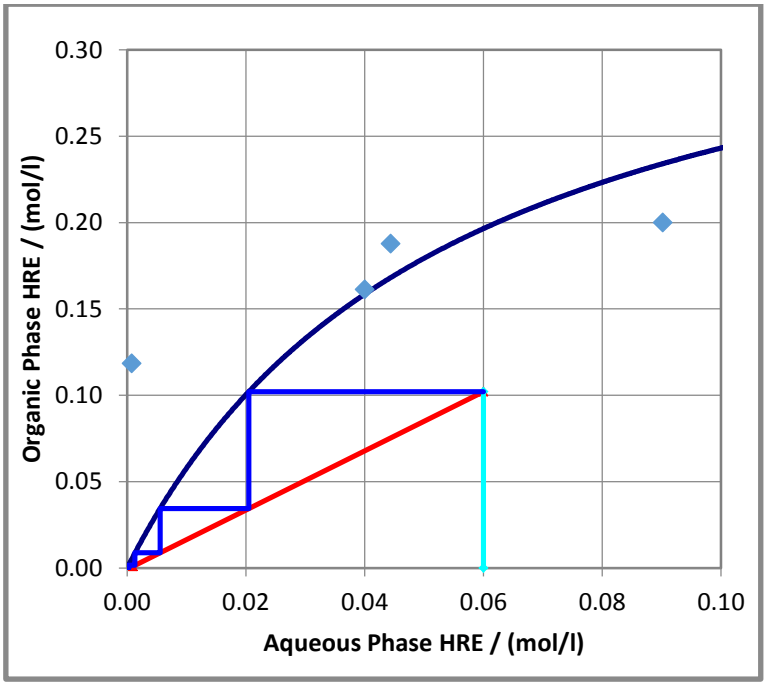

Figure 6: Extraction of HREE with 40 Vol.-% Ionquest 801 in D85. Aqueous solution: 0.06 mol/ HREE, 0.02 mol/l MREE and 0.05 mol/l LREE, initial pH 1.1

The mixer settler demonstration plant was operated according the following set-up of MSU stages.

Process Flow	Vol. Flow		Conc.
	l/h		mol/l
Feed Solution (PLS)	**12**	$c_F = c_{R,a}$	**0,06**
Raffinate		$c_R = c_{R,\omega}$	**0,001**
Solvent solution	**7**	$c_S = c_{E,\alpha}$	**0,001**
Solvent from Extraction		$c_E = c_{E,\omega}$	**0,102**
Slope operating line	tg α		1,71
Volume ratio of solvent (O/A)	v		0,58
Critical conc. loaded organic	$c_{E\omega,crit}$	g/l	0,20
Critical slope operating line	tg α_{crit}		3,31
Min. volume flow pure solvent	$V_{S,min}$	l/h	3,0
Min. ratio of solvent	v_{min}		0,30
Number of theoret. Stages	**NTS**		**4**

The prepared PLS was introduced into the extraction circuit for heavy REE separation. More than 95 % of the heavy REE and yttrium are counter-currently extracted in 4 stages with an organic solution containing 40 vol.-% Ionquest 801 dissolved in aliphatic kerosene (D85) at room temperature. The extraction was operated at pH 0.4 without pH control at organic to aqueous ratio of 1.0 to 0.8. Co-extracted light REE and medium REE accumulated in the organic phase to a concentration of about 0.01 mol/l.

The loaded organic solution was then scrubbed in 6 stages using a counter-current of weak hydrochloric acid at high organic to aqueous phase ratio. More than 99 % of the co-extracted medium REE and light REE were removed.

The resulting organic solution, containing only heavy REE and yttrium was fed to the stripping circuit. Here, heavy REE and yttrium were counter-currently stripped in 5+1 stages with strong HCl. Finally, the stripped organic solution was returned to the extraction circuit for conditioning using alkali.

Table 8: Composition of the aqueous feed and raffinate during heavy RE extraction of Kvanefjeld demo testing. Organic solution (40 vol.-% 801 in Kerosene)

Metal	Aqueous feed	Raffinate	Extraction efficiency
	g/l	g/l	%
Dysprosium	0.73	0.020	98
Holmium	0.07	0.006	92
Erbium	0.24	0.019	92
Ytterbium	0.12	0.001	99
Yttrium	4.40	0.008	>99
HRE (Dy - Yb, Y)			96

The composition of resulting strip solution, containing the heavy REE is shown in Table 9.

Table 9: Strip solution, heavy REE composition in g/l

La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Y
<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	4.5	0.9	2.2	0.7	38

The composition of resulting raffinate, containing the medium REE and light REE is shown in Table 10.

Table 10: Raffinate from heavy REE separation, composition in g/l

La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Y
15.2	25.6	5.9	8.7	0.8	0.07	0.04	0.02	0.006	0.030	0.001	0.008

Medium Rare Earth Separation

The raffinate containing MREE and LREE (Table 8) was fed to the MREE separation circuit as follows:

Alkali was added to pH of around 2.0. The prepared PLS was then introduced into the extraction circuit for medium REE separation. More than 90 % of the medium REE was counter-currently extracted in 6 stages with an organic solution containing 40 vol.-% Ionquest 801 dissolved in aliphatic kerosene (D85) at room temperature. To minimize the co-extraction of lanthanum and cerium, the extraction was operated at pH 0.7 without further pH control at organic to aqueous ratio of 1.5:1. Co-extracted light REE accumulated in the organic phase to about 0.05 mol/l.

The loaded organic solution was then scrubbed counter-currently in 6 stages with dilute HCl at a high organic to aqueous phase ratio. More than 90 % of the co-extracted light REE were scrubbed.

The resulting organic solution, containing only medium REE was fed to the stripping circuit. Here, the remaining dysprosium and other MREE were counter-currently stripped in 5 stages with strong HCl. Finally, the stripped organic solution was returned to the extraction circuit for conditioning using alkali.

Table 11: Composition of the aqueous feed and raffinate during medium Rare Earth extraction of Kvanefjeld demo testing. Organic solution (40 vol.-% 801 in Kerosene)

Metal	Aqueous feed	Raffinate	Extraction efficiency
	g/l	g/l	%
Samarium	0.80	0.010	90
Europium	0.07	0.011	95
Gadolinium	0.40	<0.002	>99
Dysprosium	0.02	<0.002	>99
MREE (Sm-Dy)			96

The composition of resulting strip solution, containing the medium REE is shown in Table 12.

Table 12: Strip solution, medium REE composition in g/l

La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Y
<0.05	0.5	0.6	5.0	7.1	0.7	4.0	0.2	<0.01	<0.01	<0.01	<0.01

The composition of resulting raffinate, containing the medium REE and light REE is shown in Table 13.

Table 13: Raffinate from medium REE separation, composition in g/l

La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Y
15.0	24.9	5.5	8.3	0.010	<0.005	<0.002	<0.002	<0.001	<0.001	<0.001	<0.001

SUMMARY

The recovery of heavy REE (and yttrium) and medium REE from the resulting heavy Rare Earths raffinate from a Kvanefjeld Rare Earths carbonate feed stock was investigated by MEAB. A liquid sample was prepared by dissolution the Kvanefjeld intermediate Rare Earth carbonates using hydrochloric acid. The resulting composition of the prepared test solution was analysed and is shown in Table 2.

pH isotherms, selectivity data as well as McCabe Thiele constructions based on equilibrium curves were obtained using a 40 Vol.-% Ionquest 801 (di(ethylhexyl)phosphonic acid) in Ketrul D85 by using our AKUVFE laboratory set-up. Continuous extraction demonstration tests showed that almost all heavy and medium REE were extracted in a multi stage mixer settler arrangement. Finally, the separation and purification parameter for neodymium were investigated using a synthetic solution, containing light Rare Earths elements.

The proposed separation and purification process starts with recovery of HREE (Dy-Yb, Y) from MREE (Sm-Gd, Dy) and LREE (La-Nd). The following three main process sections, based on laboratory development and on our MSU-0.5 mixer settler operation were proposed:

- **Section 1: HREE Separation.** Extraction of HREE from LREE and MREE by solvent extraction using di(ethylhexyl)phosphonic acid (Ionquest 801) in kerosene (D85),
- **Section 2: MREE+LREE Removal.** Scrubbing of LREE and MREE from the organic solvent by using 1.5 mol/l HCl at high O/A phase ratio, and
- **Section 3: HREE Recovery.** Stripping of HREE from the resulting organic solution in section 2 by solvent extraction using 4 to 5 mol/l HCl. Precipitation of the resulting HREE from the strip solution as carbonates.

The recovery of MREE (Sm-Gd, Dy) from LREE (La-Nd) resulted in the following separation procedure, based on laboratory development and on our MSU-0.5 mixer settler operation were proposed:

- **Section 1: MREE Separation.** Extraction of MREE from LREE by solvent extraction using di(ethylhexyl)phosphonic acid (Ionquest 801) in kerosene (D85),
- **Section 2: LREE Removal.** Scrubbing of LREE from the organic solvent by using 1 mol/l HCl at high O/A phase ratio, and
- **Section 3: MREE Recovery.** Stripping of MREE from the resulting organic solution in section 2 by solvent extraction using 3 to 4 mol/l HCl.

The resulting MREE raffinate will be further treated the separate praseodymium and neodymium from lanthanum and cerium.

CONCLUSIONS

Our experimental findings with laboratory and bench scale demonstration tests using our mixer-settler MSU-0.5 equipment resulted in a better understanding of the separation and purification of REE generated from European deposits. An application of Rare Earths separation and purification that now has gained great interest in the metallurgical processing industry is solvent extraction. The process is carried out by occurring acidic extractants of organo-phosphorus including functional groups.

We also have shown the application of the solvent extraction procedure for the separation and purification of Rare Earths elements with the aim to improve of the metal product quality.

ACKNOWLEDGEMENTS

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RECOVERY OF SCANDIUM FROM BAUXITE RESIDUE BY SELECTIVE PRECIPITATON FROM LEACH SOLUTIONS

By

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ABSTRACT

As a member of EU H2020 ETN Red Mud Project which aims to recover all constituents of bauxite residue (BR) and adopts a zero-waste valorisation point of view, this study focuses on maximized recovery of Scandium in the BR. The red mud investigated was obtained from Aluminium of Greece and contains 130ppm of Sc in its composition which makes it a valuable Sc resource. Previous studies showed that a remarkable amount of Sc (~90%) could be extracted by direct acidic leaching of BR and in this study selective precipitation was investigated on obtained pregnant leach solution (PLS) from BR. Three different approaches; (a) direct precipitation with selected agents from highly impure PLS obtained directly from red mud, (b) pre-purified and enriched PLS in terms of Sc by solvent extraction and (c) cascade type continuous precipitation process to reach various Sc products will be compared and assessed. Advantages and drawbacks of those mentioned approaches will be discussed in cooperation with experimental results.

Keywords: Scandium, Bauxite Residue, Precipitation, Recovery

OUTLINE

1. INTRODUCTION
2. AIMS
3. EXPERIMENTAL
4. RESULTS
    i. SYNTHETIC SOLUTION
    ii. HYDROXIDE PRECPITATION
    iii. PHOSPHATE PRECIPITATION
    iv. SOLVENT EXTRACTION
5. CONCLUSIONS

INTRODUCTION

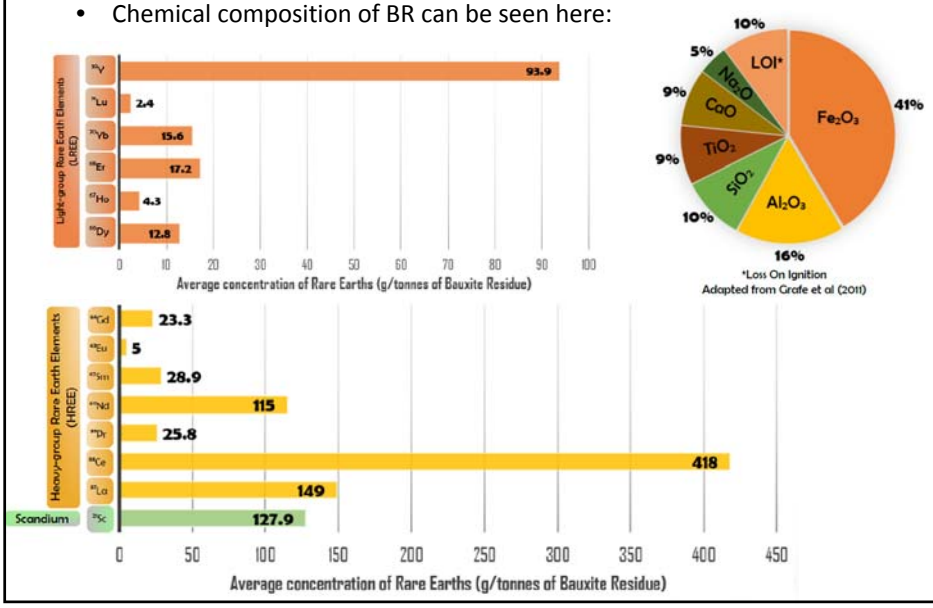
- Despite scandium (Sc) being extremely expensive, the demand of Sc is increasing worldwide owing to recent developments in promising applications in a wide range.
- Due to very limited and rare direct sources of Sc ores, it can be extracted as a by-product which will lead complex metallurgical processes and high production and purification expenses.
- Bauxite residue (BR) is a by-product and the waste obtained from the Bayer Process and stockpiled in huge amounts all over the world.
- Estimated amount of red mud stocks are around four billion tonnes and it is growing unceasingly.

INTRODUCTION (CONT.)

- Producing 1 tonne of Aluminum results in 1 to 1.5 tonnes of bauxite residue.
- Depositing this amount of heavily alkaline waste affects both production costs and the environment.
- However, it can also be considered as a valuable resource for metals.
- BR contains numerous valuable elements such as Ti, Sc, Y, Nd, Ce, etc., it can also be counted as a significant resource.
- The low concentration of Sc in leachates, extraction studies have mainly focused on solvent extraction and ion-exchange processes.

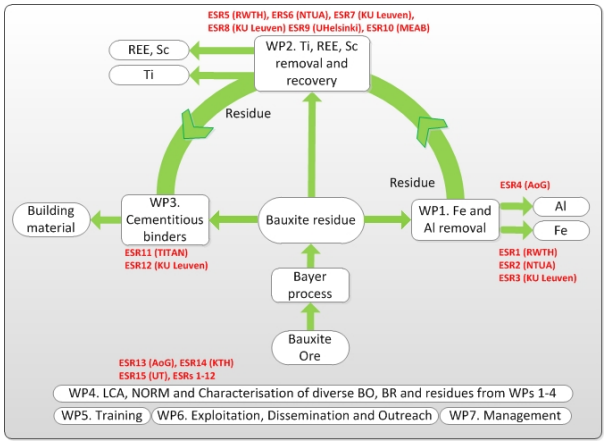
INTRODUCTION (CONT.)

- Chemical composition of BR can be seen here:



INTRODUCTION (CONT.)

- EU H2020 ETN Red Mud Project aims to recover all constituents of BR and adopts a zero-waste valorisation point of view.



AIMS

- The main aim of this study is to develop a continuous process of chemical precipitation.
- Obtaining high purity Sc complexes with >90% precipitation efficiency.
- Investigating the behaviours of different precipitation agents for Sc and comparing their selectivities and the co-precipitation behaviours.
- Comparing different processes for Sc extraction and achieving a low cost high efficiency Sc process.

EXPERIMENTAL

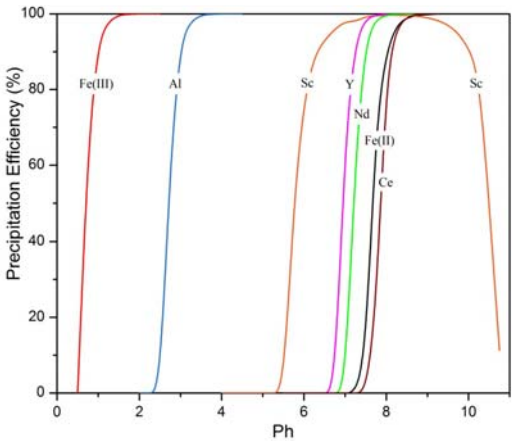
- All experiments were carried out using solutions prepared from analytical grade reagents and de-ionized water.
- The concentrations of the constituent ions were determined by microwave plasma optical emission spectroscopy (Agilent MP-AES 4100).
- The precipitation agents was carefully dripped by sensitive burette into 50ml of the synthetic PLS while controlling pH and temperature.
- The resulting suspension in each case, stabilized and homogenized at given pH and temperature for 2h and filtered via suction filtration.

RESULTS – SYNTHETIC PLS

- This study considers the expected pregnant leach solutions (PLS) obtained by sulfuric acid leaching after recovering Fe, Al and Ti according to recent developments by linked studies in the project.
- Predicted values were used to synthesize the PLS.

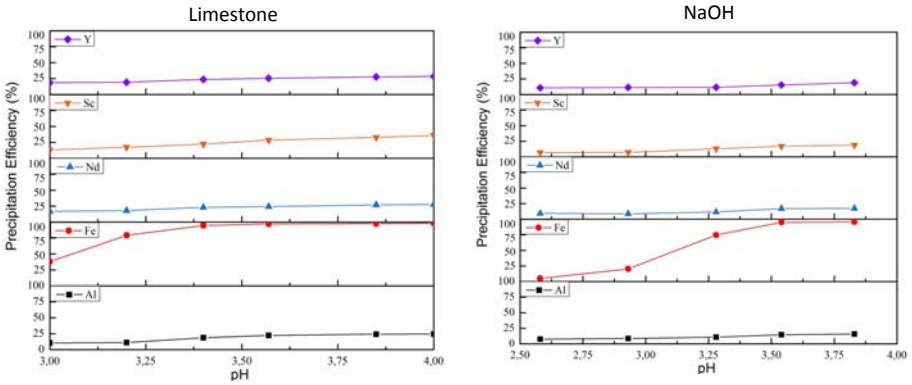
Constituent Ions	Concentration (mg/L)
Al	450
Fe (III)	400
Ca	250
Sc	100
Y	100
Nd	100

RESULTS – HYDROXIDE PRECIPITATION



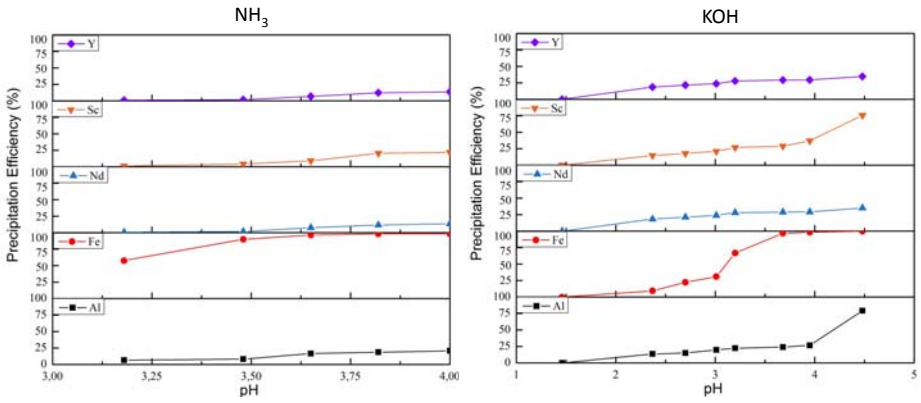
Theoretical precipitation behaviour of the constituent ions according to thermodynamical calculations

RESULTS – HYDROXIDE PRECIPITATION



Addition of Limestone and NaOH to the synthetic solution

RESULTS – HYDROXIDE PRECIPITATION



Addition of NH_3 and KOH to the synthetic solution

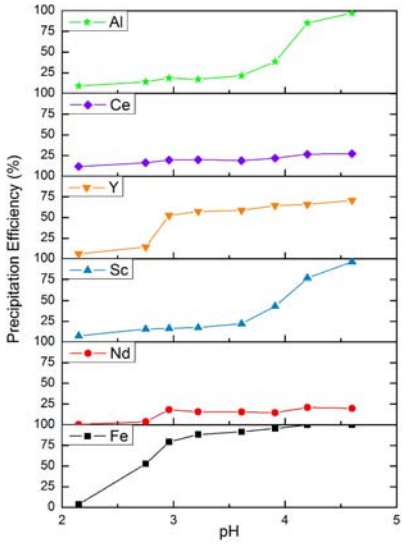
RESULTS – HYDROXIDE PRECIPITATION

Precipitation Agent	pH	Fe (%)	Sc (%)	Al (%)	Y (%)	Nd (%)
Limestone	3.5	95	17	15	15	17
NaOH	3.4	95	22	19	24	23
NH_3	3.5	90	4	8	2	2

- The selectivity of a agent for two different metals M_1 and M_2 is represented by the separation factors S. This is calculated as quotient of the distribution coefficients D of the two metals. Selectivity of Fe/Sc was compared among different precipitation agents to determine which is performed best.

Precipitation Agent	pH	Selectivity of Fe/Sc
KOH	3.7	70
NaOH	3.6	85
Limestone	3.5	95
NH_3	3.6	291

RESULTS – HYDROXIDE PRECIPITATION



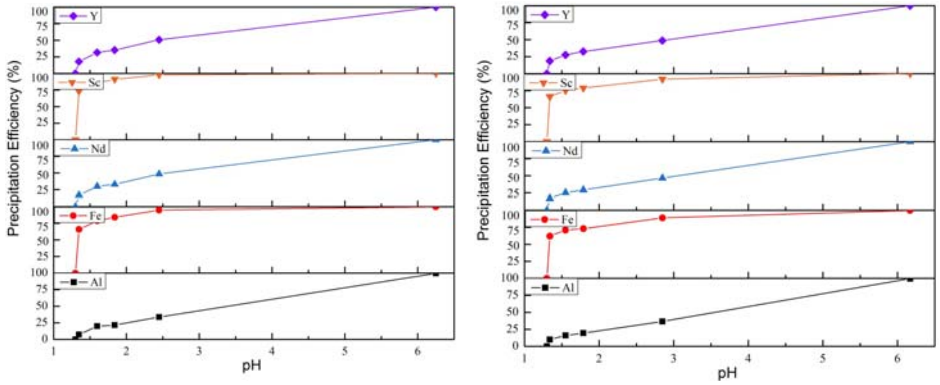
- Precipitation by NH_3 from directly simulated leachate can be seen.
- Similar trend was observed in highly impure solution.
- High co-precipitation with Y is observed.
- Sc loss is apprx. 20% while Fe precipated around 96% as hydroxide.
- NH_3 can be used as a precipitation agent for pre-purification step.

RESULTS – PHOSPHATE PRECIPITATION

- This part of study investigates the precipitation of Sc and REEs by the addition of 1mol/L dibasic phosphate solutions.
- Previous studies showed that, Y^{3+} and REE ions showed strong affinity towards PO_4^{3-} compared to SO_4^{2-} with the addition of phosphate salts to sulphate solution of Y and REEs.
- As the behavioural similarities between Sc and REEs, it was expected to trigger the precipitation with the addition of dibasic salts.
- Dibasic salts, K_2HPO_4, $(NH_4)_2HPO_4$ and Na_2HPO_4, were tested for Sc precipitation according to the expected Eq:
- $REE(SO_4)_n^{3-2n}{}_{(aq)} + PO_4^{3-}{}_{(aq)} = REEPO_{4\,(s)} + nSO_4^{2-}{}_{(aq)}$

RESULTS – PHOSPHATE PRECIPITATION

K_2HPO_4 Na_2HPO_4

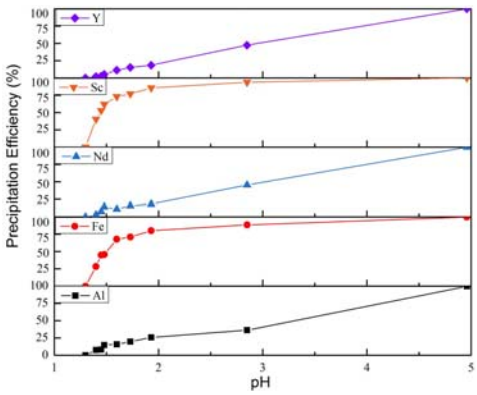


Addition of K_2HPO_4 and Na_2HPO_4 to the synthetic solution [1]

[1] Yagmurlu B. et al. (2016), Precipitation trends of scandium in synthetic red mud solutions with different precipitation agents, (submitted to Journal of Sustainable Metallurgy)

RESULTS – PHOSPHATE PRECIPITATION

$(NH_4)_2HPO_4$

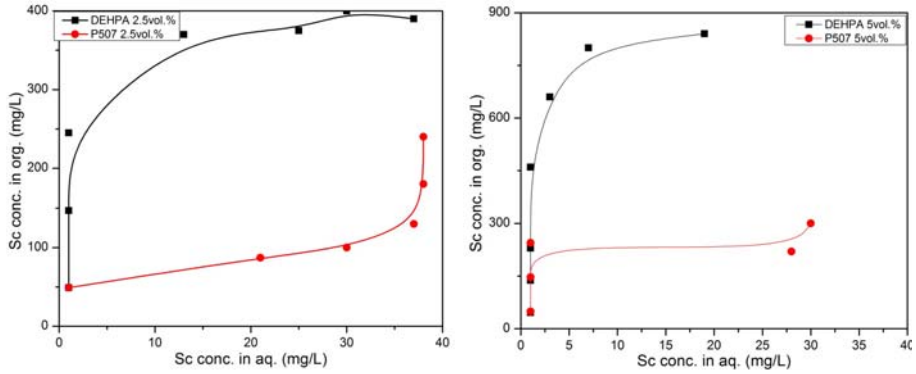


- Highly selective precipitation for Fe and Sc between 1-3 pH
- Rate of precipitation changes with pH
- Reacting constituents changes with pH

Addition of $(NH_4)_2HPO_4$ to the synthetic solution [1]

[1] Yagmurlu B. et al. (2016), Precipitation trends of scandium in synthetic red mud solutions with different precipitation agents, (submitted to Journal of Sustainable Metallurgy)

RESULTS – SOLVENT EXTRACTION

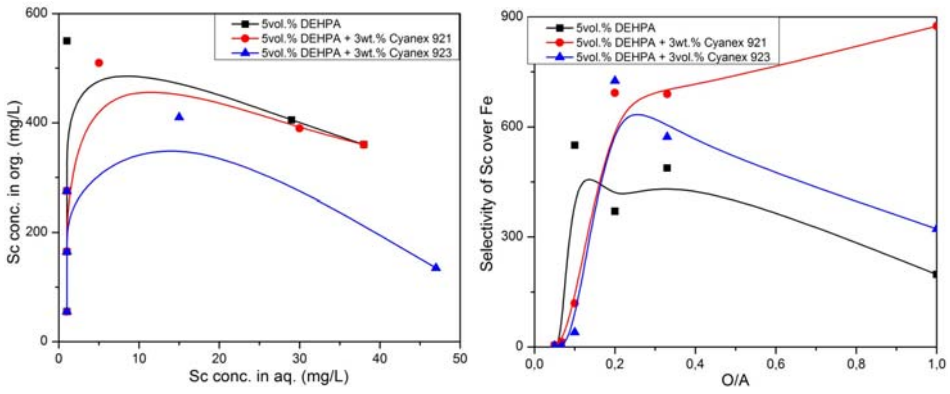


Solvent Extraction of BR Leachate with Di-(2-ethylhexyl)phosphoric acid (DEHPA) and (2-Ethylhexyl)phosphonic acid (P507)

RESULTS – SOLVENT EXTRACTION

- Fe is one of the most problematic elements for Sc extraction.
- While DEHPA extracts apprx.15%, P507 extract 15-25% Fe in the solution.
- In all O/A ratios, DEHPA showed better selectivity than P507.
- 5vol.% in D60 of both organics performed better than 2.5vol.%.
- DEHPA performed superior in all concentrations and O/A ratios compared to P507.
- To solve the co-extraction problem of DEHPA, blended organics were tried.

RESULTS – SOLVENT EXTRACTION



Comparison of selectivities of fresh DEHPA, blended DEHPA+Cyanex 921 and blended DEHPA+Cyanex923

RESULTS – SOLVENT EXTRACTION

- To reduce Fe co-extraction, Cyanex 921 & 923 added to 5vol.% DEHPA.
- Extraction behaviour of Sc remained almost the same.
- Fe co-extraction decreased from 10-15% to 5-6% when both Cyanex organics added to fresh DEHPA.
- Selectivity of Sc over Fe increased noticeably.

CONCLUSIONS

- Synthetic solutions was prepared considering the leachates of BR.
- Limestone, NaOH, NH_3 and KOH was compared to remove Fe(III) from the solution.
- Fe in the system was removed selectively and achieved low co-precipitation levels by the help of ammonia.
- Dibasic phosphates showed high selectivity towards Fe and Sc while other constituents had low co-precipitations.
- DEHPA showed superior performance for Sc extraction compared to P507.
- To solve Fe co-extraction problem of DEHPA, blended organics were tried and co-extraction was decreased to 5-10%.

SYERSTON SCANDIUM PROJECT: LONG TERM SUSTAINABLE SCANDIUM SUPPLY USING CLEAN TEQ'S CONTINUOUS RESIN-IN-PULP TECHNOLOGY

By

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ABSTRACT

Clean TeQ is developing its Syerston Scandium Project in New South Wales, Australia. The Syerston ore body hosts the richest known natural concentration of scandium at scale in the world.

Scientists and metallurgists have known for decades that scandium has a range of unique properties, notably as an alloying agent for aluminium. Aluminium-Scandium (Al-Sc) alloys have remarkable strength, corrosion resistance and welding characteristics. As such, they hold the promise of lighter weight and more energy-efficient solutions in mainstream economic activities ranging from transportation (aerospace, rail, marine, automotive) to construction to power distribution. More recently, the substitution of scandium for yttrium in solid oxide fuel cells (SOFCs) has been critical to the emerging commercial success of these distributed power systems.

Until now, the world has derived limited benefit from scandium's unique potential because of a largely dysfunctional global supply chain. Scandium has only ever been recovered as a by-product of other mining or metal processing activities, from sources with low starting scandium concentrations. The available supply has been limited, unreliable and costly; the market has been opaque and distorted by political forces.

Clean TeQ is changing this paradigm, by combining Syerston's grade and unique hydrometallurgical processing technology to provide large-scale, low cost scandium to the market. At the core of the process is Clean TeQ's Continuous Resin-In-Pulp (cRIP) technology, which provides a simple highly efficient process route for recovery of scandium, as well as other by-product metals.

Keywords: scandium, aluminium alloys, Syerston, continuous ion exchange, resin-in-pulp, aerospace, automotive.

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Certain statements in this presentation are forward looking statements. By their nature, forward looking statements involve a number of risks, uncertainties or assumptions that could cause actual results or events to differ materially from those expressed or implied by the forward looking statements. These risks, uncertainties or assumptions could adversely affect the outcome and financial effects of the plans and events described herein. Forward looking statements contained in this presentation regarding past trends or activities should not be taken as representation that such trends or activities will continue in the future. You should not place undue reliance on forward looking statements, which apply only as of the date of this presentation.

The Syerston Scandium Project is at the Scoping Study phase and although reasonable care has been taken to ensure that the facts in this presentation are accurate and/or that the opinions expressed are fair and reasonable, no reliance can be placed for any purpose whatsoever on the information contained in this document or on its completeness.

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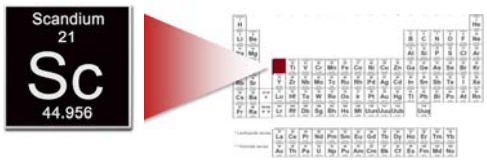
The information in this document that relates to Exploration Results, Mineral Resources or Ore Reserves is based on information compiled by Sharron Sylvester, who is a Registered Professional Geoscientist (10125) and Member (2512) of the Australian Institute of Geoscientists, and a full time employee of OreWin Pty Ltd. Sharron Sylvester has sufficient experience that is relevant to the style of mineralisation and type of deposit under consideration and to the activity which he is undertaking to qualify as a Competent Person as defined in the 2012 Edition of the 'Australasian Code for Reporting of Exploration Results, Mineral Resources and Ore Reserves'. Sharron Sylvester, who is a consultant to the Company, consents to the inclusion in the report of the matters based on her information in the form and context in which it appears.

For further details on the content of this presentation, please refer to the ASX releases dated 24th November 2014, 23rd January 2015 and 25th May, 2015.



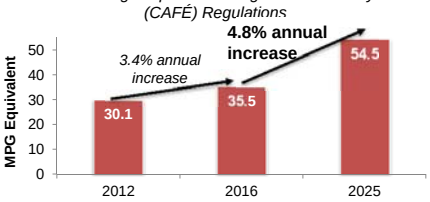
Scandium
Strategic Lightweighting Material

Scandium | Strategic Lightweighting Metal

1. The world needs lightweighting solutions:

- Regulations are driving the transport industry (particularly automotive) to become more fuel efficient.

Increasing Corporate Average Fuel Economy (CAFÉ) Regulations



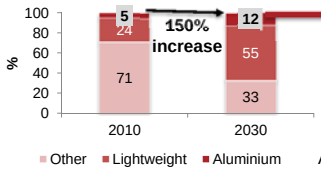
- Internal combustion engines have reached the limit of fuel efficiency.
- Further gains in efficiency can only come from lightweight materials.

Source: The International Council of Clean Transportation

2. Aluminium is a critical lightweighting material:

- Aluminium is 25% lighter than high strength steel and 75% cheaper than carbon fibre, providing the lowest cost light weighting material available today.
- While commercial aerospace uses 40-50% aluminium in planes, these materials are only just now making their way to automotive:

Automotive Material Split



The new Ford F-150 uses 25% Aluminium to meet efficiency targets

Source: McKinsey

Scandium | Strategic Lightweighting Metal

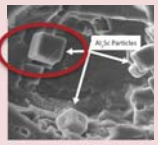
3. Scandium makes aluminium:

- **Stronger**: use less metal - *Scandium provides the greatest increase in aluminium alloy strength to weight ratio*[1]
- **Weldable**: lower manufacturing cost
- **Corrosion resistant**: lower lifecycle cost

These benefits mean that scandium will have a crucial role in the future use of aluminium in transport.

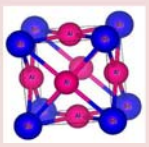
1: K. Venkateswarlu, et al, High Strength Aluminum Alloys with Emphasis on Scandium Addition, 2008

The micro structure of aluminium is fundamentally changed when scandium is added:



Source: AMG Aluminum

Cuboid Structure of Al_3Sc:

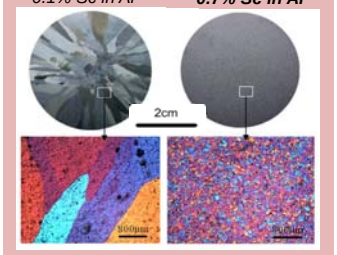


Source: Galav and Joshi, 2014

This leads to finer grains of aluminium being formed. The implications of this "grain refinement" on the performance of the alloy, including strength and weldability are enormous.

Effect of Sc Addition

0.1% Sc in Al *0.7% Sc in Al*

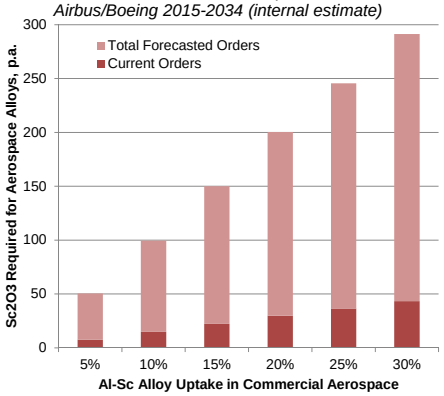


Source: Zhang et al, 2013

Scandium | Significant Potential Demand in Transport

Commercial Aerospace:

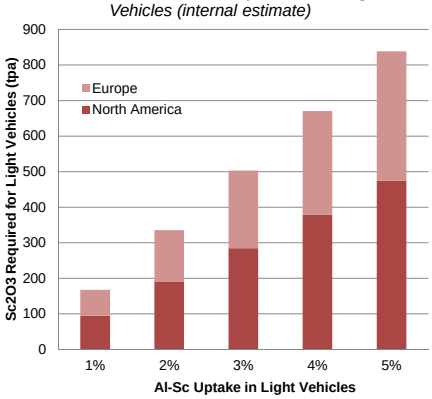
Potential Annual Sc2O3 Requirement for Airbus/Boeing 2015-2034 (internal estimate)



Assumes 0.2% Al-Sc alloy used replacing existing Al or Al alloy components.
Assumed as average Al content per empty operating weight of 60%.
Empty Operating weight, Aluminium content Source, Airbus, Boeing

Automotive:

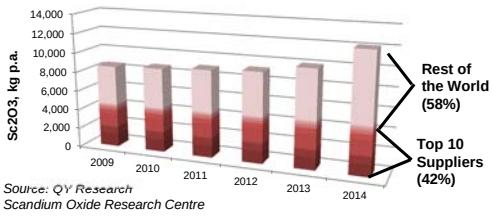
Potential Annual Sc2O3 Requirement for Light Vehicles (internal estimate)



Assumes 0.2% Al-Sc alloy used replacing existing Al or Al alloy components.
Aluminium amount source: Ducker Worldwide

Scandium | Fragmented Supply Issues Solved

Historical Global Scandium Oxide Production



Source: QY Research
Scandium Oxide Research Centre

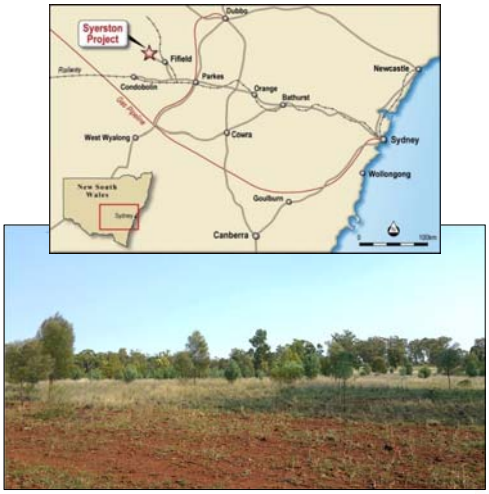
- Current scandium supply is heavily fragmented, as by-product sources generally contain low concentrations of scandium (~10-30ppm Sc)
- Total global supply of SC_2O_3 is approx. 12-15tpa
- 2014 average prices USD2,000-3,000/kg SC_2O_3:
- The majority of the world's SC_2O_3 is produced in China, Russia or the FSU, which presents inherent sourcing risks.

Requirements to establish a viable market for scandium oxide for aerospace:

- **Reliable and sustainable long term supply**
  Large resources, low political risk, supply chain diversity and readily expandable production capacity
- **A significant step change in Sc_2O_3 pricing**
  Identification of higher grade sources of Sc and more efficient extraction technologies
- **End-user preparedness to support new development**
  Supply chain collaboration, understanding potential market demand and scandium supply commitments from customers

Syerston Scandium Project
Overview

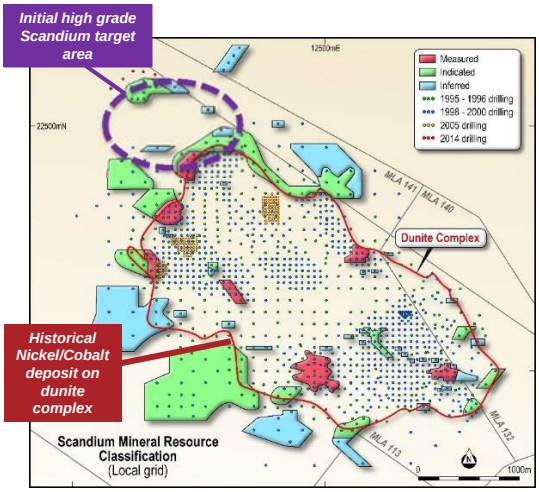
Syerston | Location and History



Project History:

1960's-1986	Regional exploration for platinum. Large laterite resource identified at Syerston, enriched with cobalt (Co), nickel (Ni) and scandium (Sc).
1986-1998	Noble Resources: ~500 holes drilled and PFS1998 completed for Ni/Co project
1998-2004	Black Range Minerals: Acquired project from Noble. 750 holes drilled and a Feasibility Study (FS) 2000 completed for a 20,000tpa Ni & 5,000tpa Co mine. EIS completed, Development Consent.
2004-2014	Ivanhoe Nickel and Platinum: Acquired Black Range, revising the FS 2005 and drilling an additional 200 holes. Due to plant capex and metal prices, Ivanhoe elected not to proceed with project. No development after 2007. Development Consent trigged 2005, Project ready to construct.
2014-present	Clean TeQ acquired Project holding company in Nov, begins development of Scandium project, incl. drilling of over additional 100 holes in high grade Sc zones.

Syerston | World Class Scandium Deposit



- Scandium is found at the periphery of the Cobalt/Nickel deposit, allowing for separate development
- Shallow resource amenable to simple low cost open pit mining
- High grade pods can be targeted in early years
- Significant potential for further increasing scandium resource in the future

Syerston | Scandium Mineral Resource

- The Syerston Project has almost 200 years supply at a production rate of 40tpa Sc_2O_3
- Cut-off grade can be adjusted to accommodate various production scenarios
- Potential resource upgrade once new scandium-targeted drilling is included.
- Syerston will be the world's first primary scandium mine.

Measured, Indicated and Inferred Scandium Resource (JORC 2012):

*Scandium cut-off of **300ppm** Sc:*

Category	Tonnage, Mt	Sc Grade, ppm	Sc Tonnes	Sc_2O_3 Equiv Tonnes*
Measured	5.8	454	2,635	4,032
Indicated	15.9	420	6,697	10,247
Inferred	6.4	386	2,487	3,805
Total	**28.2**	**419**	**11,819**	**18,083**

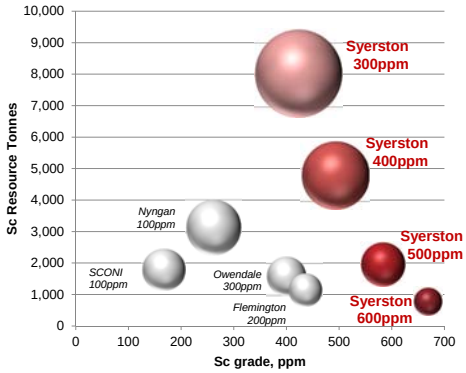
*Scandium cut-off of **600ppm** Sc:*

Category	Tonnage, Mt	Sc Grade, ppm	Sc Tonnes	Sc_2O_3 Equiv Tonnes*
Measured	0.6	685	394	603
Indicated	0.8	663	545	834
Inferred	0.1	630	57	87
Total	**1.5**	**670**	**996**	**1,524**

** Sc multiplied by 1.53 to convert to Sc_2O_3.*

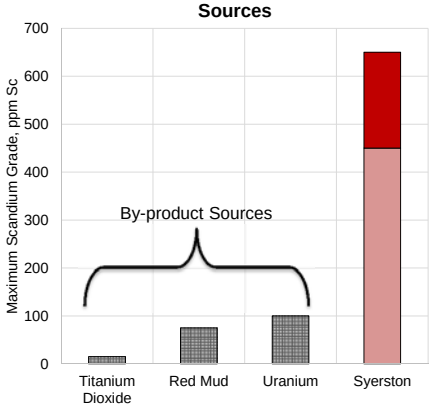
Syerston | High Grade Significant Scandium Resource

Australian Scandium Mine Measured & Indicated Resource with Scandium cut-off



Syerston contains the largest and most developed resource of all Australian scandium mines, with over 75% of its scandium resource in the measured and indicated categories.

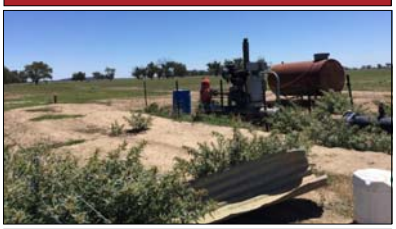
Grade Estimates for Other Scandium Sources



Compared to other current and potential sources, which only produce small amounts as by-products, Syerston's primary scandium provides more cost effective long term supply.

Syerston | Development Ready

Established water bore fields

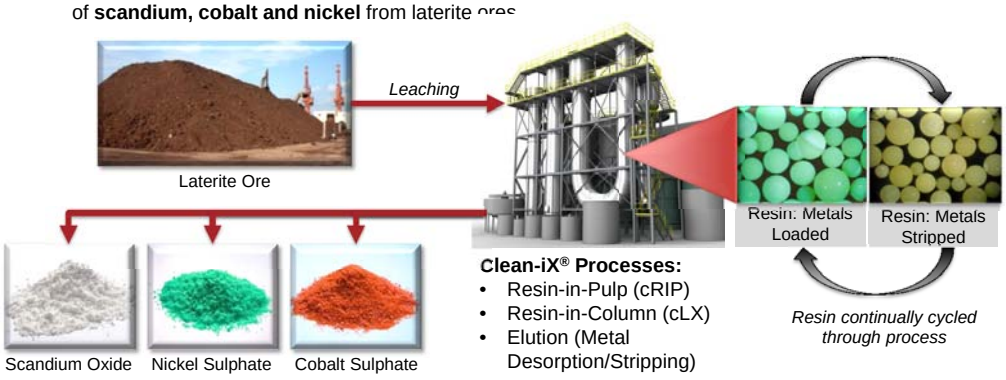


- Project, including EL's, MLA's and freehold land underlying the project area 100% owned
- Key permits already in place:
  - **Environmental approvals (EIS)**
  - **Mining approval (Development Consent)**
  - **Water License (existing 3.2GLpa water allocation)**
  - **Mining Lease Applications lodged**
- Site is well connected to infrastructure (roads, gas, rail and power)
- Water is critical for development - established borefield with a licensed water allocation sufficient for initial production plus expansions
- **Existing permitting significantly accelerates development**

Clean-iX® Technology
Overview

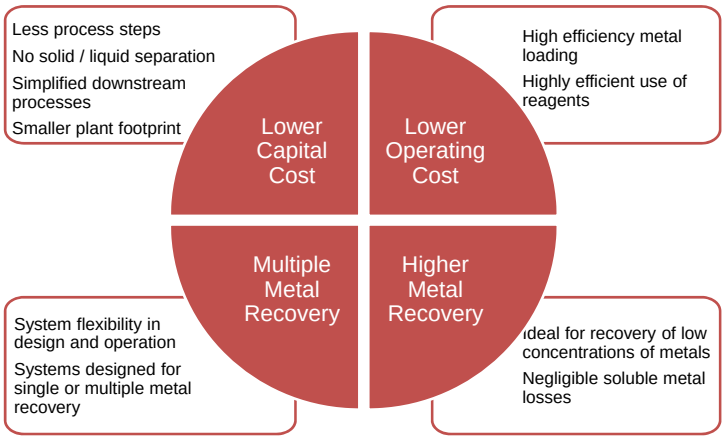
Clean TeQ Technology | The Clean-iX® Process

- **Platform technology** for leaching, extraction and concentration of metals.
- Clean-iX® uses **ion exchange resin** to extract and concentrate metals from slurries and liquors – IX more cost effective and efficient than SX for low grade metal recovery.
- **Continuous Counter current** processes used, which increase the efficiency of extraction and reduce overall cost.
- Clean TeQ has built on 40 years of R&D and commercial operations to develop a process for recovery of **scandium, cobalt and nickel** from laterite ores

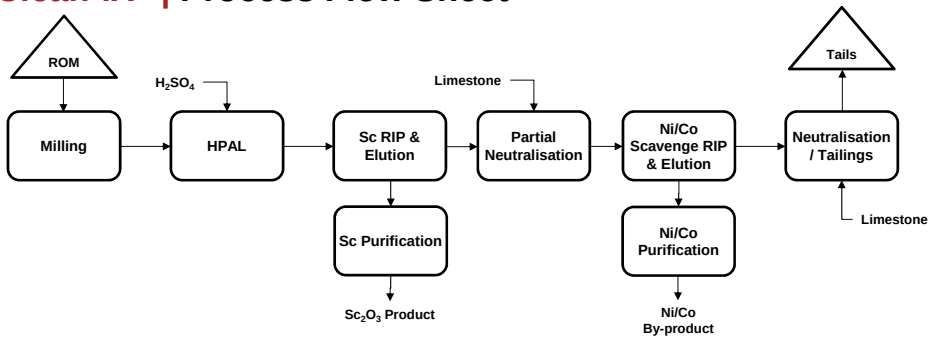


Clean-iX® | A Step Ahead for Metal Recovery

The most efficient and cost effective process for metal recovery from ores:



Clean-iX® | Process Flow Sheet



HPAL:

- 250°C, 90 mins, >85% Sc extraction

Scandium RIP & Elution:

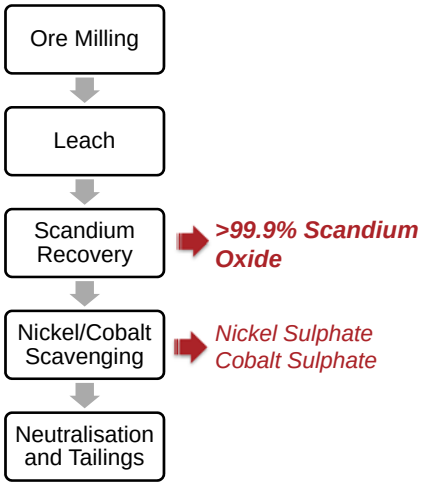
- Proprietary Clean-iX® continuous counter-current process.
- Patented scandium recovery process
- Purification process produces >99.9% Sc_2O_3
- Total initial production: 40tpa Sc_2O_3

Nickel & Cobalt Scavenging:

- Recovery of low grades of nickel and cobalt which leach with scandium.
- Aiming to produce either sulphate or cathode products.

Feasibility Study underway, aiming to be completed in in end of June, 2016

Syerston | Feasibility Study Underway



- Small-scale simple mining for 65,000tpa plant feed
- ~40tpa of Sc_2O_3 initial production capacity at USD$1,500/kg
- Over 150 years mine life at assumed production rate and resource base
- Production rate can be significantly expanded as demand grows – reducing scandium oxide price
- Feasibility Study on track to be completed by June 2016.

Syerston | Scandium Samples Produced

- CLQ completed a large scale Scandium Pilot Plant, as shown, in Aug-Oct
- The Pilot Plant was a fully automated continuous operation and integrated HPAL plus RIP circuit
- 12 tonnes of Syerston material processed through plant
- 99.9% samples of produced Sc_2O_3 have been sent to potential customers for certification and qualification testing.

Scandium | Scoping Study Summary

Parameter	Assumption / Output
Resource Base used for Mine	Measured & Indicated Resource
Processing Plant Throughput	64,000tpa (1.28Mt over 20 yrs)
Processing Plant Average Feed Grade	510g/t Sc [1]
Sc_2O_3 Average Production (Years 1-20)	42.5tpa Sc_2O_3
Processing Plant Recovery	85%
Life of Mine	20 years
Long Term Sc_2O_3 Price (99.9% purity)	USD$1,500/kg Sc_2O_3
Exchange Rate	0.78USD:1AUD
Total Capital Cost	AUD$78.4M [2]
Average Sc_2O_3 Unit Operating Cost (Yr 1-20)	AUD$571/kg Sc_2O_3 USD$446/kg Sc_2O_3
Average Annual Revenue	AUD$81.8M
Net Present Value (NPV) – post tax	**AUD$279.1M [3]**
Internal Rate of Return (IRR) – post tax	**53% [3]**

1. Pit selection, dilution and mining factors applied
2. 20% contingency on direct capital costs
3. Post Tax, 8% discount rate, 100% equity, real terms
All $ are in Australian Dollars (AUD) unless otherwise stated.

- Robust project economics for long term scandium production – lowest cost scandium mine currently being developed
- Key assumptions are output and price - unit opex is sensitive to production volume – larger volumes will lead to lower cost of production
- Low mining, processing and permitting risk
- Feasibility Study to provide updated project economics based on additional drilling, metallurgical testwork and piloting

Scandium | Collaboration to Build Off-take

APWORKS by Airbus Group — *Collaboration on development of Al-Sc powder (Scalmalloy®) applications for 3D Printing*

KBM AFFILIPS MASTER ALLOYS — *Collaboration on supply of scandium to master alloy production and optimisation of process*

UAC UNIVERSAL ALLOY CORPORATION, A COMPANY OF MONTANA TECH COMPONENTS AG — *Collaboration on use of Al-Sc on extruded parts for aerospace.*

with more agreements to come…

Uranium-REE Proceedings

Lithium Processing

THE SILEACH™ PROCESS - LITHIUM RECOVERY FROM SILICATES, WITHOUT ROASTING

By

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ABSTRACT

Lithium Australia NL initially developed the hydrometallurgical Sileach™ process specifically for the digestion of spodumene, a mineral only commercially processed by roasting and leaching. The conventional processing mechanisms are energy intensive and require high-grade ore for a positive commercial outcome whereas competitive lithium production processes recovering lithium, as carbonate, from brines, generate the final product for about half the cost.

Development of Sileach™ was aimed at reduced operating costs to make lithium chemicals from spodumene competitive with chemicals from brines. The process has been further successfully tested on other lithium minerals, including a wide range of micas. More recently it has been used on refractory gold slags to remove mineral coatings that blind the gold particles from cyanide solutions.

Keywords: Lithium, Processing, By-products, Roasting, Hydrometallurgy

Outline

TRADITIONAL SOURCES OF LITHIUM

A BRIEF HISTORY OF THE LITHIUM INDUSTRY

SILEACH™ - COMPLETE FLEXIBILITY

THE FORGOTTEN RESOURCES

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Certain statements contained in this presentation, including information as to the future financial or operating performance of Lithium Australia NL ('LIT' or 'the Company') and its projects, are forward-looking statements. Such forward-looking statements are necessarily based on a number of estimates and assumptions that, while considered reasonable by LIT, are inherently subject to significant technical, business, economic, competitive, political and social uncertainties and contingencies, involve known and unknown risks and uncertainties that could cause actual events or results to differ materially from estimated or anticipated events or results reflected in such forward- looking statements, and may include, among other things, statements regarding targets, estimates and assumptions in respect of commodity prices, operating costs and results, capital expenditures, ore reserves and mineral resources and anticipated grades and recovery rates and are, or may be, based on assumptions and estimates related to future technical, economic, market, political, social and other conditions.

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Many known and unknown factors could cause actual events or results to differ materially from estimated or anticipated events or results reflected in such forward-looking statements. Such factors include, but are not limited to: competition; mineral prices; ability to meet additional funding requirements; exploration, development and operating risks; uninsurable risks; uncertainties inherent in ore reserve and resource estimates; dependence on third-party smelting facilities; factors associated with foreign operations and related regulatory risks; environmental regulation and liability; currency risks; effects of inflation on results of operations; factors relating to title to properties; native title and Aboriginal heritage issues; dependence on key personnel, and share-price volatility. They also include unanticipated and unusual events, many of which it is beyond the Company's ability to control or predict.

Photographs in this presentation do not depict assets of the Company.

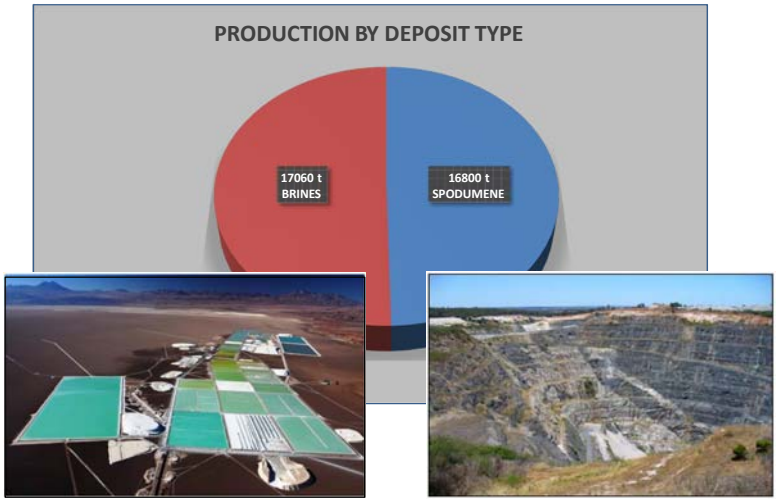
COMPETENT PERSON'S STATEMENT

The information in this report that relates to reporting of Exploration Results is based on and fairly represents information and supporting documentation prepared by Adrian Griffin, a member of the Australasian Institute of Mining and Metallurgy. Mr Griffin is a shareholder in, and managing director of, LIT and has sufficient experience relevant to the style of mineralisation and type of deposit under consideration. He is qualified as a Competent Person as defined in the 2012 edition of the Australasian Code for Reporting of Exploration Results, Mineral Resources and Ore Reserves. *Mr Griffin consents to the inclusion in this report of the matters based on information in the form and context in which it appears.*

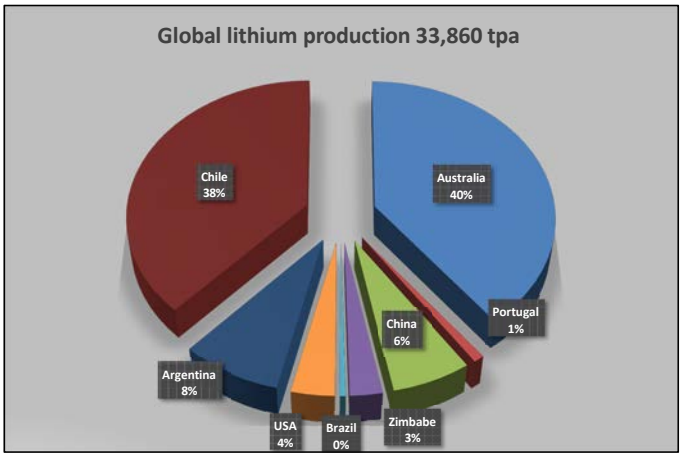
The reporting of mineral species is generic in nature, and the term 'lepidolite' – as it is applied to mineral species, and not necessarily locality names – includes mineral species widely considered to be part of the solid solution series of polylithionite/trilithionite, of which the Competent Person considers lepidolite to be approximately a median member. It is also acknowledged that material processed from Lepidolite Hill has bulk compositions tending towards trilithionite, although the rubidium concentration is outside the range generally expected in such minerals.

Similarly, the term 'zinnwaldite' has been applied to minerals approximating the accepted composition of zinnwaldite but with variations tending towards lepidolite. This terminology is considered acceptable by the Competent Person.

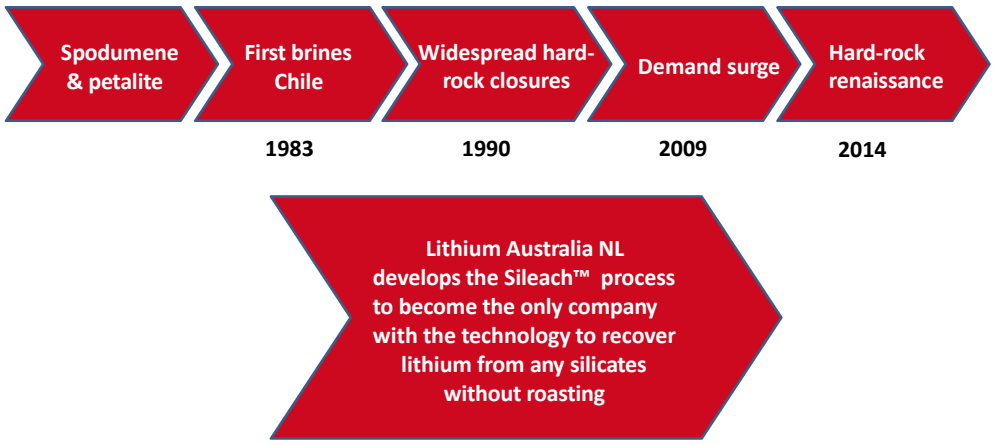
Lithium chemicals originate from two sources – brines and hard rock



Feed is dominated by two countries



A brief history of lithium production



Processing innovation creates a paradigm change

Broken Hill Proprietary Company Ltd about 1888

"Broken Hill led the world in the profitable treatment of zinc-lead sulfides. At the turn of the 20th century, three out of every four tons that came out of the mine could not be treated. It was stacked in huge dumps along the line of lode; dumps that would mark the grave of Broken Hill unless silver, zinc and lead could be separated cheaply,

In 1902 D.G. Delprat, the general manager of Broken Hill Proprietary Company Limited, invented a process that promised to extract the treasure in the dump. He added oil, salt cake and other chemicals to a tank of pulped ore, and pumped air in through a blower at the bottom. He was delighted to observe that the particles of minerals clung to the rising air bubbles and overflowed the tank which the barren particles sank to the bottom. His company erected the first efficient flotation plant in the world

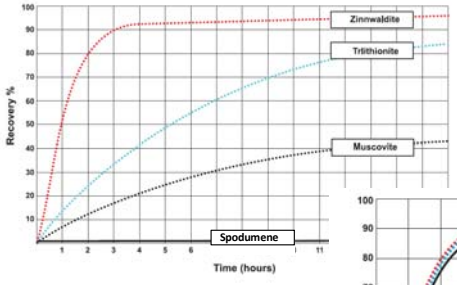
Taken from StumpJump Plough to Interscan, A. Walsh, Australian Academy of Science, 1977.

Fusion of thought – a retrospective

"In terms of economic value, no Australian invention can have been of more importance to Australia than the flotation process for the separation of minerals. It had been known since the late eighteenth century that powdered ores could be made to float by generating bubbles which attached them to the ore particles and raised them to the surface. But the first person to succeed in the large scale commercial exploitation of the flotation process was Charles Vincent Potter, a Melbourne brewer and chemist. His process was patented in 1901 and shortly afterwards was put into operation at Broken Hill, where it produced over six million tons of zinc concentrate, assaying up to 42 per cent zinc. Potter's invention was the forerunner of several flotation processes to be developed and put into operation at Broken Hill." Taken from StumpJump Plough to Interscan, A. Walsh, Australian Academy of Science, 1977.

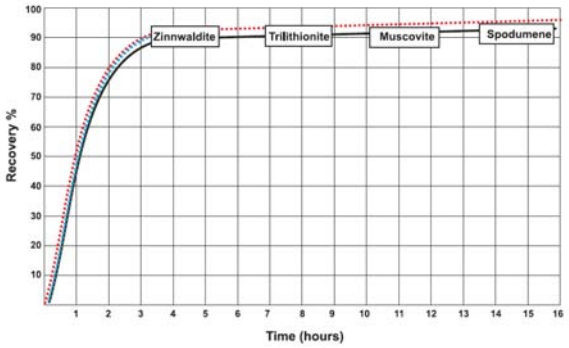
The ability to recover lithium from silicates, without roasting will again put Australia, through the application of the Sileach™ process, at the forefront of mineral processing technology, the importance of which may eclipse froth flotation.

From alpha-spodumene to zinnwaldite Sileach™ ultimate processing solution



Lithium bearing mineral species have a range of leach performances in sulphuric acid, from very reactive in the case of zinnwaldite, to completely unreactive in the case of spodumene.

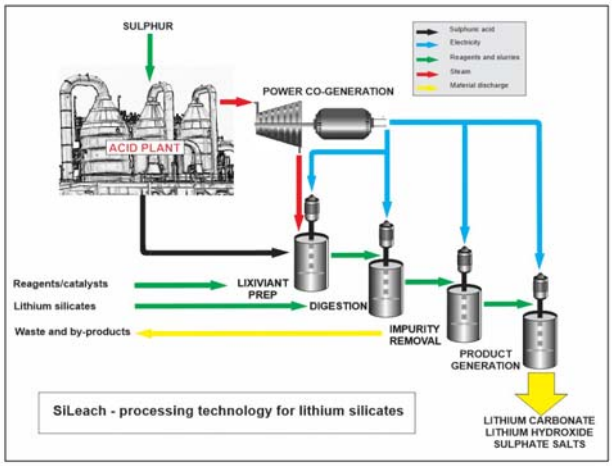
Bespoke lixiviants used in the Sileach™ process optimize the dissolution curves for most silicates, allowing spodumene to achieve the processing performance of the less refractory lithium silicates.



Inside the Sileach™ process

MATCHING CHEMISTRY TO MINERALOGY

The Sileach™ process success resides in identifying the chemical reactions required to release metals from silicates. The process is easily adapted to silicates containing lithium or other metals of value. The process is energy efficient and has the potential to capitalize on high by-product credits.

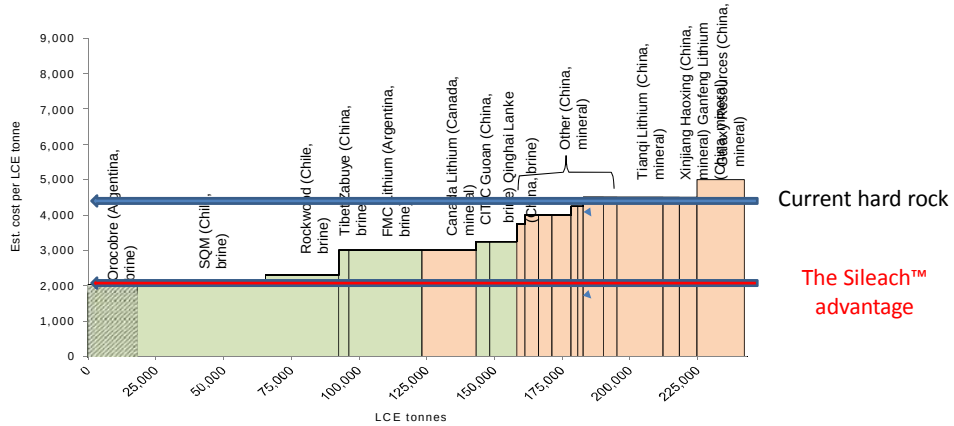


Sileach™ is 100% owned by Lithium Australia NL. The process was initially designed to recover lithium from spodumene (the most commonly produced hard rock lithium concentrate). Subsequent testing proved the flexibility of the process, which has since been adapted to recovery of lithium from all lithium silicates.

The process derives all of its energy requirements from the production of the lixiviant, that has a sulphuric acid base (produced in a sulphur burning acid plant) with additional reagents added in accordance with the specific mineral chemistry of the feed material.

The lixiviant can be tailored to the mineral feed to achieve optimum results. A range of mineral chemistries has been processed generally with lithium extractions around 90% with residence times around 4 hours.

Current cost profile and the Sileach™ advantage



Estimated global lithium cost curve [sources: Roskill (with modifications) and Orecobre 2014 presentation].

Lithium chemical operating profile

THE BRINES
- Low operating cost
- Large resources
- By-product credits
- Long commissioning times
- High capital costs
- Climate dependant
- Variable solution chemistry
- Unpredictable aquifer performance
- Expansion failures
- Low resource/reserve conversions
- Reliance on by-product credits

SPODUMENE
- High operating cost
- Smaller resources
- No by-product credits
- Short commissioning times
- Capital efficiency
- No Climate risk
- Simple – fixed chemistry
- Quantified resource risk
- Simple expansions
- High conversion rate
- Only one product

THE MICAS
- Low operating cost
- Smaller resources
- Very high by-product credits
- Commissioning risk
- Moderate capital
- No Climate risk
- Complex solutions
- Quantified resource risk
- Simple expansions
- High resource/reserve conversions
- Multiple high-value products

The forgotten resources

TRADITIONAL PROCESSING REQUIRES ROASTING PRIOR TO LEACHING

THE GRADE OF MICAS IS TOO LOW TO PAY THE ENERGY BILL

SILEACH™ CAN RECOVER LITHIUM FROM MICAS COST EFFECTIVELY

THIS PROCESSING BREAKTHROUGH PROVIDES ACCESS TO:
- Micas in mine dumps
- Micas in tailings dams
- Micas in unmined deposits, and
- Micas in tails discharge of current mining operations

AND WHAT ABOUT LOW-GRADE AND CONTAMINATED SPODUMENE?

JADARITE, TOURMALINE, CLAYS

SILEACH™ HAS EVEN BEEN USED ON REFRACTORY GOLD ORE

Battery performance – the great enabler

Source: Solar Impulse

BENEFICIATION OF SPODUMENE ORE INTO A CONCENTRATE AND FURTHER PROCESSING TO PRODUCE BATTERY GRADE LITHIUM CARBONATE

By

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ABSTRACT

The demand for high purity battery grade lithium carbonate is expected to grow significantly in the future.

The mining and processing of spodumene involves a number of challenges in order to achieve a high grade and recovery with minimal impurities. This paper discusses the value adding beneficiation step of processing spodumene and challenges.

This spodumene concentrate is then processed through the traditional sulphuric acid route and the challenges involved in achieving battery grade lithium carbonate are discussed. In addition, the evolving new alternative process routes are listed as options for consideration.

The lithium-ion battery sector is one of the largest consumers of lithium, currently estimated to be at approximately 26% of total global lithium demand. Originally used in computing and mobile communication devices, lithium-ion batteries are being increasingly used to power electric bicycles (e-bikes), vehicles and mass energy storage devices. Lithium-ion batteries have superior energy density, are more efficient and environmentally friendly than traditional acid batteries.

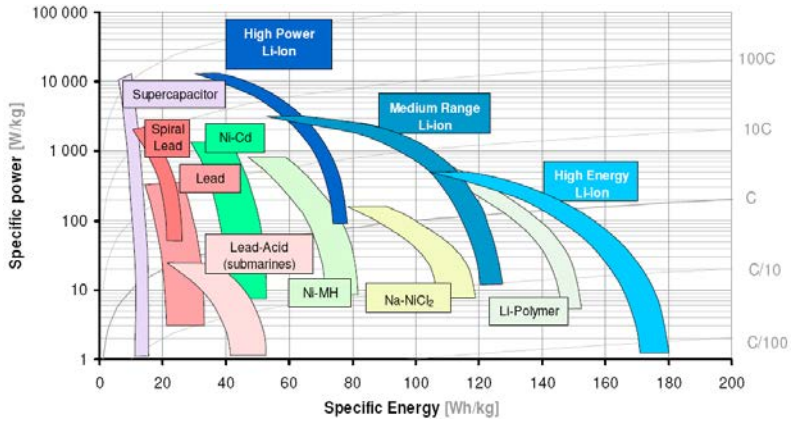
Keywords: Spodumene beneficiation, sulphuric acid processing, production of battery grade lithium carbonate

Introduction

Lithium aluminium silicate – spodumene - $LiAl(SiO_3)_2$

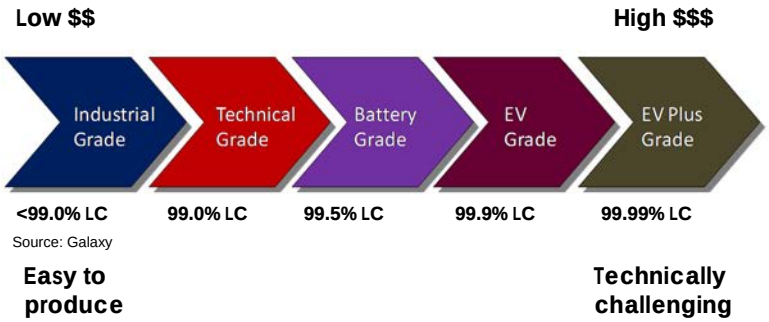
- Specific Gravity 3.0-3.23, flotation fatty acids
- Demand for high purity battery grade lithium carbonate is expected to grow with the development of electric, motorcycles, cars, and other devices.
- Beneficiation of spodumene involves a number of challenges to produce high recovery and a concentrate with minimal impurities.
- Mt Catalin and Pilgangoora projects are discussed with reference to beneficiation and the issues to produce a marketable concentrate
- Several lithium carbonate plants are discussed.
- New technology associated with lithium carbonate production is discussed

Battery Alternatives



Source: Nemaska lithium

Lithium Carbonate Products

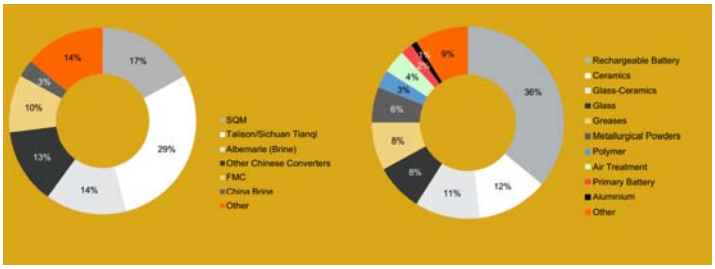


Source: Galaxy

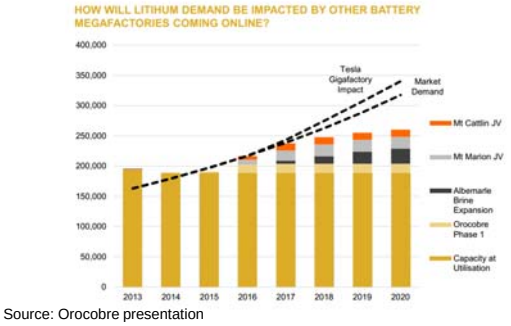
Easy to produce

Technically challenging

Supply and Demand

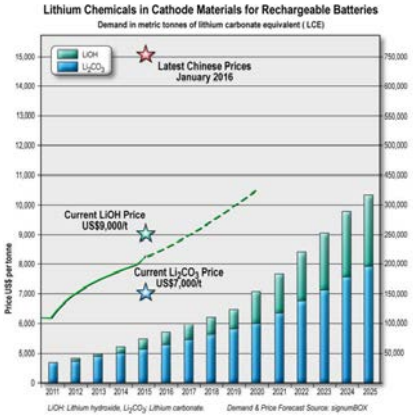


Source: Orocobre presentation

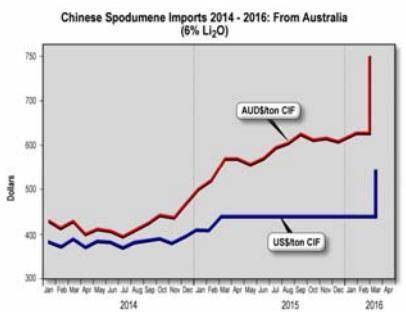


Source: Orocobre presentation

Lithium Prices

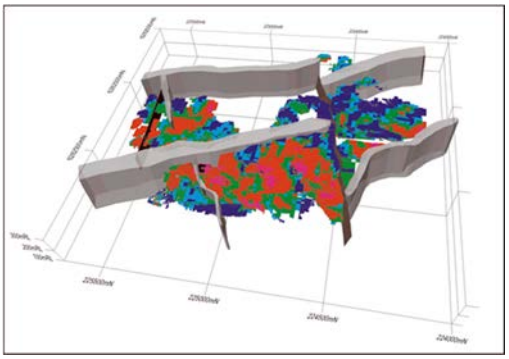


Source: Neometals website



Source: Neometals website

Mt Catalin Deposit



Category	Tonnes	Li_2O %	Ta_2O_5 ppm
Measured	2,260,000	1.19	143
Indicated	7,064,000	1.10	156
Inferred	5,044,000	1.01	152
TOTAL	**14,368,000**	**1.08**	**153**

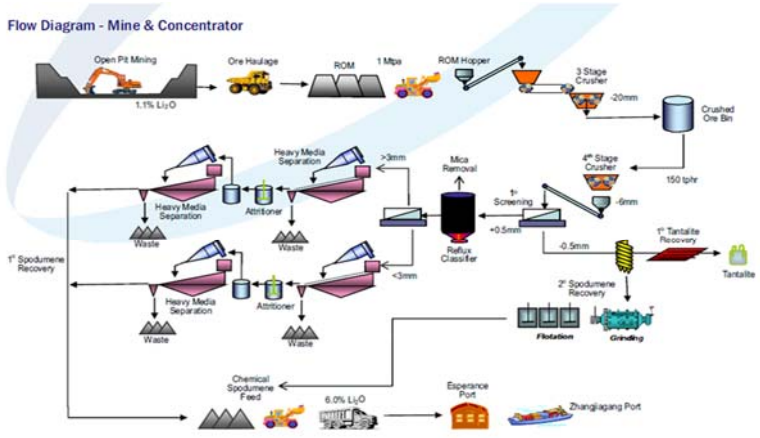
Source: Galaxy ASX announcement

Processing Mt Catalin

The key process steps are:

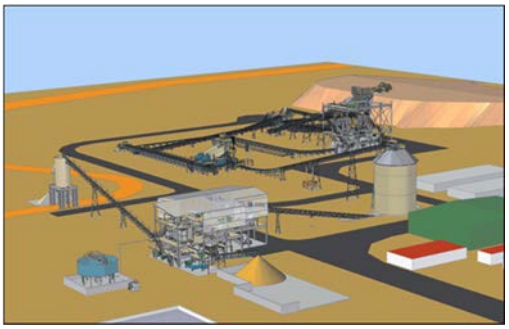
- Open pit mining
- Crushing and screening of ROM ore to -6mm
- Reflux Classifier to remove mica flakes
- Two stage heavy media separation (HMS) in two separate size streams
- Gravity concentration (spirals and wet tables) of tantalite minerals
- Grinding and flotation of - 0.5mm stream to remove residual spodumene
- Contract dressing and packaging of tantalite concentrates (in Perth)
- Production of 137,000 tonnes of spodumene concentrate @ 6.0% Li2O
- Shipment of bulk concentrate through Esperance to Zhangjiagang in China

Mt Catalin Deposit



Source: Galaxy ASX announcement

Process Plant 3D



Source: Galaxy ASX announcement

Crusher

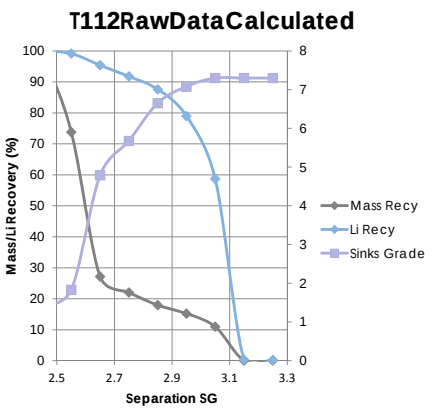
Source: METS site photo

Source: METS site photo

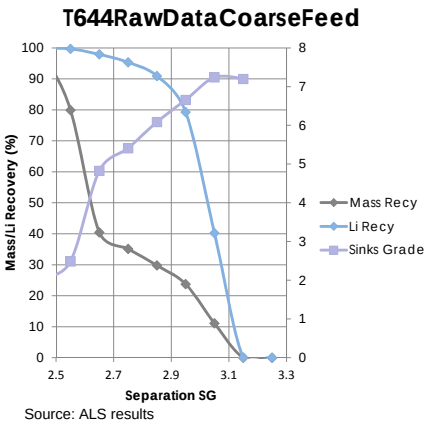
Source: METS site photo

Source: METS site photo

DMS Feed Densimetrics : Selected Results

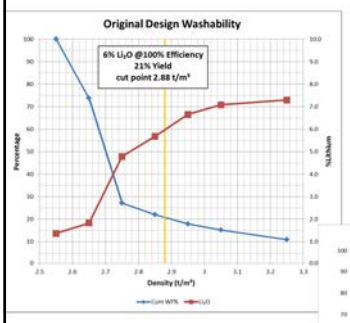


Source: ALS results



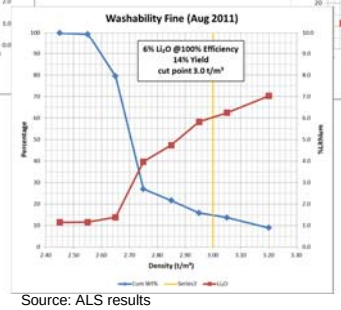
Source: ALS results

Washability Comparison



Source: ALS results

Source: ALS results



Source: ALS results

Differences From Design (Original Plant)

- Presence of weathered spodumene not taken into account. Poor recovery.
- Flotation not included in the flowsheet resulted in low recoveries (50%) being achieved
- Ore variability not addressed in the flowsheet
- Physical dilution of concentrate with mica could not be managed in the existing flowsheet
- Plant closed and concentrate purchased from Talison for Jiangsu lithium carbonate plant
- Plant has since reopened

Cons Dilution / Weathered Spodumene

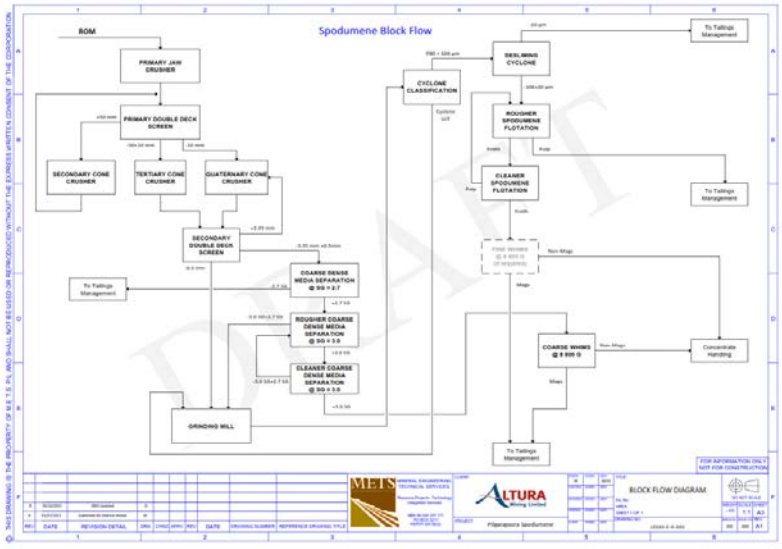
Source: Site Samples whiteboard

Altura Pilangoora

Source: Altura ASX announcement

METS core photo

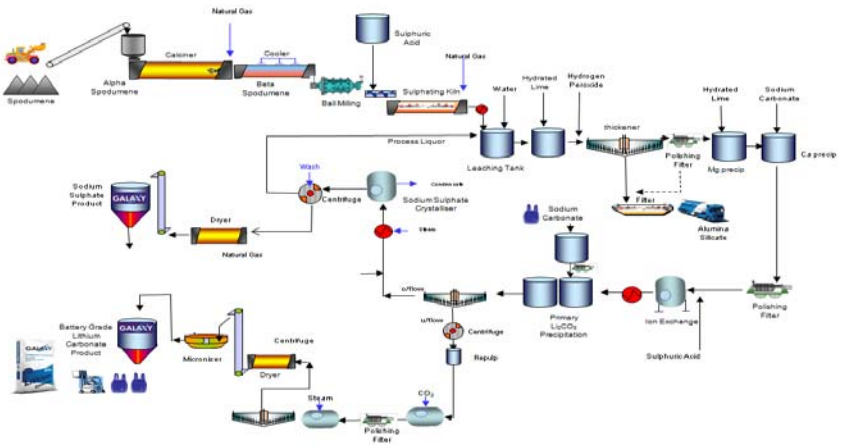
Altura Block Flowsheet



Testwork Outcomes

- The comminution results indicated that the Pilgangoora ore is of medium-hard hardness, is abrasive, and has a strong resistance to failure by compression. The head assays of each composite were measured to be 1.35% Li2O and 1.15% Li2O respectively.
- Beneficiation testwork was successful. Over 90% lithium recovery was achieved at concentrate grades of 6-7% Li2O.
- Dense media cyclone separation after a rougher and a cleaner stage, concentrates assaying 6.6% and 6.9% Li2O were collected from feed samples of the LGC and the HGC respectively.
- To further upgrade the coarse concentrate, magnetic separation by Rapid disc magnet was performed on the dense media cyclone SG 3.0 cleaner underflow. This successfully upgraded the aforementioned dense media cyclone cleaner concentrates to 7.0% and 7.5% Li2O for the high grade and low grade composites respectively, at >99% lithium recoveries.
- The flotation concentrates collected exhibited grades of 5.95% and 6.75% Li2O from the LGC and the HGC flotation tests respectively.
- Significant value may be added to the Pilgangoora Project through optimisation testwork on several processing areas.

Jiangsu Process Plant Flowsheet



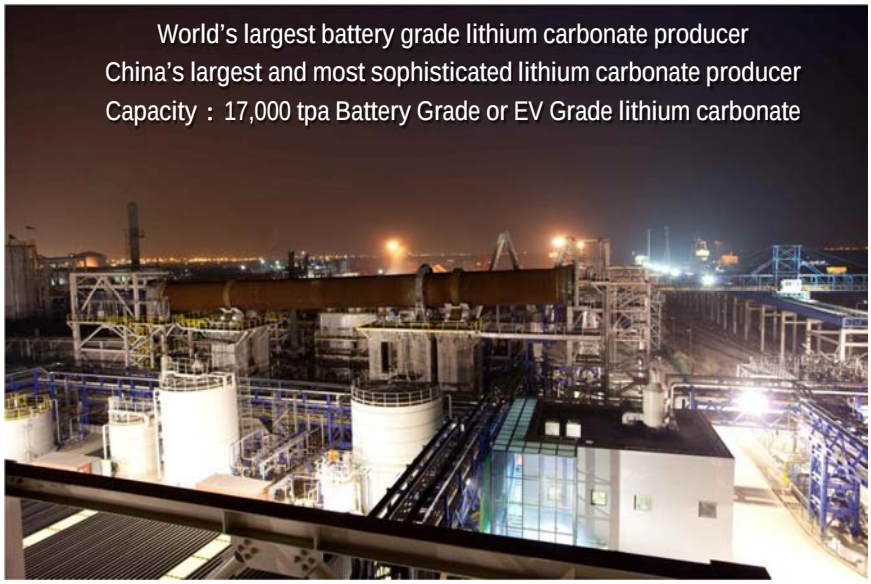
Source: Galaxy ASX announcement

Jiangsu Location on Yangtse River

- Zhangjiagang Free Trade Zone
- Chemical Industrial Park
- 120 top foreign companies
- Adjacent to a wharf, unloading spodumene directly to plant
- Bonded stockpile
- Sulfuric acid supplied via pipeline
- Close supply of soda ash & other reagents
- Close to markets & convenient logistics

Source: Galaxy ASX announcement

Jiangsu Process Plant



Source: Galkaxy presentation

Jiangsu Process Plant

All Pictures need a Source: Galaxy presentation


Spodumene


Calcination


Sulphation


Leaching

Slag


Li_2SO_4 Solution


LiC production


Carbonization

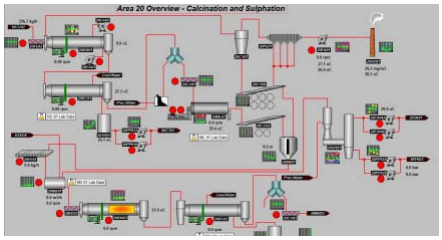

Precipitation


Crystallization

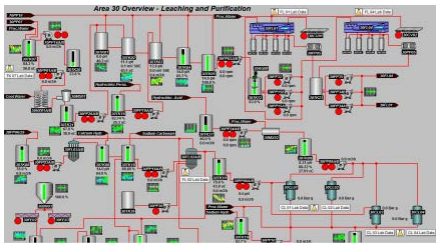

Impurity Removal

Process Control


Source: METS site photo



Source: METS site photo



Source: METS site photo

Ore unloaded at Jiangsu

Area 10 – Ore stockpile area

Senior management team on site

Ore feed conveyor to kiln

Purification plant

Lithium carbonate production plant

Commissioning in lithium carbonate production plant

Sodium sulphate plant


Calciner and reagent plant in background
Galaxy operators cold commissioning
Control room checking bulk I/Os
Pipework and slag filter building


Lithium carbonate centrifuge
Site laboratory in full operation
Product storage bins
Microniser and packaging building


Laboratory testwork in progress
Laboratory building in background
Packaging building
Microniser unit


Whole plant controlled from central control centre
Highly process controlled plant
HAVER
Full automatic bagging machine
Automated packing plant

Battery Grade Specification

Lithium Carbonate

Battery Grade

Batch Number: 1102140001
Production Date: 14 February 2011
Shift: Day Shift
Dispatch Date: 23 February 2011

Quality Status: Passed
Date: 16 February 2011

Product Analysis

CHEMICAL CONTENT					
Lithium	Li_2CO_3	99.8%	Calcium	Ca	0.002%
Beryllium	Be	0.001%	Tin	Sn	0.001%
Boron	B	0.001%	Manganese	Mn	0.002%
Sodium	Na	0.041%	Iron	Fe	0.001%
Magnesium	Mg	0.004%	Niobium	Nb	0.005%
Aluminium	Al	0.002%	Bismuth	Bi	0.001%
Phosphorus	P	0.01%	Chloride	Cl	0.002%
Sulphur	S	0.16%	Sulphate	SO_4	0.34%
Potassium	K_2	0.01%			

Source: METS photo shift result

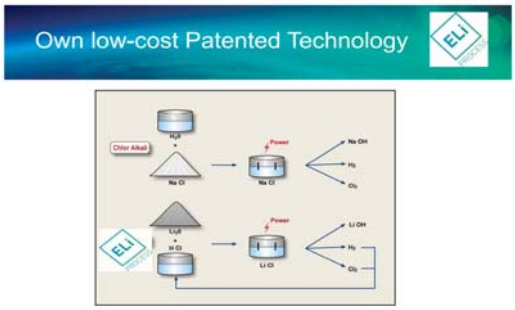
Eli Process

NEOMETALS - "ELi Process"

- The Neometals process ("ELi Process") is as follows (Yatendra Sharma's patent: http://www.google.com/patents/WO2014026217A1?cl=en):
- **Roasting** - at ~1000 degC to convert alpha-spodumene to beta-spodumene
- **Leaching** - 20% hydrochloric acid is mixed with beta-spodumene at 108 degC (boiling point of 20% HCl) and 40% solids for 6-12 hours
- Solid liquid separation
- **Pyrohydrolysis -** at 300 degC to convert Al and Fe chlorides into insoluble hydroxides. Excess HCl is also recovered here. It doesn't say how – potentially done by condensing and absorbing the off-gas from the pyrohydrolysis – this is the way we would do it at Direct Nickel with nitric vapour.
- Solid liquid separation
- **Precipitation** - Further impurity removal (Mn and Mg and remaining Fe and Al) precipitated by raising the pH to 9 with LiOH.
- Solid liquid separation
- **Precipitation 2** - Further impurity removal – (Ca) using soda ash
- Solid liquid separation
- **Ion exchange** - to remove any residual Ca, Mg – bring conc. Of these elements down to below 10 ppm.
- **Electrolysis** - Saturated LiCl sent to an electrolysis cell at 90 degC where chlorine gas is produced (and recycled back to make hydrochloric acid for leaching) and lithium migrates across a membrane as the concentration of lithium increases in the LiCl brine. The lithium from the LiCl solution migrates into a weak solution of LiOH and increases it from 4 to 6% (see picture I found on a youtube video. The weak LiCl ("depleted brine") is recycled to the leach step
- The LiOH solution undergoes either evaporation process to give crystalline LiOH or it goes to carbonation with CO2 to produce Li2CO3 depending on which product you want to produce.

Mt Marion Project

Source: Neometals website



Source: Neometals website

Cost Comparison

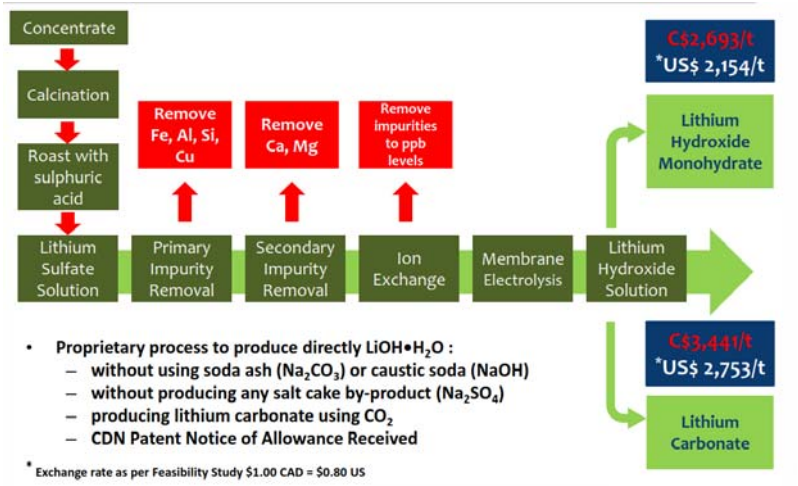
Source: Neometals website

Nemaska Process

NEMASKA Process

- From the Feasibility study (http://www.nemaskalithium.com/Documents/files/43-101/nemaska-lithium-whabouchi-feasibility-study.pdf)
- The alpha-beta spodumene roasting step is the same as above.
- **Acid Roast** – This is the traditional 200 degC, 98% sulphuric acid roasting step. Impure lithium sulfate is produced
- **Water Leach** – This is again a part of the traditional pathway. pH ends up around 1.7.
- **Purification 1** – pH elevated with hydrated lime – Fe, Al and Si came out as insoluble hydroxides.
- Solid/Liquid sep
- **Purification 2** – Ca, Mg, and Mn precipitated with NaOH in first two tanks, sodium carbonate (soda ash) used in third tank to precipitate any remaining impurities as carbonates.
- Solid/Liquid sep
- **Ion exchange** – to remove Ca and Mg
- **Membrane Electrolysis** – The difference here is that its lithium sulfate solution as opposed to lithium chloride as is the case with the Neometals process. Sulphuric acid is produced instead of chlorine gas (and therefore hydrochloric acid).
- **Crystallisation** – to produce LiOH.H2O or again sent to carbonation to produce Li2CO3.

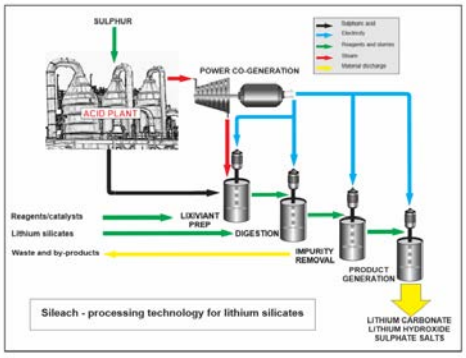
Nemaska Flowsheet



Source: Nemaska Presentation

Sileach Process

- Leaching for Li silicate ores
- Low energy, no roasting required
- Low CAPEX, OPEX
- Low temperature /atmospheric leach
- Rapid reaction times
- Patent application lodged



Source: Lithium Australia ASX announcement

Ceramatec Patent

Ceramatec Patent (2012)

- This process seems to cover both lithium sulfate and lithium chloride solution into an electrolysis electro-dialysis cell. A method for recovering and extracting lithium from a feed liquid (110) that may have a mixture of lithium and non-lithium salts present in the feed liquid.
- Salts of varying solubility are precipitated (120) out of the feed liquid (110) using water evaporation (140) or other techniques. Pure lithium hydroxide (190) is obtained using electrolysis or electro-dialysis processes (180) in combination with a lithium ion selective inorganic membrane such as LiSICON.
- The negative effect of sodium and potassium on the lithium ion selective inorganic membrane is reduced by reversing the polarity of the current placed across the membrane.

Conclusions

- Crushing, dense media separation and flotation are the standard unit operations applied.
- Not all spodumene ores are amenable to beneficiation to produce the required concentrate specification
- Technology has improved where some concentrates can be further beneficiated to remove excess mica.
- The standard lithium concentrate flowsheet is proven over time however the technical operating difficulties of producing better grade lithium carbonate should not be underestimated
- New technologies are emerging which may result in alternative process options

Acknowledgements

- Thanks to ALTA 2016 for the opportunity
- Thanks to companies for permission to publish
- Thanks also to all colleagues, laboratory staff and other consultants for their help and contribution
- Thanks to vendors for the photos

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- ACKNOWLEDGEMENTS

This document is a dynamic record of the knowledge and experience of personnel at Mineral Engineering Technical Services. As such it has been built upon over the years and is a collaborative effort by all those involved. We are thankful for the material supplied by and referenced from various equipment manufacturers, vendors, industry research and project partners.

Uranium-REE Proceedings

Ion Exchange

ACID RECOVERY FROM URANIUM ELUATES USING ION EXCHANGE RESIN

By

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ABSTRACT

An experimental study using ion exchange resin for acid recovery from sulfuric acid uranium eluates is described in this work. Commercial grade chromatographic particle size anion and cation resin of the Dow Chemical company was used to investigate whether uranium and sulfuric acid could be separated and recovered by the principle of ion retardation. Results demonstrate the possibility to recycle acid and recover uranium from the eluate by an ion exchange mechanism rather than by ion retardation (patent application filed).

INTRODUCTION/BACKGROUND

The cost, consumption and potential recovery/recycling of reagent chemicals (otherwise known as lixiviants and eluents as termed in hydrometallurgy) has become ever increasingly under the spotlight as uranium mines try to reduce operating costs in a depressed metals market since the slump of the uranium price post the Fukushima disaster.

Acid retardation as a process was already introduced in 1963 by Hatch and Dillon to separate strong acids from their salts. The feed solution is passed through a strong base anion exchange resin which shows greater affinity for the acid, thereby retaining/retarding it whilst the salt comes out first. Subsequently the acid is eluted from the resin with water. This process is based on the Donnan exclusion (Helfferich 1962) effect that it is more efficient with co-ions of higher valence and with solutions of low concentration. The acid crosses the Donnan potential and enters the resin while the salts (metal ions) are excluded. A strong base anion having a small particle size of chromatrographic grade is preferred due its improved kinetics. The resin is placed in compact short columns. In an upflow mode the acid is sorbed by the resin and the remaining salt solution comes out the top of the resin bed, followed by a downflow of water eluting the acid so that purified acid comes out the bottom of the column.

Inversely, a strong acid cation exchange (SAC) resin would exclude the acid more than positive or neutral uranyl species.

In this work, this ion exclusion mechanism was investigated for the separation of uranium from sulfuric acid using SAC resins.

Complex-ion equilibrium – Uranium in acid leach solution forms the following complexes

(1) $UO_2^{2+} + SO_4^{2-} \Leftrightarrow [UO_2SO_4]$

(2) $UO_2^{2+} + 2SO_4^{2-} \Leftrightarrow [UO_2(SO_4)_2]^{2-}$

(3) $UO_2^{2+} + 3SO_4^{2-} \Leftrightarrow [UO_2(SO_4)_3]^{4-}$

Also;

(4) $SO_4^{2-} + H^+ \Leftrightarrow HSO_4^-$

Uranyl and sulfate ions form anionic complexes which makes it possible to remove/recover uranium from acidic sulfate leach liquors with strong or weak anion exchangers.

(5) $2R\text{-}X + SO_4^{2-} \Leftrightarrow R_2\text{-}SO_4 + 2X^-$

(6) $R\text{-}X + HSO_4^- \Leftrightarrow R\text{-}HSO_4 + X^-$

(7) $[UO_2(SO_4)_3]^{4-} + 2R_2\text{-}SO_4 \Leftrightarrow R_4\text{-}[UO_2(SO_4)_3] + 2\ SO_4^{2-}$

(8)

Elution of uranium was done with but not limited to:

- Acidified NaCl solutions,
- Acidified NH_4NO_3 solutions,
- Sulfuric acid solutions.

Uranium is recovered from pregnant eluates by neutralization and precipitation in the first two cases and by solvent extraction (SX) in the latter case.

Other technologies used in the latter case include the use of chelating resins[1] and the use of nano-filtration technology\[2].

EXPERIMENTAL

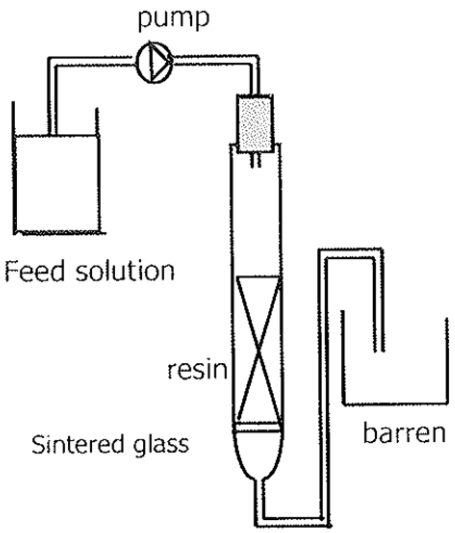

Figure 1: Column trials

A given volume of ion exchange resin, fully hydrated and converted to the required ionic form before introduction, was added into a 2cm internal diameter column.

Feed solution approximating a pregnant eluate with composition of 5gU/L and 8% H_2SO_4.

Experiment 1 - using anion exchange resin with small uniform particle size, loading cycle profile for acidity and uranium plotted.

Experiment 2 - using cation exchange resin with small uniform particle size, loading cycle and stripping cycle for acidity and uranium plotted.

The eluate was analyzed for uranium and acid content using ICP/EOS, Varian 720-ES and a Metrohm 716 DMS potentiometric titrator.

ICP installation

1- Argon gas valve 2- Gases evacuation system (chimney) 3- Plasma torch compartment 4- Ultrasonic nebulizer + spray chamber 5- Pump tubing for wastes 6- Auto sampler + peristaltic pump	7- Computer (ICP expert II software) 8- Liquid Wastes evacuation 9- Water cooling system 10- Power & safety 11- Evacuation system control

RESULTS AND DISCUSSION

The first lab experiment using small particle size anion exchange resin gave a broad peak of acidity <3.5% and uranium loading with zero leakage (Figure 2). This is indicative that the interaction of the anion exchange resin was complex ion formation according to reaction (7). The trial was not run to uranium breakthrough as the complexation reaction with uranylsulfate and anion exchange resins are well documented. This approach where acid retardation was not working and uranium was found again fixed on the resin as uranylsulfate was therefore abandoned.

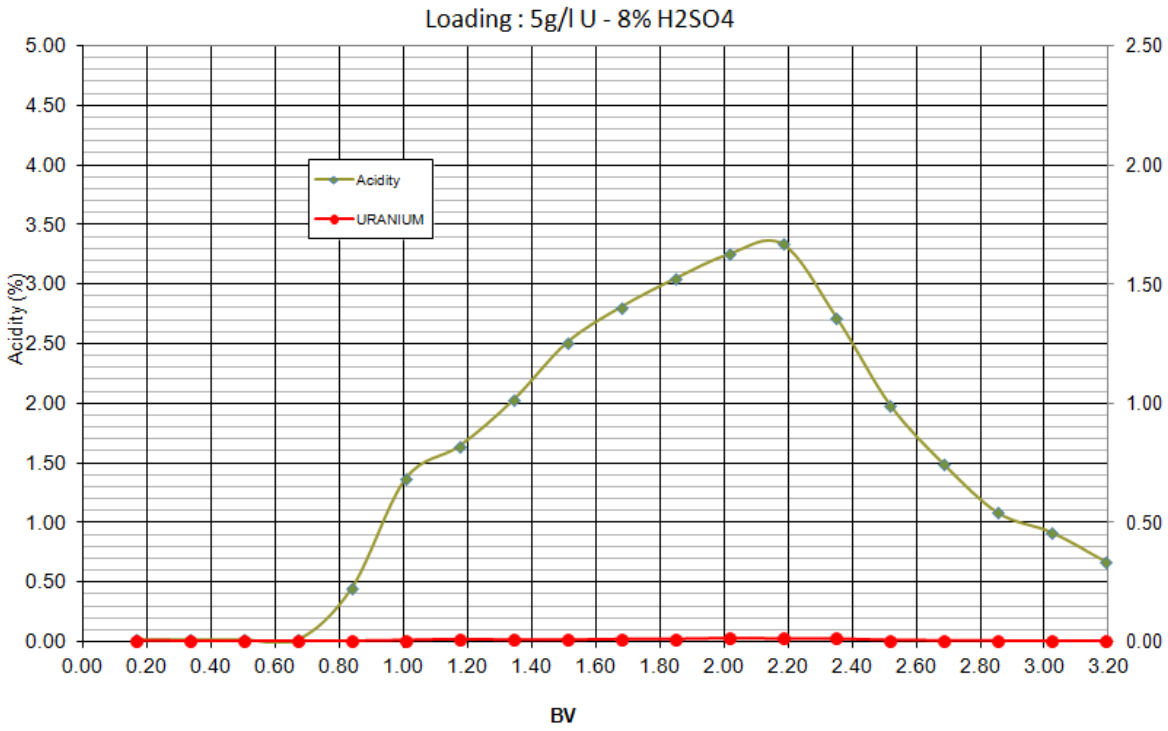

Figure 2

The second lab trial using small particle size cation exchange resin in the H+ form in elution chromatography mode with water elution showed that uranium was fixed strongly by the SAC resin and could only be eluted by an eluent such as 10% Na_2SO_4 (Figure 3).

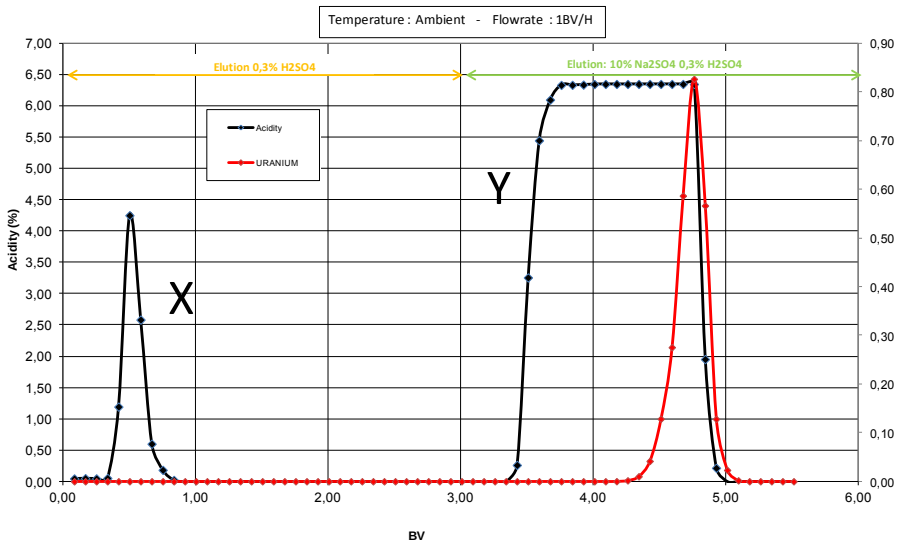

Figure 3

This result suggested that the way to proceed further was with a SAC ion exchange resin in a continuous flow mode. Figure 4 shows such an experiment, the obtained capacity however was only 1.0 BV with a feed solution containing 8% H_2SO_4 and 5g U_3O_8/L (Figure 4). This was due to the low selectivity coefficient UO_2^{2+}/H^+ and a low total volume capacity of the chromatographic resin used.

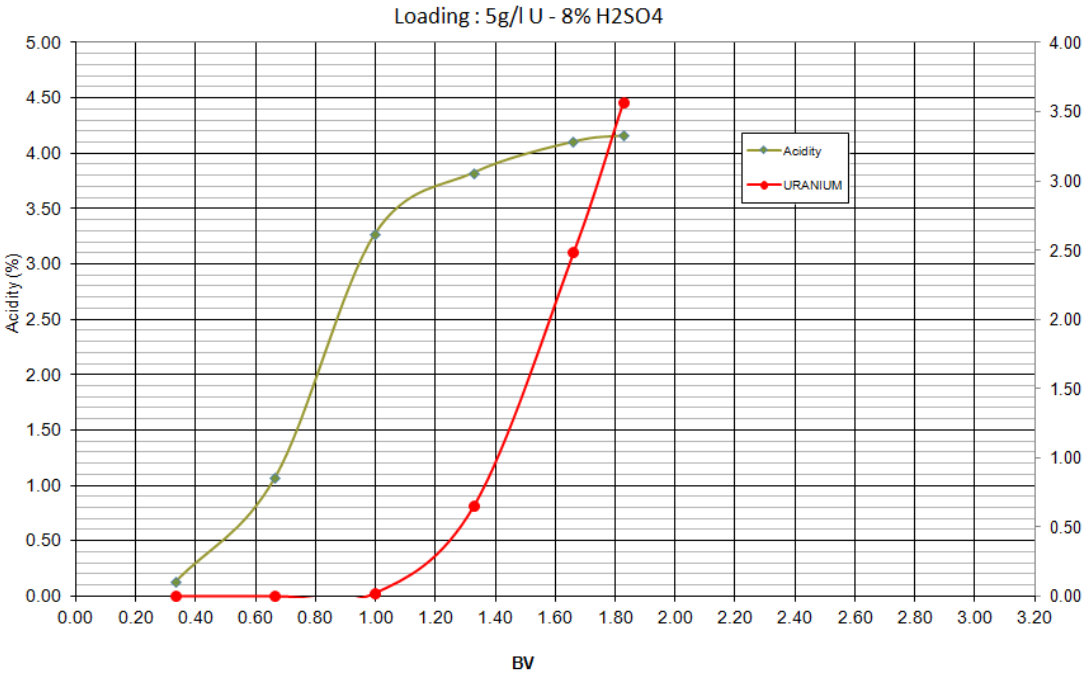

Figure 4

Elution (Figure 5) shows free sulphuric acid and uranium come out together and therefore difficult to separate them from the eluate.

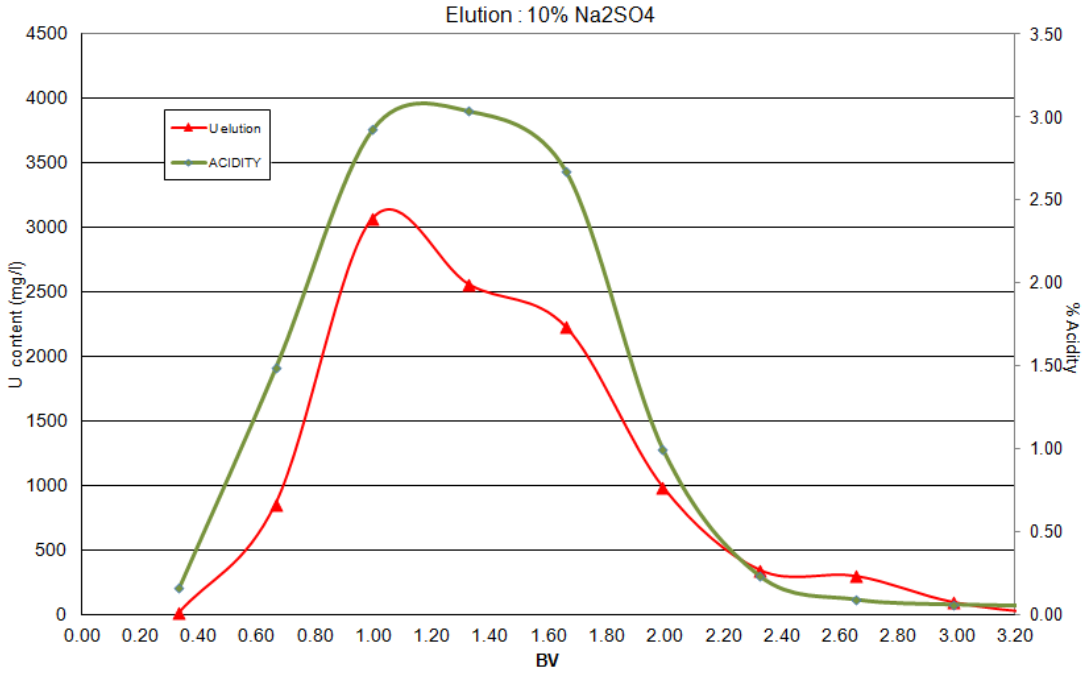

Figure 5

The pregnant eluate (under investigation) at the exit of the elution column has a composition depending on the specific operating conditions of the system but typically it can be 8-10% H_2SO_4 and 5-10 g U/L. H_2SO_4 being a diprotic acid with dissociation constants $K_1=2.4*10^6$ and $K_2=1.2*10^2$ the predominant species of H_2SO_4 in the pregnant eluate solutions would be HSO_4^-. It is therefore expected that uranium in H_2SO_4 solutions will be found as cation, UO_2^{2+} rather than as anionic uranyl sulfate complexes. As such, it should therefore be able to be fixed on a strong acid cation exchanger, according to the equation:

(9) $2\ R\text{-}SO_3^-H^+ + UO_2^{2+} \Leftrightarrow (R\text{-}SO_3^-)_2UO_2^{2+} + 2\ H^+$

CONCLUSIONS

Investigation has pointed to the use of Strong Acid Cation resins to remove uranium from H_2SO_4 eluates and recovery of the H_2SO_4. In order to improve the efficiency of this process, work in a more optimal way has been carried out. Patent application has been filed for the use of strong acid cation resin (whereby uranium is fixed on the resin as cation) and proposed processes to recover uranium from sulfuric acid eluates.

ACKNOWLEDGEMENTS

Dow Water & Process Solutions wish to acknowledge and thank Dr. Emmanuel Zaganiaris for his passion and dedication in making valuable contributions to the business.

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POLYAMINE FUNCTIONALISED CHELATION ION EXCHANGE RESINS FOR URANIUM EXTRACTION

By

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ABSTRACT

Ion exchange (IX) techniques are ubiquitous in industrial processes throughout the world, being used in areas such as desalination, mineral extractions and the nuclear fuel cycle. In the nuclear fuel cycle IX has been implemented at the front end for the extraction of uranium from pregnant leach liquors, chemical control of the coolant water within reactors and also at the back end in spent fuel reprocessing and waste treatment[1,2,3]. Though there is a major competitor to this technology in solvent extraction (SX), IX has always been a major workhorse technology in the nuclear industry. This is due to IX not having some of the drawbacks of SX such as the lower ability for preconcentration, potential for solvent loss, phase disengagement in multiple contact stages, third phase formation and the generation of large volumes of liquid aqueous and organic waste streams.

Chelation is a thermodynamic effect inferring an enhanced stability for a multidentate ligand and metal complex when compared with a complex containing the same metal ion and a group of similar monodentate ligands. Chelation IX resins have also been shown to resist uptake suppression due to the ionic strength of uptake media[4]. This effect can aid in potentially producing selective extractants which could be tailored to specific metals in a range of aqueous feeds. N-donor functional groups (ethylenediamine (EDA), diethylenetriamine (DETA) and pentaethylenehexamine (PEHA)) have been grafted onto the Merrifield resin (chloromethylated polystyrene). Soft N-donor ligands are well known to bind to uranium[5], with N-donor functional groups being commonly used at the front end of the nuclear fuel cycle for uranium extraction from pregnant leach liquors[3]. These IX resins are classed as weak base resins, which are commonly found to be effective when sulphuric acid leach conditions have been used[6]. There are reports of like resins being used in the literature[7,8,9], however, a comprehensive analysis of uptake (loading isotherms, pH dependence) and direct comparison between the homologous functional groups has not been published.

The three synthesised resins and a commercial resin, Purolite S985, have been assessed for their uptake behaviour towards uranium (as UO_2SO_4) in sulphuric acid media. Purolite S985 is also a polyamine resin, which was designed for the selective removal of heavy metals. It has been shown to extract platinum, palladium, rhodium, nickel, copper and zinc[10,11,12] under varying conditions, but its uptake towards uranium is relatively unknown. Uranium loading isotherms have been performed at constant pH, as well as studies to explore the effect of pH and SO_4^{2-} concentration. Isotherm models have been derived using data from extended x-ray absorbance fine structure (EXAFS) data and compared with well known isotherm models such as Langmuir and Dubinin-Radushkevich. Elution methods will also be investigated.

Keywords: Uranium Recovery, Chelation, Ion Exchange, EXAFS, Polyamine, S985

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Introduction

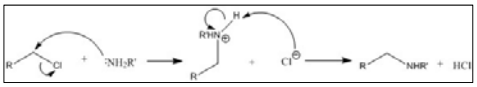
- Context
- Synthesis and characterisation
- Uptake studies
  - pH/sulphate
- Isotherms
  - Uptake/fits
- EXAFS studies
- Future work

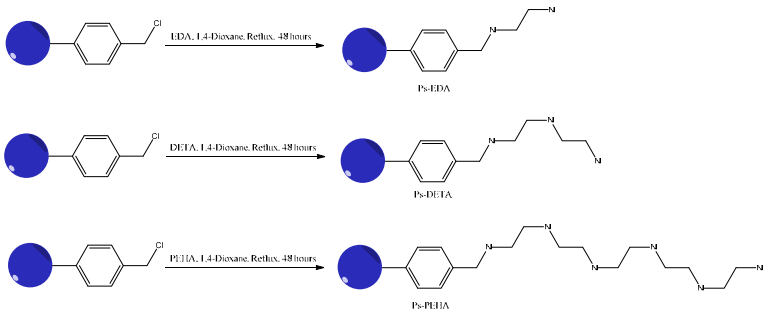
Why?

- Research group has experience synthesising and testing amine compounds for SX
  - Interested in trying IX
- IX does have some advantages over SX
  - Ability to work with lower quality feeds
  - Does not produce large volumes of organic waste
  - Removes possibility of third phase formation
  - Safety considerations (large solvent volume)
- IX resins with SBA or WBA functional groups are already employed in uranium processing circuits
  - Amines are used

Resin Synthesis

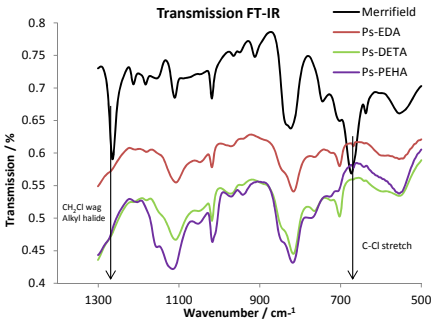
- Three related ligands were grafted onto the Merrifield resin
  - EDA, DETA, PEHA
  - Soft, N-donors
  - Weak base anion exchange

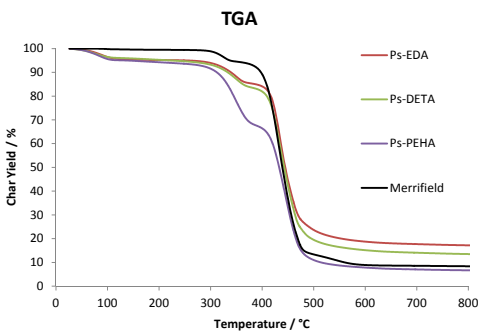




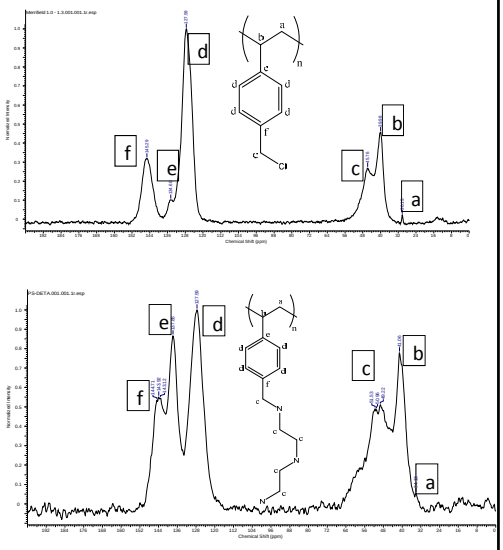
Resin Characterisation

- Resin products were characterised for assessment of the synthetic method
  - Transmission FT-IR
  - TGA
  - Solid State ^{13}CNMR



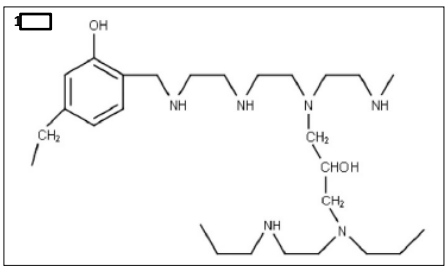


- SS ^{13}CNMR spectra show evidence of direct functionalisation
  - C-Cl peak removal
- Peak assignments based on similar aqueous phase molecules
  - Peak broadening effects resolution



Uptake Studies

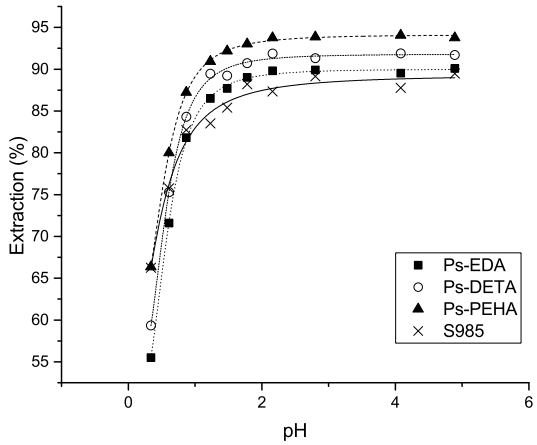
- As well as the synthetic resins, the commercial polyamine resin Purolite S985 was also tested for comparison
  - 1 g L^{-1} Uranium
- pH effects
- Sulphate effects



1 A. N. Nikoloski, K. L. Ang and D. Li, *Hydrometallurgy*, 2015, **152**, 20–32.

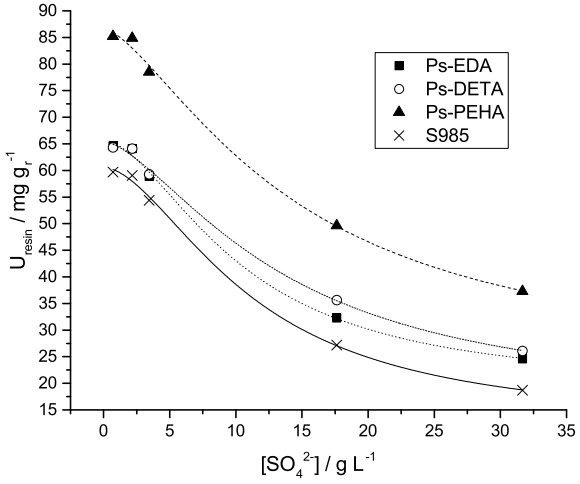
pH

- Uptake suppression above pH 2 for all resins
- Synthetic resins behave similarly to S985



Sulphate

- Uptake is suppressed by relatively small increases in $[SO_4^{2-}]$

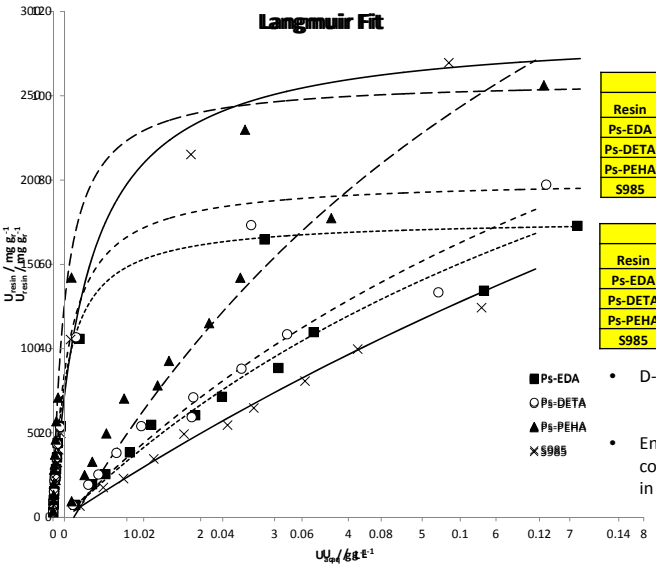


Isotherm Studies

- The Langmuir and Dubinin-Radushkevich isotherm models were fit to the data
  - Langmuir showed a slightly better fit ($r^2 > 0.99$)
- Isotherm model based on IX has been derived for the synthetic resins

$$2\overline{[RN_2H_2(HSO_4)_2]} + [UO_2(SO_4)_3^{4-}] \rightarrow \overline{[(RN_2H_2)_2(UO_2(SO_4)_3)]} + 4[HSO_4^-]$$

Fitting



Dubinin-Radushkevich				
Resin	q_m / mg g^{-1}	B_{DR}	E / kJ mol^{-1}	r^2
Ps-EDA	382.616	5.534E-09	9.505	0.976
Ps-DETA	404.528	5.456E-09	9.572	0.983
Ps-PEHA	553.079	5.303E-09	9.710	0.974
S985	654.034	7.001E-09	8.446	0.990

Langmuir			
Resin	q_m / mg g^{-1}	b	r^2
Ps-EDA	177.147	1226.428	0.999
Ps-DETA	200.762	1143.701	0.998
Ps-PEHA	259.767	1461.987	0.999
S985	289.821	510.0406	0.998

- D-R does not fit as well as Langmuir
  - Predicts higher loading capacities
- Energy values from D-R are in consistent range with IX processes in the literature

Derived Model

- Isotherm model derived based on an IX mechanism
  - Fixed pH, fixed sulphate

$$2\overline{[RN_2H_2(HSO_4)_2]} + [UO_2(SO_4)_3^{4-}] \rightarrow \overline{[(RN_2H_2)_2(UO_2(SO_4)_3)]} + 4[HSO_4^-]$$

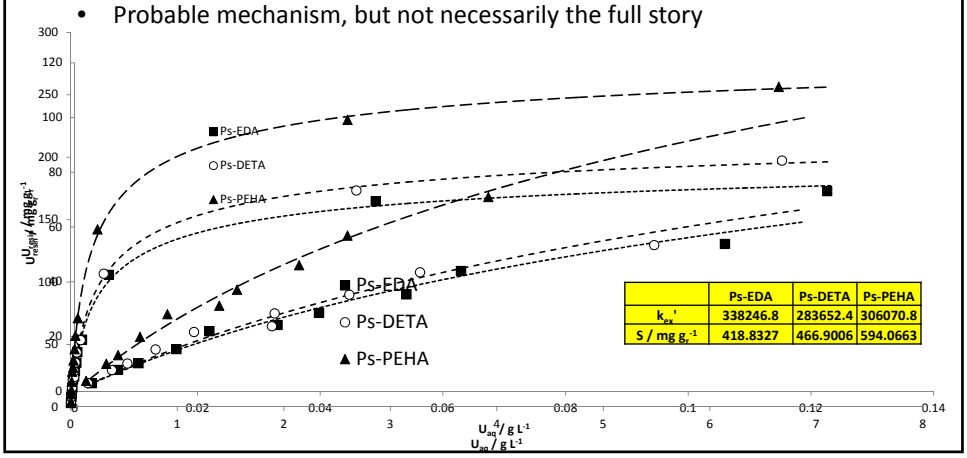
$$k_{ex} = \frac{\overline{[(RN_2H_2)_2(UO_2(SO_4)_3)]}[HSO_4^-]^4}{\overline{[RN_2H_2(HSO_4)_2]}^2[UO_2(SO_4)_3^{4-}]}$$

$$\boldsymbol{y = \frac{-(4k'_{ex}xS + 1) - \sqrt{(4k'_{ex}xS + 1)^2 - (4k'_{ex}xS)^2}}{8k'_{ex}x}}$$

$S = initial\ functionality\ concentration$
$x = total\ aqueous\ uranium\ at\ eq.$
$y = uranium\ on\ resin\ at\ eq.$

$$\boldsymbol{k'_{ex} = \frac{k_{ex}k_3[SO_4^{2-}]^3}{[HSO_4^-]^4(1 + k_1[SO_4^{2-}] + k_2[SO_4^{2-}]^2 + k_3[SO_4^{2-}]^3)}}$$

- Model fits with uptake suppression with increasing $[SO_4]^{2-}$
- However, long amine chains could result in a more complicated mechanism
  - Different types of uptake sites
- Probable mechanism, but not necessarily the full story

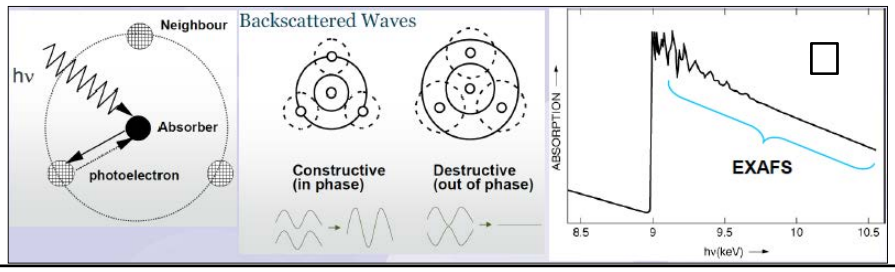


	Ps-EDA	Ps-DETA	Ps-PEHA
k_{ex}'	338246.8	283652.4	306070.8
S / mg g_r^{-1}	418.8327	466.9006	594.0663

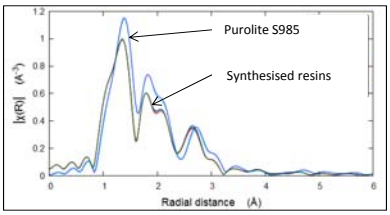
EXAFS

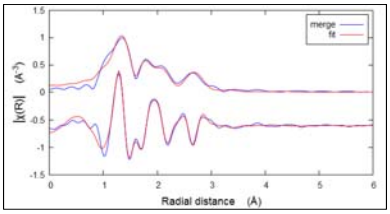
- **E**xtended **X**-ray **A**bsorption **F**ine **S**tructure
- Uses high energy X-rays
  - Only done at synchrotrons
- Structural and electronic information
- Element selective
- Bulk technique
  - Gives an average of all structures present

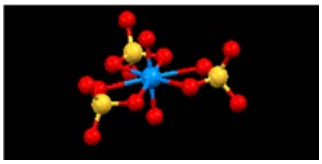

- Acceleration of electrons gives off X-rays
- Beam hits sample
- Core electron is excited
  - Photoelectron produced
  - Atom left in excited state
- Photoelectron propagates as a wave and interacts with neighbouring atoms
  - Interference gives structural information



Comparison of EXAFS data for U uptake on resins







- All synthetic resins appear to have the same structure
  - Very similar to S985
- Four prominent peaks
  - Sulphur peak at about 2.6 A
  - Equatorial oxygen peak at about 2 A
  - Equatorial oxygen peak at about 1.8 A
  - Axial oxygen peak at about 1.3 A
- Fitted structure is $[UO_2(SO_4)_3]^{4-}$
  - Fits agree with collected data
  - All synthetic resins and S985 fitted with the same structure
    - All WBA resins
  - Structure used to derive isotherm model for the system

Conclusions

- Uptake in all resin systems is pH and $[SO_4^{2-}]$ dependant
- The synthesised resins extract uranium from aqueous solution
  - Via an anion exchange mechanism
    - Possibly bisulphate with uranyl(tris)sulphate
- EXAFS experiments can give an indication of resin surface species
- Using all these techniques combined could allow for the designing of resins for specific waste streams

Future Work

- Mass spec of TGA off gas
- Assess uptake kinetics
  - Kinetic model
- Further resin tests
  - Real world process water
  - Saline/phosphoric acid conditions
- Cu/Au uptake
  - EPR spectroscopy
- EXAFS experiments from difficult aqueous streams
  - Saline/phosphoric acid

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- EPSRC

Uranium-REE Proceedings

Solvent Extraction

NEW SOLVENT EXTRACTION SYSTEM FOR URANIUM RECOVERY FROM LEACH SOLUTIONS USING SEAWATER

By

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CSIRO Mineral Resources, Australia

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ABSTRACT

Uranium resource processing using seawater is highly demanded due to the shortage of underground water. Currently there is no solvent extraction (SX) system suitable for uranium recovery from leach solutions containing high chloride concentrations comparable to seawater.

In order to develop a suitable solvent extraction system for uranium recovery from leach solutions using seawater, a number of SX systems were studied in terms of uranium extraction and separation from impurities, especially iron(III). A new SX system has been developed with which >99% uranium was extracted from a synthetic leach solution using seawater, while only about 10% iron(III) was extracted, leading to the separation factor of uranium over iron(III) >1000. With the new SX system, uranium was almost completely extracted (>99%) in a pH range of 0.5-1.5 tested. Therefore, no pH adjustment may be needed for uranium extraction. Uranium maximum loading in 1% (v/v) of the organic system was >1.3 g/L. The kinetics of uranium extraction was fast, reaching equilibrium within 3 min. Except for vanadium, all other commonly associated impurities could be readily separated from uranium. After uranium extraction, the discharged raffinate solution can be recycled to the leach step due to the high chloride tolerance of the new SX system. This can significantly reduce the water usage and the environmental concern as well. Scrubbing with 0.5 M H_2SO_4 is efficient to remove the co-extracted iron. In a single contact, uranium stripping was 80% with 4 M H_2SO_4 solution, and almost complete (>98%) with 0.5 M Na_2CO_3 or $(NH_4)_2CO_3$ solution. A process using the new SX system has been proposed.

Keywords: Solvent extraction, New system, Uranium, Seawater-leaching, Chloride.

INTRODUCTION

Except for carbonaceous types of ores, all other uranium ores are processed based on sulphuric acid leaching [1]. Solvent extraction (SX) is more preferable for uranium recovery from the resultant leach solutions [1-3]. Up to now, only tertiary amines are commercially used for uranium SX from acidic leach solutions due to their high selectivity for uranium over impurities, especially iron which is often present in a large amount. However, tertiary amines face a great challenge when chloride concentrations are high in the solution. Chloride can cause significant decrease in uranium loading capacity due to its strong affinity for amines [1,2]. Usually, when chloride concentration is greater than 3 g/L, tertiary amines will lose its applicability due to the low uranium loading capacity [4,5].

With the shortage of groundwater, seawater is considered to be employed for uranium processing in some practices located near coastal areas [6,7]. Currently, desalination of seawater must be operated to meet the requirement of uranium SX using tertiary amines. It will significantly increase the capital and operating cost. In addition, it also will raise a serious environmental concern since a large amount of concentrated brine will be sent back to the sea [7]. It is greatly advantageous using seawater to directly process uranium ores. However, new solvent extraction system is required to replace amine systems to suit high chloride concentrations.

A number of SX systems have been investigated previously in attempt to replace tertiary amines for uranium solvent extraction when high chloride concentration is present. Among them, the mixture of D2EHPA and Alamine 336 has been used for a large scale pilot plant in the Honeymoon uranium project in South Australia, where the processing solution contains about 8 g/L Cl [3,8]. The uranium loading capacity is significantly increased with the mixed organic system and the separation of uranium from iron is also improved compared to an Alamine 336 or D2EHPA alone system. Other SX systems, including the mixtures of D2EHPA with Cyphos IL 101 [9], Cyanex 272 [10,11] and Cyanex 923 [12] also have been investigated. All these systems showed potential capability for uranium extraction and separation from iron and other impurities from solutions containing high chloride concentrations. However, iron(III) was still largely extracted with all these SX systems, resulting in a poor separation of uranium from iron(III), and consequently, resulting in difficulty in iron removal.

A new organic system has been developed in the present paper. The performance of the new organic system for uranium extraction from a synthetic solution using seawater was evaluated. Uranium separation from commonly associated impurities, particularly iron(III) was studied.

SYNTHETIC FEED SOLUTION

In order to mimic uranium leach solution using seawater, a synthetic solution was prepared by dissolving the corresponding chemicals in seawater obtained from Fremantle (Western Australia) (Table 1). Metal concentrations in the synthetic solution were based on the leach solution reported elsewhere [8]. Chloride concentration in the seawater was 20.8 g/L obtained with standard $AgNO_3$ titration and it was consistent with those reported elsewhere [13]. Other elements in the seawater were not determined. Based on the reference [13], the concentrations of some major elements in the seawater were (g/L): ~11 Na, ~1.3 Mg, ~0.5Ca and ~0.4 K.

Table 1: The composition of uranium synthetic solution with seawater

Metal	**U**	**Fe**	**Al**	**Mn**
Conc. (g/L)	1.21	9.17	3.94	1.38
Chemical	$Na_2U_2O_7{\cdot}6H_2O$	$Fe_2(SO_4)_3$	$Al_2(SO_4)_3{\cdot}18H_2O$	$MnSO_4{\cdot}4H_2O$
Purity	>99%	AR grade	AR grade	AR grade
Metal	**Cu**	**Zn**	**Zr**	**V**
Conc. (g/L)	0.50	0.60	0.19	0.23
Chemical	$CuSO_4{\cdot}5H_2O$	$ZnSO_4$	$ZrOCl_2$	$NH4{\cdot}VO_3$
Purity	AR grade	AR grade	AR grade	AR grade

SELECTION OF URANIUM SX SYSTEM

In order to select a suitable organic system, a number of SX systems were evaluated in the scoping tests using the synthetic solution in terms of uranium extraction and its separation from iron(III) (Table 2). The scoping tests were carried out using 5% (v/v) extractant in each single or mixed

systems with ShellSol D70 (aliphatic compound) as the diluent. The organic and aqueous solutions were mixed at an A/O ratio of 1:1 and room temperature (~22°C) for 10 min in a shaking incubator. The initial aqueous pH was adjusted to 1.70

In Table 2, D2EHPA, Ionquest 801, Cyanex 272 and Cyanex 572 are acidic organophosphorus reagents. The structures of New-SX reagent and additives A1and A2 will not be disclosed in this paper. From Table 2, it can be seen that uranium extraction was >97% with all tested SX systems, except A1 and A2 alone systems, whereas iron(III) extraction varied from 11.49% to 78.02%. This resulted in significant difference in separation factors of uranium over iron with different organic systems. The addition of Alamine 336 (a tertiary amine) or Aliquat 336 (a quaternary amine salt) into an organic system containing D2EHPA, Ionquest 801, Cyanex 272 or Cyanex 572 did not reduce the iron extraction (Table 2). Contrarily, the addition of Alamine 336 to Cyanex 572 or Cyanex 272 systems significantly increased the iron(III) extraction, leading to a poorer uranium selectivity over iron. However, with the addition of A1 or A2 in the tested SX systems, the separation factor of uranium over iron ($SF_{U/Fe}$) was significantly increased due to the increase in uranium extraction. This suggested that A1 or A2 as an additive could improve the separation of uranium from iron. In Table 2, uranium extraction was 98.8% with the New-SX reagent alone system, while iron extraction was only 11.5%, resulting in $SF_{U/Fe}$ of 631 which was much larger than those obtained using other single extractant system. Although higher $SF_{U/Fe}$ was obtained with the addition of A1 or A2, the New-SX alone system was selected for further test considering its simpler compositions.

Table 2: Comparison of organic systems for uranium extraction and separation from iron from the synthetic solution using seawater.

Organic system	Uranium extraction (%)	Iron(III) extraction (%)	$SF_{U/Fe}$
D2EHPA+Alamine 336	99.03	51.21	97.3
D2EHPA+Aliquat 336	97.43	66.27	19.3
Ionquest 801+Alamine 336	99.13	78.02	32.2
Cyanex 572	98.13	34.42	100
Cyanex 272	98.58	21.72	250
New-SX	98.79	11.49	631
Cyanex 572+Alamine 336	99.75	75.53	127
Cyanex 272+Alamine 336	99.59	68.17	112
Cyanex 272+A1	99.15	18.53	514
Cyanex 272+A2	99.76	23.26	1364
New-SX+A1	99.31	13.56	919
New-SX+A2	99.73	15.03	2057
A1	0	0	-
A2	3.69	0	-

METAL DISTRIBUTION pH ISOTHERMS WITH NEW SX SYSTEM

Metal extraction pH isotherms were determined using 5% New-SX system at an A/O ratio of 1:1 and room temperature (Fig. 1). The pH was adjusted using a 200 g/L NaOH solution. In Fig. 1, uranium was almost completely extracted (extraction >98%) in the tested pH range of 0.5-1.7. Large amounts of vanadium were also extracted, increasing from 32% to 56% with pH increasing from 0.5 to 1.7. Iron extraction slightly increased from 3% to 6% when pH was increased from 0.5 to 1.4, and increased to 13% at pH 1.7. About 10% Zr was co-extracted and the extraction of other metals were <5%. The separation factors of uranium over iron, vanadium and zirconium were calculated (Table 3). It is clear that uranium can be readily separated from the impurities with the New-SX system, except for vanadium.

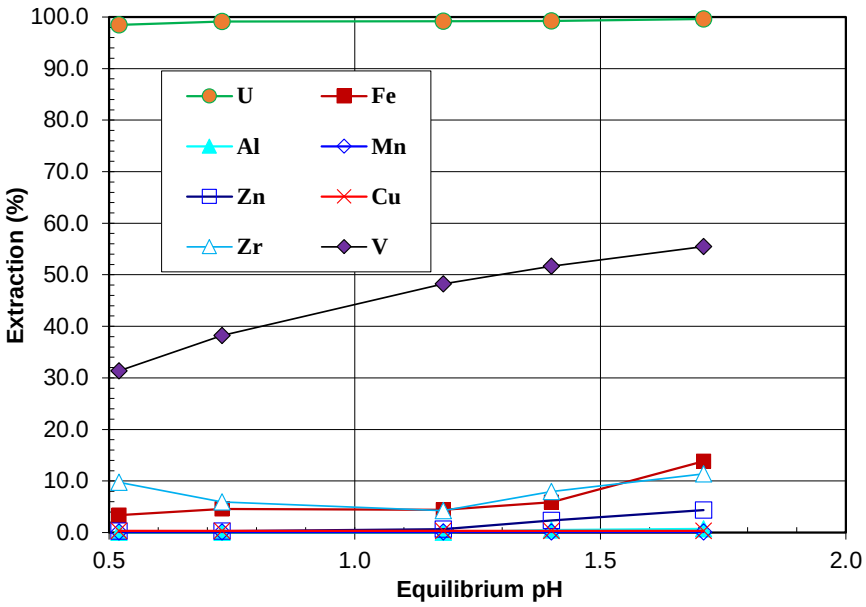

Fig. 1: Metal extraction pH isotherms with 5% New-SX system and the synthetic solution.

Table 3: Separation factors (SF) of uranium over metals at various pH usingNew-SX system.

pH	$SF_{U/Fe}$	$SF_{U/Zr}$	$SF_{U/V}$
0.52	1877	604	143
0.73	2293	1755	179
1.18	2665	2787	133
1.40	2093	1505	122
1.71	1602	2002	206

Effect of New-SX Concentration

Uranium extraction and separation from the impurities were tested using various New-SX concentrations at an A/O ratio of 1:1 and room temperature (Fig. 2). The extraction pH was adjusted to 1.50 with a 200 g/L NaOH solution. In Fig. 2, all extractions of uranium, vanadium and iron were increased with the increase in organic concentration due to the increase in extractant availability. Zirconium extraction was almost unchanged, indicating that it is not dependent on the organic concentration.

The separation factors of uranium over iron and vanadium under various New-SX concentrations are given in Table 4. The separation factors of uranium over iron and vanadium both decreased with decreasing organic concentration due to the lower uranium extraction. This indicated that lowering organic concentration to increase organic saturation (rate occupied by metal loading) could not improve uranium separation from iron and vanadium. At New-SX concentration of 0.5%(v/v), uranium loading in the organic solution was 0.67 g/L, translating 1.34 g/L in 1% (v/v) organic concentration. This suggested that uranium maximum loading capacity in the organic system can reach 1.34 g/L or higher in 1% (v/v) organic solution.

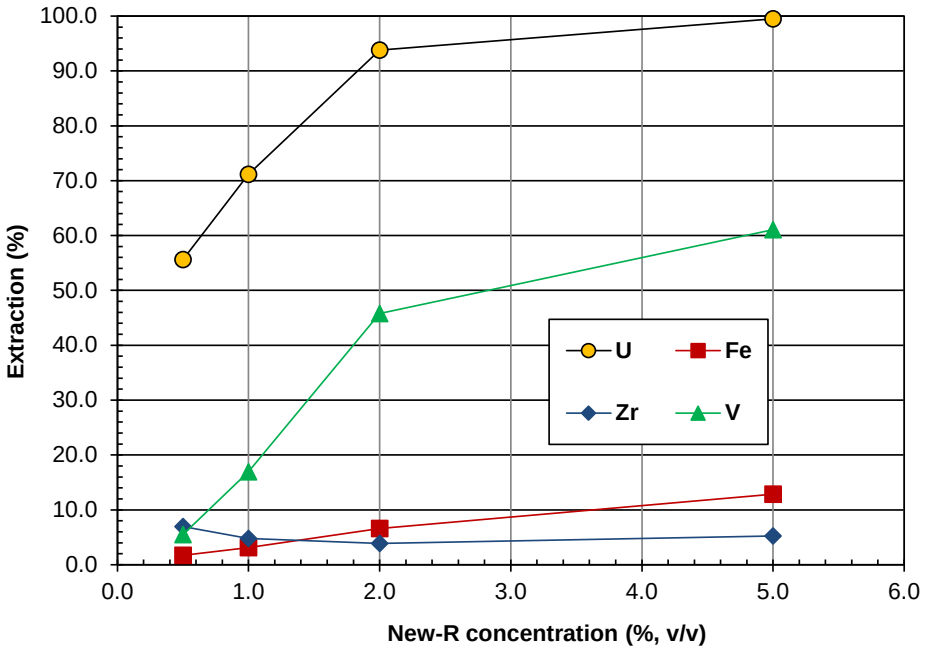

Fig. 2: Effect ofNew-SX concentration on metal extraction at pH 1.50.

Table 4: Selectivity of uranium over Fe, Zr and Vat various New-SX concentrations

New-SX Conc. (% v/v)	$SF_{U/Fe}$	$SF_{U/Zr}$	$SF_{U/V}$
0.5	74	17	22
1.0	76	49	12
2.0	209	372	18
5.0	1277	3485	123

Effect of Chloride Concentration

Although the chloride concentration in seawater is constant at around 20 g/L[13], the concentration may be elevated to some extent in the process by evaporation. Therefore, the effect of raising chloride concentration on uranium extraction and separation from other metals was tested by adding sodium chloride in the synthetic solution to a chloride concentration range of 20-60 g/L. The 5% New-SX system was used for the extraction at an A/O ratio of 1:1, pH 1.5 and room temperature (Fig.3). In Fig. 3, chloride concentration in the initial synthetic solution was 20.0 g/L. It was found that with the increase in chloride concentration, the extraction of uranium and zirconium was almost unchanged and vanadium extraction was slightly increased. However, iron extraction was significantly increased. Therefore, the increase in chloride concentration could significantly impact the uranium separation from iron. The effect of chloride concentration under a lower pH value of 0.85 was also measured (Fig. 4). It can be seen that iron extraction was significantly suppressed at pH 0.85. Therefore, lowering pH is favourable to the uranium separation from iron at a high chloride concentration.

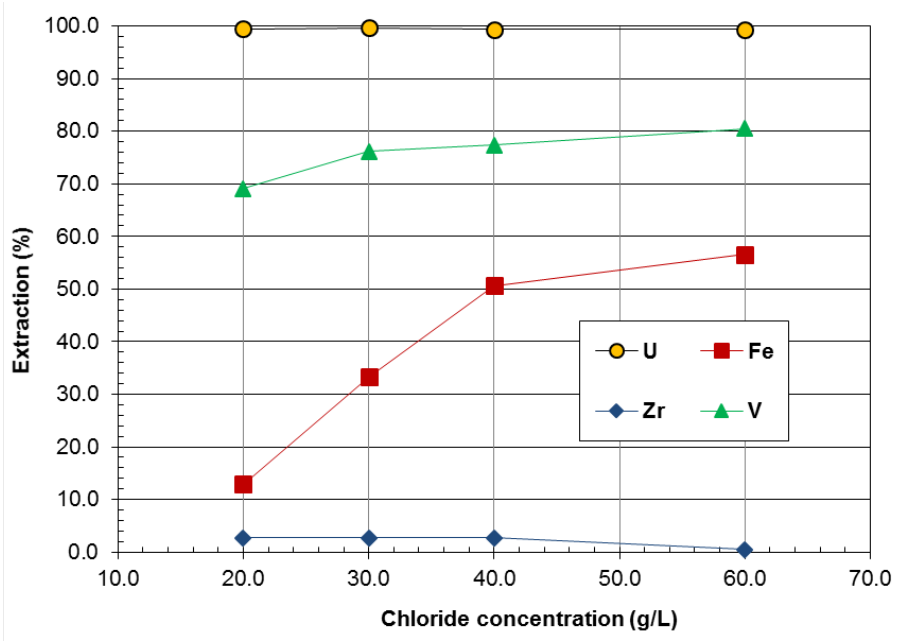

Fig. 3: Effect of chloride concentration on metal extraction at pH 1.50.

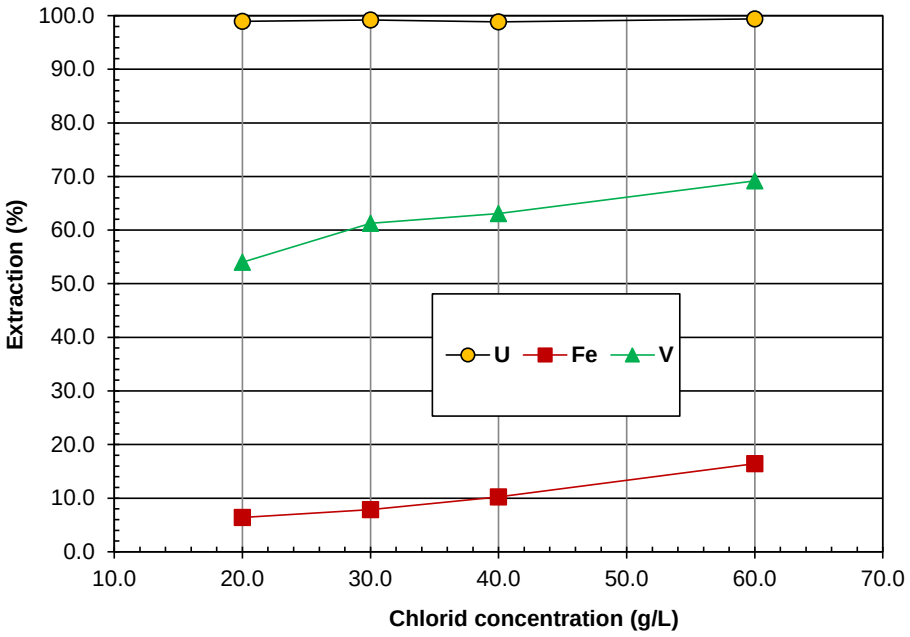

Fig. 4: Effect of chloride concentration on metal extraction at pH 0.85.

Effect of Temperature

The effect of temperature on the extraction of uranium and iron was measured using 2% New-SX system at an A/O ratio of 1:1 and pH 1.50 (Fig. 5). It was found that temperature in the range of 22-50°C has almost no effect on the extraction of uranium and iron.

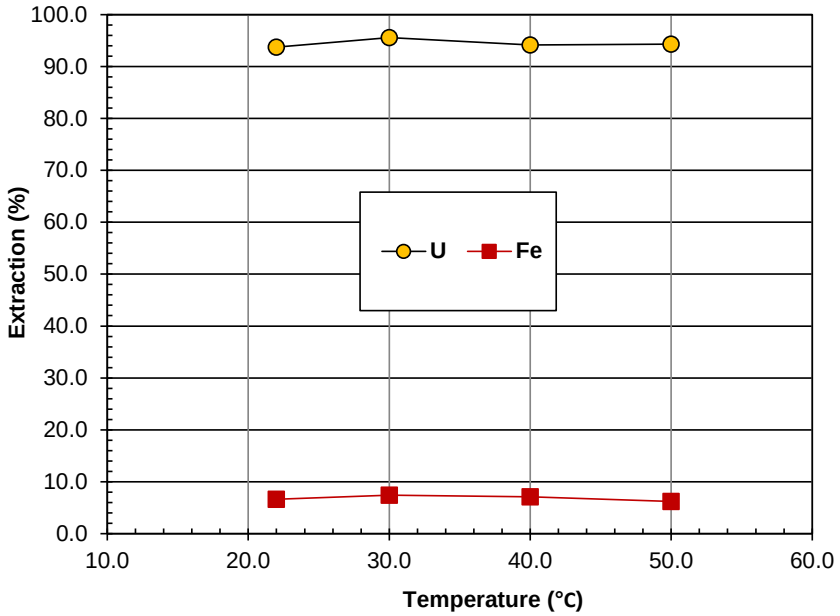

Fig. 5: Effect of temperature on metal extraction.

Effect of A/O Ratio

The extraction of uranium and iron was determined under various A/O ratios using 5% New-SX system at pH 1.50 and room temperature (Fig. 6). Uranium extraction was slightly decreased from A/O ratio 1:2 to 2:1 and rapidly decreased when A/O ratio higher than 2:1. At A/O ratio of 2:1, uranium in the loaded organic solution (5% extractant) was 2.4 g/L, meaning 0.48 g/L U in each 1% extractant. It is suggested that if uranium loading is greater than 0.48 g/L in per unit (1%) of the organic solution, its extraction could be reduced rapidly due to the reduced availability of the extractant. Iron extraction decreased gradually with increasing A/O ratio, indicating that high organic loading can suppress the iron extraction.

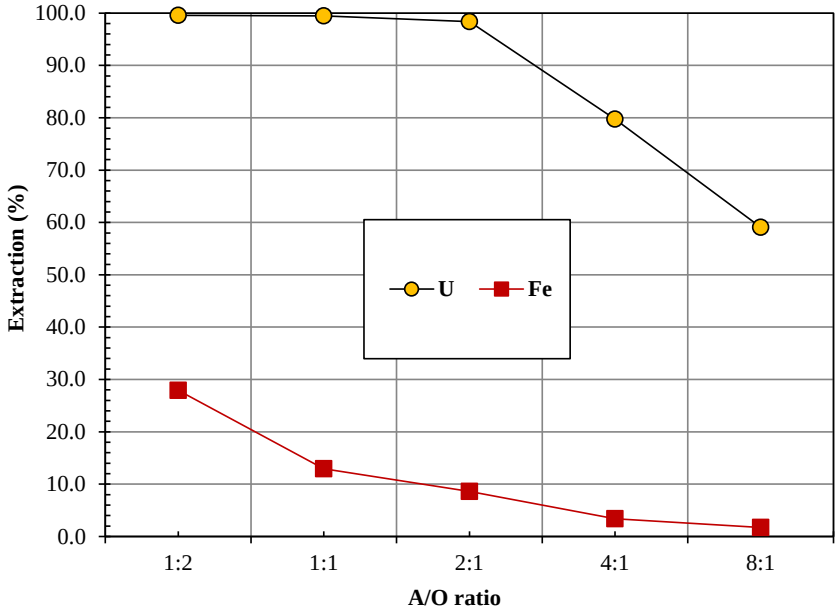

Fig. 6: Effect of A/O ratio on metal extraction.

Extraction Kinetics

Metal extraction kinetics is important to the process design. The extraction kinetics of uranium and iron were determined with the 5% New-SX system and the synthetic solution under various contacting time at A/O ratio of 1:1, pH 1.50 and room temperature (Fig. 6). Two phase solutions were mixed by stirring using an overhead stirrer. It is shown that uranium extraction was very fast, reaching equilibrium within 3 min. Iron extraction was relatively slow and the extraction still increased after 10 min (Fig. 6). This suggests that using shorter contact time is favourable to uranium separation from iron.

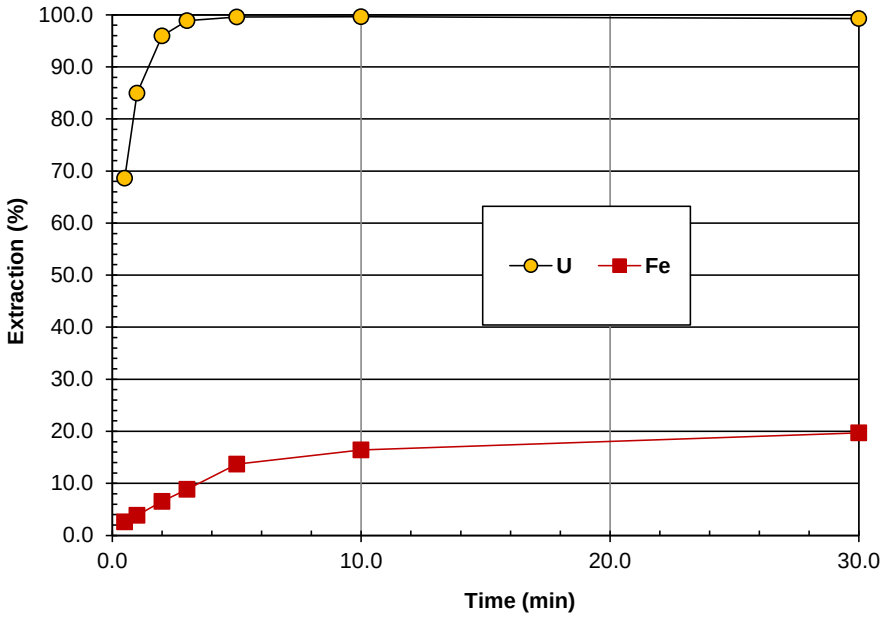

Fig. 6: Metal extraction kinetics at room temperature (22°C).

Uranium Extraction Distribution Isotherm and McCabe Thiele Diagram

Based on the uranium extraction under various A/O ratios, the distribution isotherm and McCabe Thiele diagram for uranium extraction were obtained and are shown in Fig. 7. It can be seen that two theoretical stages are required to completely extract uranium from the synthetic solution containing 1.21 g/L U using 5% New-SX system at an A/O ratio of 4:1, leaving a negligible amount of uranium in the raffinate. As the result, a loaded organic solution containing 4.84 g/L U can be obtained.

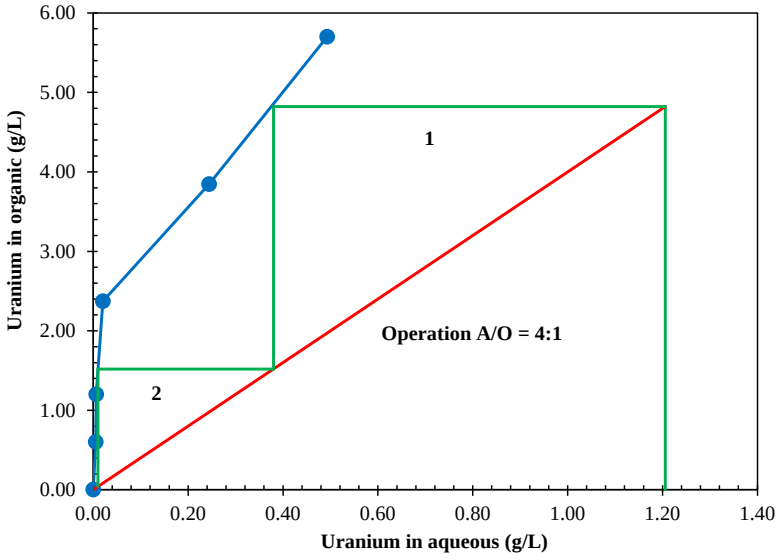

Fig. 7: Uranium extraction distribution isotherm and McCabe Thiele diagram

Uranium Stripping

From above discussion, it is known that only uranium, vanadium and iron were substantially extracted with the New-SX system. Other impurities could be readily separated from uranium. Uranium separation from vanadium is difficult due to their poor separation. If vanadium is present in the practice, further investigation is required. The stripping of uranium and iron from the loaded 5% New-SX system containing 1.2 g/L U and 0.38 g/L Fe were studied using 2 M, 4 M H_2SO_4 and 5 M HCl solutions (Table 5). For comparison, a loaded organic system of 5% Cyanex 272 containing 1.2 g/L U and 0.71 g/L Fe was also studied under similar conditions. It was found that uranium was difficult to be stripped using acidic solutions from both New-SX and Cyanex 272 systems. Uranium stripping was only 74.2% and 81.9% using 4 M H_2SO_4 solution from the 5% New-SX and the 5% Cyanex 272 SX systems, respectively, and it was only about 20% from both organic systems using 5 M HCl solution. The stripping of iron was efficient with acidic solutions from the New-SX system. Almost 100% iron was stripped using all acidic solutions tested. However, it was found that iron could not be completely stripped from the 5% Cyanex 272 system with H_2SO_4. Iron stripping was about 90% using both 2M and 4 M H_2SO_4 solutions, leaving around 10% iron in the stripped organic solution. Using 5 M HCl solution, iron stripping was only 50%. It is suggested that iron removal by scrubbing using acidic solution could be ready from the New-SX system, but may be difficult from the Cyanex 272 system.

Table 5: Stripping of uranium and iron with acidic solutions

Strip solution	5% New-SX reagent		5% Cyanex 272	
	U Stripping (%)	Fe Stripping (%)	U Stripping (%)	Fe Stripping (%)
2M H_2SO_4	34.4	~100	44.0	90.2
4M H_2SO_4	74.2	~100	81.9	91.6
5 M HCl	25.8	~100	22.5	50.0

The stripping of uranium and iron was tested using alkaline solutions (Table 6). Significant amounts of iron co-loaded in organic solution can be stripped together with uranium with alkaline solutions and then form precipitation, resulting in organic emulsion. It has occurred in the Honeymoon uranium project [8]. Therefore, a loaded 5% New-SX system was first scrubbed with 0.5 M H_2SO_4 at an A/O of 1:2 to remove the co-extracted iron. After scrubbing, the resultant organic system contained 1.1 g/L U and 0.03 g/L Fe from the initial concentration of 1.2 g/L U and 0.38 g/L Fe. It indicated that 0.5 M H_2SO_4 is efficient to scrub iron. After scrubbing, the organic solution was stripped with some alkaline solutions (Table 6). It can be seen that 0.5 M $(NH_4)_2CO_3$ and Na_2CO_3 are efficient for uranium stripping with >98% U stripped.

Table 6: Stripping of uranium and iron by basic solution

Strip solution	U Stripping (%)	Fe Stripping (%)
0.5 M NH_4Ac	0.1	59.6
0.5 M $(NH_4)_2CO_3$	~100	~100
0.5 M Na_2CO_3	98.1	92.8

PROCESS DISCUSSION USING THE NEW-SX SYSTEM

Using the New-SX system, uranium can be completely extracted in two theoretical stages due to its efficient extraction. However, three stages are more recommended in the practice. The pH adjustment is not needed if the feed solution pH is in the range of 0.5-1.5. The A/O ratio is controlled depending on the concentrations of organic and uranium in the feed solution to obtain about 1.0 g/L uranium loading in each percentage unit (1%) of organic concentrations. Although 0.5 M H_2SO_4 is efficient for iron scrubbing at an A/O of 1:2, high concentration acid solutions, such as 2 M H_2SO_4, is suggested for iron scrubbing at a lower A/O ratio to reduce the volume of scrub solution. As good uranium extraction and separation from iron can be still achieved when chloride concentration is up to 60 g/L at pH 0.85, the raffinate solution after uranium extraction can be recycled to the leach step if the accumulation of other impurities is tolerable. Sulphuric solution at 4 M or higher can be used for uranium stripping. Uranium in the resultant loaded strip liquor can be recovered using the method developed by Zhu *et al.* [14]. However, alkaline solution of Na_2CO_3 or $(NH_4)_2CO_3$ is more recommended due to their high efficiency.

The process using the New-SX system for uranium recovery from seawater leach solutions is proposed as shown in Fig. 8. The following advantages can be expected using the proposed process.

1) Good separation of uranium from iron can be obtained. No iron reduction is required as performed in the reported process[8],

2) Iron can be readily removed from the organic system by scrubbing. Crud formation arising from iron precipitation during uranium stripping can be avoided.

3) No pH adjustment is needed for uranium extraction.

4) Raffinate solution can be recycled due to the high chloride tolerance with New-SX system. It can significantly reduce water consumption and environmental pollution.

As discussed previously, uranium separation from vanadium is poor, resulting in difficulty in its removal. If vanadium presents in the solution, further investigation is required. In addition, if titanium and thorium are associated in the process, further investigation is also required.

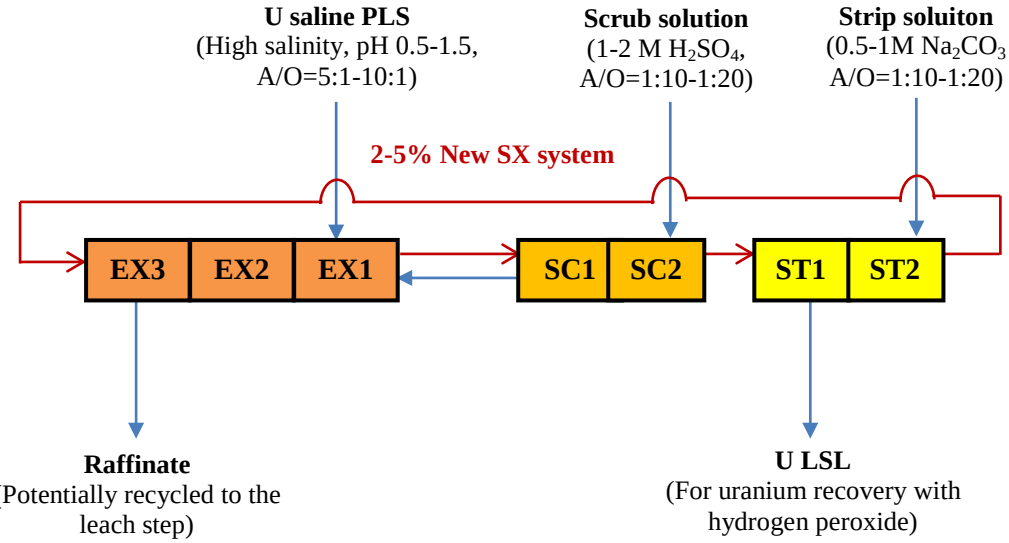

Fig. 8: A proposed process flowsheet

CONCLUSIONS

A new SX system has been developed which is suitable for the uranium recovery from saline leach solutions containing high chloride concentrations comparable to seawater. The SX system has high uranium selectivity over iron(III) with separation factor reaching >1000 in pH range of 1.0-1.5. Except vanadium, other commonly associated impurities, including Al, Mn, Cu, Zn, and Zr are not largely extracted and can be readily separated from uranium. Uranium separation from vanadium was poor and further investigation is required if it presents in the leach solution. More than 98% uranium could be extracted in the pH range of 0.5-1.5. Uranium extraction kinetics was fast, reaching equilibrium within 3 min. Two theoretical stages are required to completely extract uranium from the synthetic leach solution containing 1.2 g/L U at an A/O ratio of 4:1 using 5% New-SX system. About 74% uranium was stripped with 4 M H_2SO_4 solution in a single contact at an A/O ratio of 1:1. More than 98% uranium was stripped using 0.5 M Na_2CO_3 or $(NH_4)_2CO_3$ solution. A process flowsheet using the New-SX system is proposed.

ACKNOWLEDGMENTS

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APPLICATION OF MIXED PHOSPHONIC/PHOSPHINIC ACID REAGENTS FOR SEPARATION OF RARE EARTHS

By

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ABSTRACT

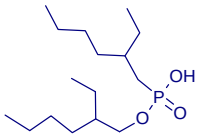
The separation of rare earth elements from each other is commonly achieved by solvent extraction, using EHEHPA (2-ethylhexyl phosphonic acid 2-ethylhexyl mono-ester, also known as P507, PC-88A and Ionquest 801). In recent years, mixed reagents containing EHEHPA and Cyanex 272 (a weaker, phosphinic acid reagent) have been put forward for this task. This work examines the extraction and separation of rare earths by EHEHPA, Cyanex 272, Cyanex 572 (a commercially available phosphonic/phosphinic acid reagent) and mixtures of EHEHPA and Cyanex 272.

We present results of a detailed study on the effect of pH and extractant concentration on distribution ratios of mixed reagents. The observed antagonistic impacts of mixed phosphonic/phosphinic reagents were studied by the method of continuous variation and supported by ^{31}P NMR and electrospray ionization-mass spectrometry (ESI-MS).

In this presentation we discuss the pros and cons of using these reagents for the production of high purity rare earths.

Keywords: rare earths, solvent extraction,

Rare Earth Solvent Extraction



EHEHPA – 2-ethylhexyl phosphonic acid
mono 2-ethylhexyl ester
('P507', 'PC88A', 'Ionquest 801')

Extraction consumes base

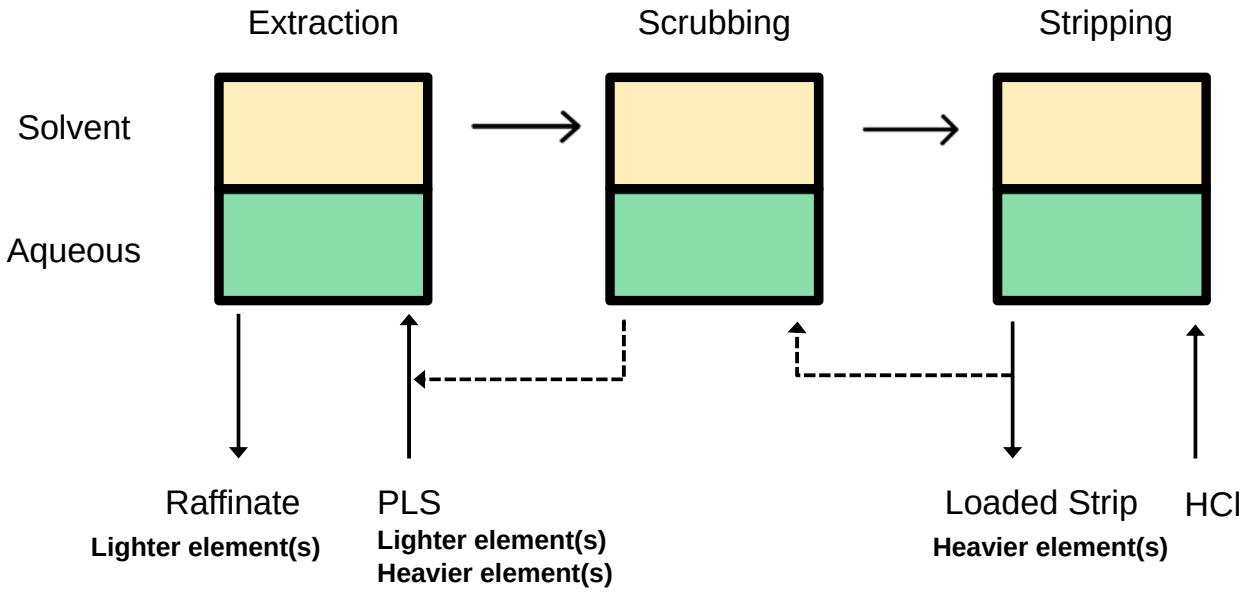
$$RE^{3+} + 3\ \overline{H_2A_2} \rightleftharpoons \overline{RE(HA_2)_3} + 3\ H^+$$

Stripping consumes acid

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Heavier elements are extracted in preference to lights

Rare Earth SX Circuits



Research Topic

Can mixed reagents improve the current RE SX process?

- Stripping Acidity → *Reduce reagent consumption.*
- Separation Factors → *Reduce number of stages.*
- Loading Capacity → *Reduce size of equipment.*

Quinn, J. E.; Soldenhoff, K. H.; Stevens, G. W.; Lengkeek, N. A., Solvent extraction of rare earth elements using phosphonic/phosphinic acid mixtures. *Hydrometallurgy.* **2015,** *157*, 298–305.

Problems With Current Process

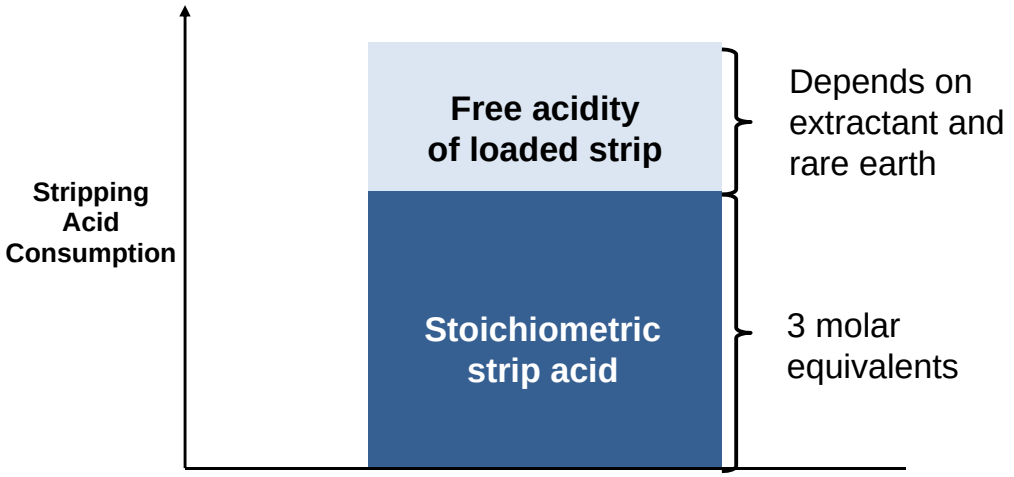
Small separation factors

System	Separation Factor
U / Fe (III) (tertiary amine)	>9000
Co / Ni (Cyanex 272)	~7000
Nd/Pr (EHEHPA)	**1.6**

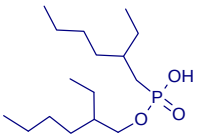
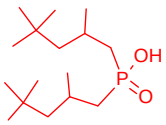
Many stages required

Problems With Current Process

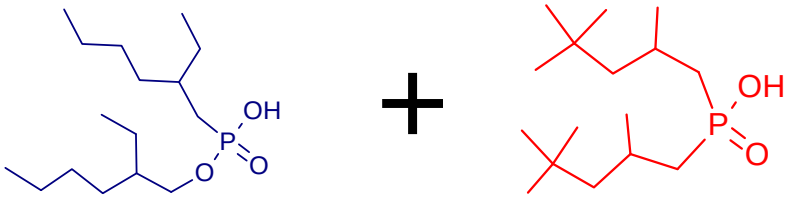
Large acid consumption for HRE



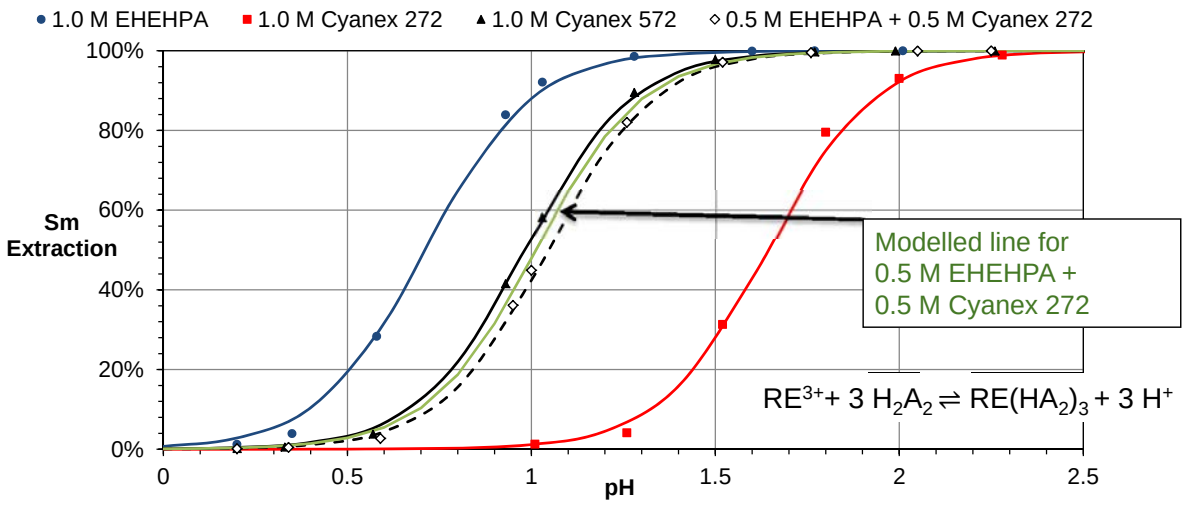
Phosphonic and Phosphinic Acids

Phosphonic (EHEHPA)	Phosphinic (Cyanex 272)	
		
Moderate pKa → high stripping acidity for heavy RE	Higher pKa = low stripping acidity	✓
Reasonable separation factors	Similar separation factors	–
Good loading capacity	Poor loading capacity	✗
Widely used industrially for RE separations	*Not commonly used industrially for RE separations*	

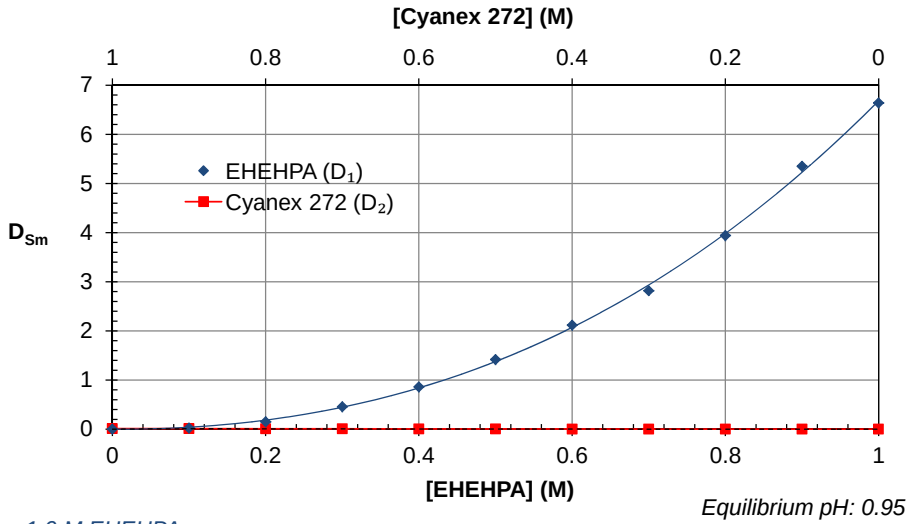
What about a mixture of **phosphonic** + **phosphinic** acids?



Effect of pH on extraction



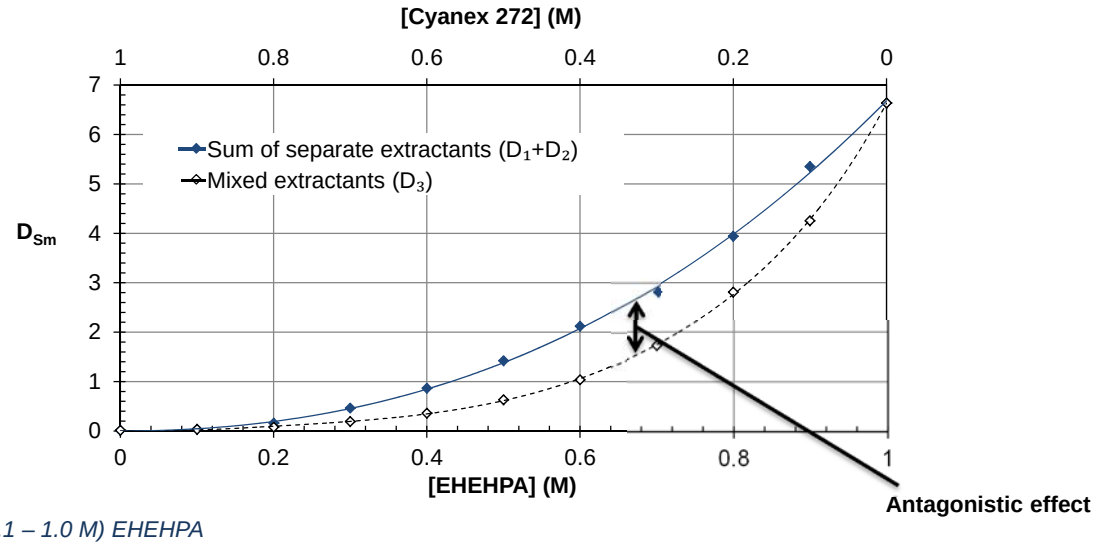
Effect of Solvent Composition



Equilibrium pH: 0.95

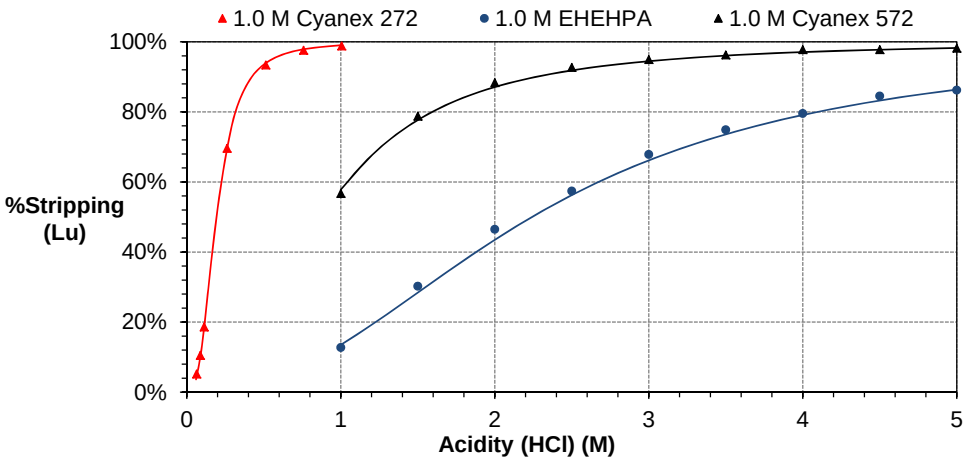
D_1: 0.1 – 1.0 M EHEHPA
D_2: 1.0 – 0.1 M Cyanex 272

Antagonistic Interaction



D_1: (0.1 – 1.0 M) EHEHPA
D_2: (1.0 – 0.1 M) Cyanex 272
D_3: (0.1 – 1.0 M) EHEHPA + (1.0 – 0.1 M) Cyanex 272

Impact on Stripping

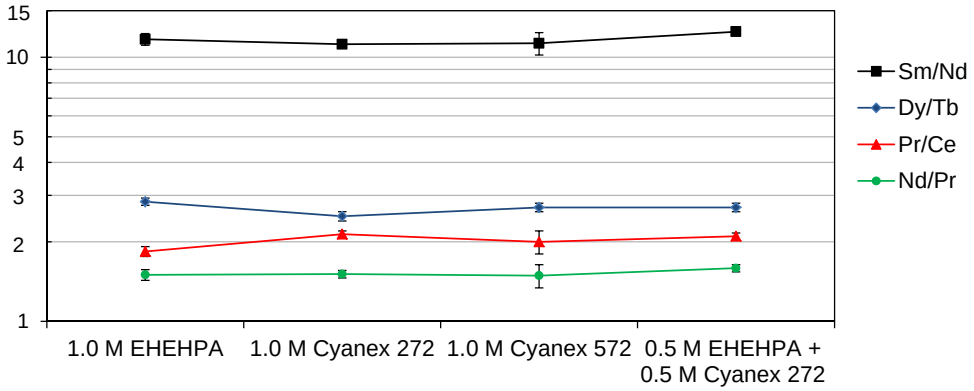


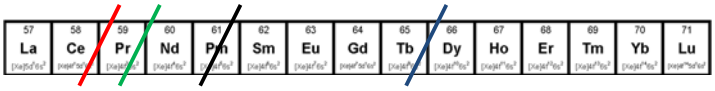
$$RE^{3+} + 3\,\overline{H_2A_2} \rightleftharpoons \overline{RE(HA_2)_3} + 3\,H^+$$

Performance of Mixed Reagent

- ✓ Reduction in stripping acid
- Separation Factors?
- Loading Capacity?

Separation Factors





Performance of Mixed Reagent

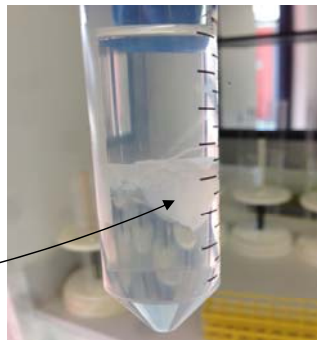
- ✓ Reduction in stripping acid
- ≈ Similar separation factors
- Loading capacity?

Loading Capacity

Theoretical loading capacity = $^1/_6$ × the extractant molarity:

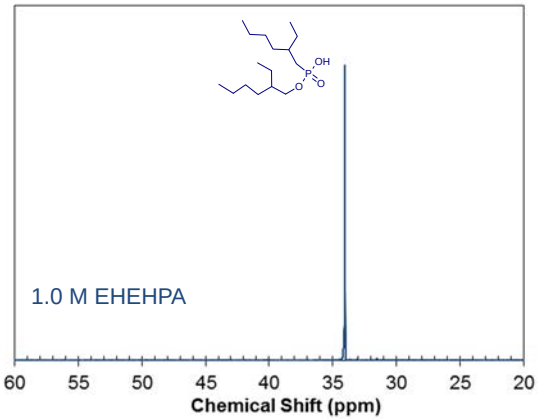
$$RE^{3+} + 3\ \overline{H_2A_2} \rightleftharpoons \overline{RE(HA_2)_3} + 3\ H^+$$

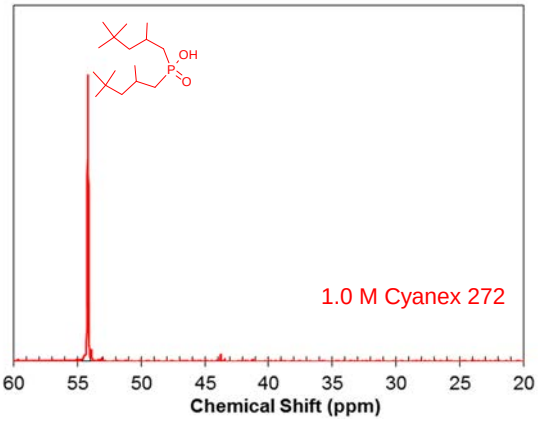
Precipitation of metal complex at high loading



Solubility of metal complex changes with reagent

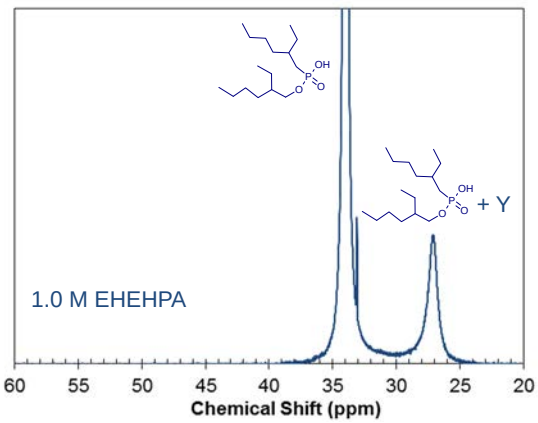
$^{31}P\{^1H\}$ NMR Study

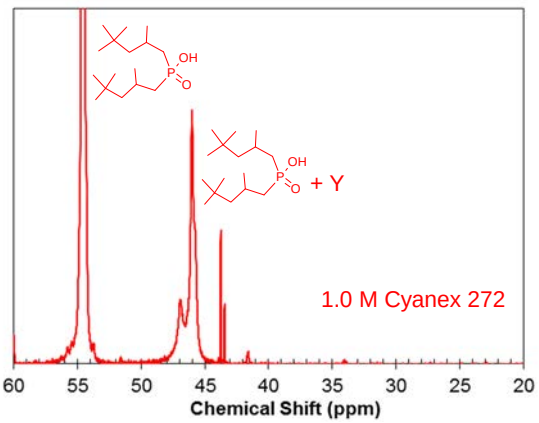




Before partial loading with yttrium

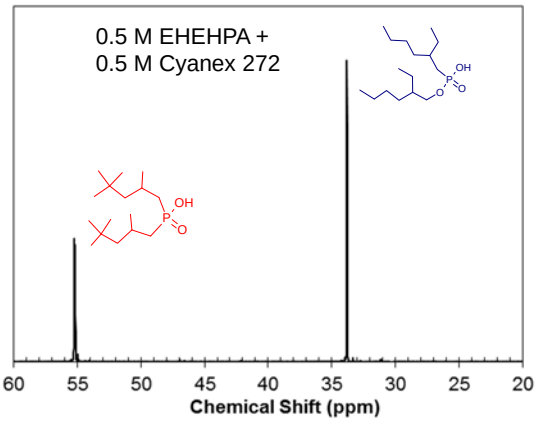
$^{31}P\{^{1}H\}$ NMR Study





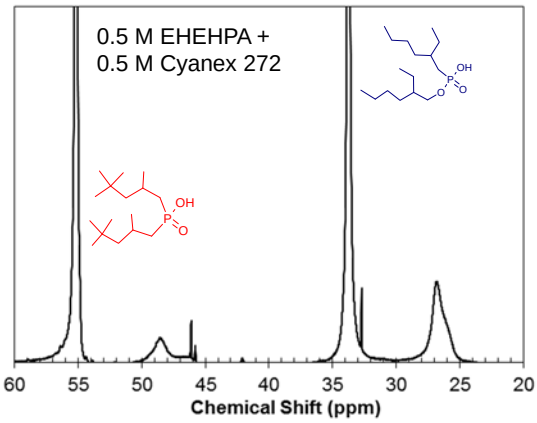
After partial loading with yttrium

$^{31}P\{^{1}H\}$ NMR Study



Before partial loading with yttrium

$^{31}P\{^{1}H\}$ NMR Study



After partial loading with yttrium

Loading Capacity

Solvent	[Yttrium] in organic phase when ppt. forms	Percentage of theoretical capacity
1.0 M EHEHPA	0.13 M	**78 %**
1.0 M Cyanex 572	0.048 M	**29 %**
1.0 M Cyanex 272	0.033 M	**20 %**

Diluent: Shellsol D60 (low aromatic kerosene)

Summary

Compared with EHEHPA, using mixed phoshonic/phosphinic reagents would result in:

- ✓ Reduction in stripping acid
- ≈ Similar separation factors
- ✗ Reduction in loading capacity

PROCESS DEVELOPMENTS FOR THE RECOVERY OF URANIUM AND MOLYBDENUM IN KAROO SANDSTONE DEPOSIT VIA SULPHURIC ACID LEACHING

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ABSTRACT

Low grade uranium deposits such as the Karoo Sandstone deposit in South Africa have remained unexploited to date, due to the low uranium price and high OPEX associated with the extraction of the uranium. The Karoo Sandstone deposit contains relatively high concentrations of carbonates which contributed to the high acid consumption in the sulphuric acid leach step. In order to reduce the OPEX, flotation of carbonates was investigated. Significant concentrations of molybdenum found in the deposit can cause cruds and third phases in the uranium solvent extraction unit operation which is problematic. Molybdenum removal was required prior to uranium solvent extraction and was thus considered as a potential by-product.

Laboratory test work done at Mintek showed that innovative combinations of flotation and solvent extraction process routes, resulted in promising reductions in processing costs. In order to quantify the impact of these improvements on the viability of exploiting the Karoo Sandstone deposits, a laboratory test work programme was undertaken to produce data for high level OPEX and revenue estimations.

The removal of calcite by flotation prior to leaching, had shown to reduce the acid consumption by >50% in the leach step, while still resulting in a uranium recovery of greater than 85%. Selective extraction of molybdenum from the leach liquor by the oxime extractant showed that greater than 98% of the molybdenum could be recovered without significant uranium co-extraction.

OPEX estimations indicated that the main cost component was the leach unit operation. A significant reduction (62%) of OPEX was achieved due to the removal of acid consumers by flotation. The cost of molybdenum solvent extraction (0.04 USD/tonne) was low as compared to the revenue (6 USD/tonne) generated for molybdenum recovery. This was an indication that the recovery of molybdenum as a by-product was favourable. The increase in molybdenum recovery by leaching at a lower pH value of 1.2 did not enhance the potential profit due to the higher acid consumption. Uranium recovery is thus the primary target for processing of the Karoo Sandstone deposit. Hydrometallurgical data and economic estimations based on the test work done have shown that the recovery of high purity uranium and molybdenum from the Karoo Sandstone deposit was favourable.

Keywords: Uranium, molybdenum, flotation, leaching, solvent extraction

INTRODUCTION

The Karoo Sandstone deposit occupies an area which is equivalent to about one-third the total area of South Africa. The Karoo region (see Figure 1) is arid to semi-arid and its name loosely translated into English means “land of thirst”[1].

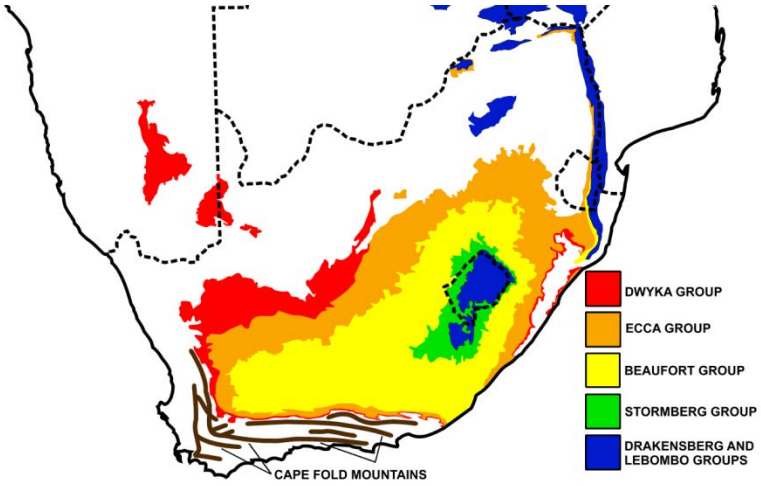

Figure 1: Map of the Karoo Supergroup[2]

The area has known resources of uranium, molybdenum and shale gas. It consists of six deposits which are collectively referred to as the Karoo Supergroup i.e. Dwyka, ECCA, Beaufort, Stormberg, Drakensberg and Lebombo[2]. Exploration of the deposit has occurred mainly in the Beaufort area, as it is believed to be amenable to open cast mining. The grades of uranium and molybdenum are 1.2 kg/tonne of ore and 0.6 kg/tonne of ore, respectively[3]. The South African government intends to add 9 600 MW of nuclear power to the national grid over the next 15 to 20 years, and it is crucial that there is feed- stock available to power these plants. The uranium needed for South Africa’s new nuclear power plants could come from the Karoo Sandstone deposit[4].

Mintek has been tasked to evaluate process options for unlocking the Karoo Sandstone deposit. The recovery of uranium from the Karoo Sandstone deposit via atmospheric acid and alkaline leaching conditions had been investigated, and the results from this research indicated that the acid leach resulted in higher uranium recoveries within a reasonable residence time[3]. However, high acid consumptions associated with uranium acid leaching affected the economic viability of processing the deposit. Since the Karoo Sandstone deposit contains relatively high concentrations of carbonates, the rejection of carbonates are likely to have a significant impact on the viability of mining this resource. Molybdenum removal prior to uranium solvent extraction is essential, as it causes third phases and crud formations when using Alamine®336 in conventional uranium recovery circuits[5, 6, 7]. Hence, the recovery of molybdenum as a by-product was evaluated.

Currently, Mintek is investigating various process options to unlock the Karoo Sandstone deposit to recover uranium and molybdenum. The focus was on the removal of carbonates via flotation, followed by leach optimisation and solvent extraction test work for uranium and molybdenum recovery. A simplified block flow diagram of the process evaluated is shown Figure 2.

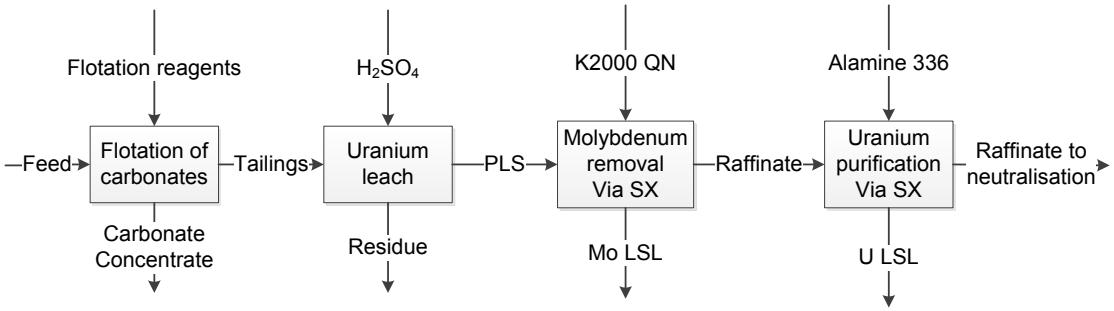

Figure 2: Simplified block flow diagram for the processing of the Karoo Sandstone deposit for uranium and molybdenum recovery

Laboratory and bulk test work presented in the current paper were done using a sample obtained from the Beaufort-West area in the Karoo Basin. The results obtained were used in a high level economic evaluation to determine the viability of processing the Karoo Sandstone deposit.

EXPERIMENTAL

Analytical Methods

Solid samples were analysed for U_3O_8 via X-ray Fluorescence (XRF) spectroscopy and analysed for base metals via Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Aqueous and organic samples were analysed using ICP-OES. The respective detection limits for the methods are given in Table 1.

Table 1: Chemical analyses and detection limits

Analysis	Method	Detection Limit
U_3O_8	XRF 15	10 mg/kg (matrix dependant)
Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn & Pb	ICP-OES	Lower limit 0.05%,Upper limit 40%-solids 2mg/L -solutions
Mo	ICP-MS	0.1 mg/kg
CO_3^-	Combustion	0.5%
Fe^{3+},Fe^{2+}, H_2SO_4	Titration	

Mineralogical Assessment

The Karoo feed sample was crushed to 100% passing 1.7 mm using a jaw crusher and thereafter by a cone crusher. The mineralogical assessment of the feed sample was done using the Mineral Liberation Analyzer (MLA) method. The method can quantify a wide range of mineral characteristics, such as mineral abundance, grain size and liberation. The MLA was used to ascertain information such as the type of uranium minerals present, their liberation characteristics (in terms of volume percentage liberation), grain size distributions and mineral associations, particularly with molybdenum, carbonates, any carbonaceous matter and other minerals.

Flotation

Reverse flotation was used to reject the carbonates upfront before the leach circuit. The products of the reverse flotation process were a carbonate rich flotation concentrate and a uranium rich flotation tailings. The milled Karoo feed material (80% passing 106 µm) was transferred into a 2.5 L Denver flotation cell at an impeller speed of 1200 rpm. Carbonate removal was conducted in accordance with the flowsheet as shown in Figure 3.

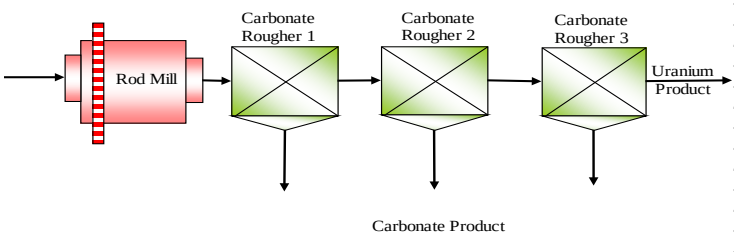

Figure 3: Flowsheet for the flotation of carbonates

The flotation conditions used for carbonate removal are presented in Table 2.

Table 2: Flotation conditions tested

Solids	Grind (P80)	Dosage		
		Dextrin	Soda Ash	Na_2SiO_3
%	µm	g/t	g/t	g/t
38	106	140	50	200

Leach Test Work Procedures

The flotation tailings (uranium rich product) were used as a feed material for the leach tests. The parameters which were varied during optimization were pH and temperature of the leach. The flotation tailings sample (1 kg) was slurried to 40 (m/m)% solids in a synthetic barren solution/raffinate. The synthetic raffinate solution contained 2 g/L ferric sulphate, and was at a pH value of 1.5 and a redox potential of 450 mV [Ag/AgCl]. Leach tests were done according to the conditions stipulated in Table 3.

Table 3: Optimization of leach conditions on flotation tailings

Test #	Name	pH	Temperature	Eh (Ag/AgCl)	Oxidant addition	Solids	Time
			°C	mV [Ag/AgCl]		%	Hrs
1	pH Scoping	1.5	25	450	added	40	24
2	pH Scoping	1.2	25	450	none	40	24
3	Temperature Scoping	1.2	50	450	none	40	24

The slurry was stirred with an overhead stirrer while the pH was maintained at the targeted value using 800 g/L of sulphuric acid (H_2SO_4). Manganese dioxide (MnO_2) was added for the first hour of the leach Test 1, to maintain a redox potential greater than 450 mV [Ag/AgCl]. The pH and Eh were measured and recorded hourly. After 24 hours, the slurry was filtered and washed. The residue was re-pulped washed twice with pH 2 adjusted water and finally with deionised water at a mass of wet cake ratio to water ratio of 1:2. The feed, washed residues and filtrates were submitted for analyses.

Solvent Extraction Test Work Procedures

Organic and Aqueous Solutions

The composition of the organic phase used for molybdenum extraction was 15 (v/v) % K2000 QN and 7.5 (v/v) % phase modifier (Isodecanol) in an aliphatic diluent (Shellsol D70). A composition of 5 (v/v) % Alamine®336 and 2.5 (v/v) % Isodecanol in Shellsol D70 was used for uranium extraction. The organic extractants and diluent were not treated prior to use.

Colloidal Silica Removal from Pregnant Leach Solution (PLS)

Silica removal was carried out by contacting a portion of concentrated coagulant with the Karoo PLS targeting a coagulant concentration of 200 mg/L in the PLS. The solutions were contacted by rapid stirring using an overhead stirrer in a reactor which was fitted with baffles at ambient temperature. The solution was stirred for 30 minutes and left overnight for the colloidal silica to precipitate out of solution. The solution was then filtered and a sample of the filtered feed solution was submitted for analysis.

Batch Contacts for Extraction and Stripping

Batch contacts were done by contacting the aqueous phase with the organic phase at the specified O/A phase ratio and pH value. Mixing of the phases was accomplished using a magnetic stirrer and stirring bar agitated at 500-750 rpm to ensure homogeneous dispersion of the two phases. The pH value (measured by means of a calibrated combined glass-reference electrode) of the aqueous phase was adjusted by the addition of a suitable acid/base. After the two phases had been contacted for a duration of 15 minutes, samples of both the aqueous and organic phases were filtered and submitted for analyses.

Extraction/Stripping Equilibrium Isotherm

Extraction/stripping equilibrium isotherms were generated by contacting the aqueous phase with the organic phase at various O/A phase ratios. Mixing of the phases was accomplished using a magnetic stirrer and stirring bar agitated at 500-750 rpm to make sure that homogeneous dispersion of the two phases occurred. The pH value (measured by means of a calibrated combined glass-reference electrode) of the aqueous phase was once again adjusted by the addition of a suitable acid/base (if required). When the suitable equilibrium pH value had been reached after mixing for 15 minutes, samples of both the aqueous phases and the organic phases were filtered and submitted for analyses.

RESULTS AND DISCUSSION

Chemical and Mineralogical Characterisation of the Sample

The average analyses of the head sample which was used as feed material for the flotation test work is shown in Table 4. The uranium minerals and relative proportions are given in Table 5.

Table 4: Average head sample analysis of Karoo Sandstone ore

Average concentration					
Al	**%**	6.27	**Ti**	**%**	0.29
Ca	**%**	3.90	**CO_3**	**%**	5.39
Fe	**%**	1.75	**Organic carbon**	**%**	0.08
Mg	**%**	0.43	**Total carbon**	**%**	1.16
Mn	**%**	0.15	**U_3O_8**	**g/t**	3830
Si	**%**	30.20	**Mo**	**g/t**	443

Table 5: Uranium minerals and relative proportions in the head grade sample

Mineral	Chemical Formulae	Mass	U normalised deportment	U content	No. of grains
		%	%	%	
Coffinite	$USiO_4\ H_2O$	99.71	99.92	72.64	984
Mourite	$UMo_5O_{12}(OH)_{10}$	0.29	0.08	22.04	8

The sample contained relatively high concentrations of carbonates as calcite (5.4%), 443 g/t Mo and 3831 g/t U_3O_8. Based on mineralogical analysis, >99 (m/m) % of the total uranium in the sample was present as coffinite, while the remaining uranium was associated with mourite (U-Mo mineral). Gangue minerals which were found in the deposit were pyrite, mica, feldspar, molybdenite, chlorite, calcite, quartz, talc and arsenopyrite.

Different liberation classes were used to define the liberation of the uranium minerals in the sample. The liberation analysis of the uranium minerals in the sample are given in Table 6. Only 1.28% of the major uranium mineral, coffinite was locked, the remaining portion was either partially exposed or liberated which would be favourable for uranium leaching.

Table 6: Liberation analyses of uranium minerals

Mineral	Locked	Partially exposed	Liberated	Total
	%	**%**	**%**	**%**
Coffinite	1.3	74.7	24.0	100
Mourite	9.6	33	57.5	100

Locked - Less than 30% of the surface of the particle was liberated;
Partially exposed - 30-80 % of the surface of the particle was liberated;
Liberated - More than 80% of the surface or the particle was liberated

Flotation

Flotation conditions as shown in Table 2 were applied to float carbonates from the feed material milled to 80% passing 106 µm. Uranium recovery of 84% and carbonate rejection of 46% was achieved. A total flotation time of 12 minutes was used to remove the carbonates. The uranium loss was 16% at a mass pull of 11.3%. The flotation results for the concentrate and tailings are shown in Table 7.

Table 7: Summarised flotation results

Products	Mass, Ret		Grade				Recovery			
			U_3O_8	Ca	Mo	CO_3	U_3O_8	Ca	Mo	CO_3
	g	%	%		g/t	%	%			
Feed	16016	100	0.38	3.9	443	5.4	100			
Carbonate Concentrate	1803	11.3	0.60	21.7	602	19	16	46	18	46
Uranium Tailings Product	14213	88.7	0.39	3.24	346	3.2	84	54	82	54

The significant reduction in carbonate content was a major improvement to the process. Further optimization test work is planned to be done at Mintek to minimize uranium losses in the flotation concentrate.

Leaching

The flotation tailings (uranium product) was used as feed solids for leach optimisation test work. The leach optimisation tests were done to achieve maximum uranium recovery and minimise reagent addition. The results for the leach optimisation tests are listed in Table 8.

Table 8: Uranium recovery and reagent consumptions

Test # and conditions	Recoveries*		H_2SO_4 consumption	MnO_2 addition
	U_3O_8	Mo		
	%	%	kg/t	kg/t
Test 1 (pH 1.5, 25 °C)	89	50	58	0
Test 2 (pH 1.2, 25 °C)	90	74	73	0.6
Test 3 (pH 1.2, 50 °C)	93	67	91	0

*Recoveries based on solids analyses

Tests 1 and 2 resulted in similar uranium extractions. Leaching at a lower pH value of 1.2 resulted in an increase in the uranium leach efficiency of only about one percent however molybdenum extraction increased to 74%. An increase in the leach temperature from 25°C to 50°C resulted in a slight increase in uranium recovery of ~3%.

Acid consumptions increased from 58 to 91 kg/tonne for Test 1 and Test 3, respectively, due to the decrease in pH combined with an increase temperature of the leach. The addition of MnO_2 was found to be unnecessary as the redox potential was well above 450 mV [Ag/AgCl]. The optimum leach conditions for uranium recovery were at a pH value of 1.5, no oxidant addition and at ambient temperature. Molybdenum extraction in the leach step was not the primary target.

A base line leach test was also conducted on the feed material prior to the flotation of carbonates and relatively high uranium extractions (90%) were obtained, but at an increased acid consumption of 143 kg/tonne.

The conditions for Test 1 were identified as the optimum leach conditions (ambient temperature and pH 1.5) as the lowest sulphuric acid consumption was achieved for this test. A bulk leach was done using optimised conditions to generate feed solution for purification test work. The acid consumption for the bulk leach was 52 kg/tonne.

Colloidal silica removal from the bulk PLS, was done prior to solvent extraction test work to prevent crud and emulsion formations. The Si concentration decreased from 376 mg/L to 172 mg/L. These results indicated that 47% of the Si was removed after the addition of the coagulant. The remaining Si could be attributed to dissolved Si. The average feed composition used for the solvent extraction test work is given in Table 9.

Table 9: Average feed composition after colloidal silica removal

Average concentration (mg/L)			
Al	283	**Mn**	270
As	85	**Mo**	81
Ca	638	**Ni**	8.1
Cd	<2	**Pb**	6.4
Co	14	**Si**	172
Cr	<2	**Ti**	<2
Cu	5.1	**V**	<2
Fe	2620	**Zn**	9.7
Li	2	**U_3O_8**	1915
Mg	98		

Solvent Extraction

Two solvent extraction reagents utilising different extraction mechanisms were used for the sequential recovery of molybdenum and uranium from the PLS.

Molybdenum Solvent Extraction

Mo(VI) is present in the aqueous solution as anionic species but in an acidic medium it partially converts to various cationic ions as presented in Figure 4.

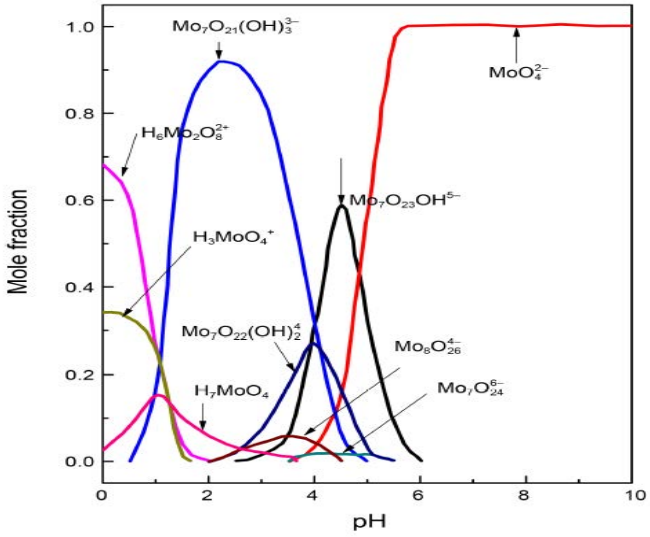

Figure 4: The distribution of molybdenum species in the Mo – H_2O system as a function of pH with a total MoO_4^- concentration of 21.20 mM[8]

The organic extractant, 2-hydroxy-5-nonylacetophenone oxime (K2000 QN), was used for molybdenum recovery which was extracted through a chelating mechanism.

Extraction Equilibrium Isotherm

The McCabe-Thiele construction for molybdenum extraction at a pH value of 1.5 (target pH of bulk leach), using 15 (v/v)% K2000 QN and 7.5 (v/v)% Isodecanol in Shellsol D70 and Karoo PLS, is presented in Figure 5.

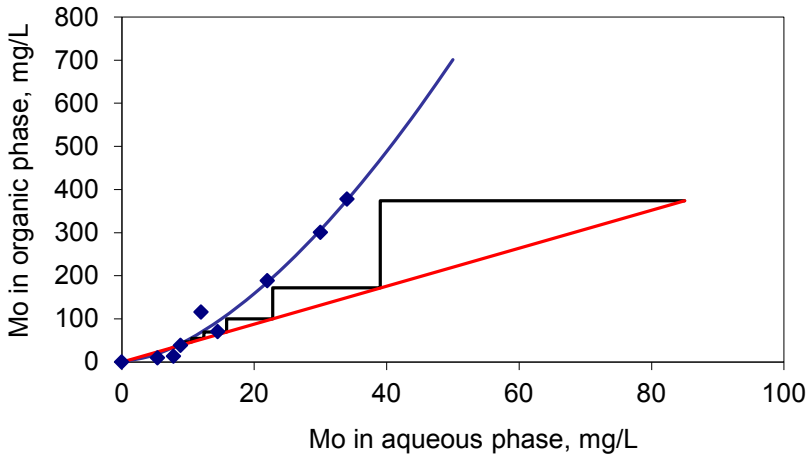

Figure 5: McCabe-Thiele construction for molybdenum extraction, using 15 (v/v)% K2000 QN and 7.5 (v/v)% Isodecanol in Shellsol D70 and Karoo Sands PLS at 25ºC (pH 1.5)

No crud formation was observed at the various O/A phase ratios tested. The McCabe-Thiele constructions which were done for the isotherm as shown in Figure 5, indicated that about 4 counter-current stages at an O/A phase ratio of 0.2 would be required at a pH value of 1.5 to achieve a molybdenum loading on the organic phase of ~374 mg/L.

Even though the shape of equilibrium isotherm indicated that molybdenum adsorption was unfavourable, it was extracted selectively from iron and uranium present in the liquor. Selectivity coefficients calculated for molybdenum extraction over uranium and iron (see Table 10 for details) were in the range of 1000-4000 and 200-700, respectively, depending on the ratio tested.

Table 10: Distribution ratios and separation factors for the extraction equilibrium isotherm using 15 (v/v)% K2000 QN and 7.5 (v/v)% Isodecanol in Shellsol D70 and Karoo Sands PLS at 25ºC

O/A phase ratio	Distribution ratios			Separation factors	
	Mo	Fe	U_3O_8	Mo-Fe	Mo- U_3O_8
0.05	1.799	0.008	0.001	231	1384
0.10	3.406	0.006	0.001	547	2597
0.50	4.750	0.007	0.001	641	3659
2.00	4.382	0.007	0.001	662	3557
10.00	1.852	0.007	0.001	264	1465

The unfavourable shape of the equilibrium isotherm can presumably be attributed to speciation of molybdenum in the leach liquor. K2000 QN extracts cationic species only, while molybdenum can form a number of cationic and anionic species at pH 1.5 as shown Figure 4.

Due to the low concentration of molybdenum in this particular feed solution to SX (only 80 mg/L was present) it could also be possible to use ion exchange for molybdenum removal to reduce OPEX and CAPEX further.

Batch loading of 15 (v/v) % K2000 QN and 7.5 (v/v) % Isodecanol in Shellsol D70 was done to generate a loaded organic phase for further scrubbing and stripping test work. The batch loading of the organic phase was done in four counter-current stages and at ambient temperature as indicated by the McCabe-Thiele construction in Figure 5. The composition of the loaded organic phase is given in Table 11.

Table 11: Composition of loaded organic phase (15 (v/v) % K2000 QN and 7.5 (v/v) % Isodecanol in Shellsol D70) after four batch contacts

Concentration (mg/L)	
Fe	58
Cu	57
Zn	<2
Mo	352

Bulk scrubbing of the organic phase was done using 50 g/L sulphuric acid at an O/A phase ratio of 20 to scrub off impurities such as copper and iron. A high O/A phase ratio was used as the spent scrub liquor stream would be recycled back to the leach unit operation. It is therefore ideal to ensure that the volumetric flow of the spent scrub liquor is as low as possible to prevent a significant dilution of the PLS in the leach step. The impurities which were reported in the loaded organic phase were most likely due to the detection limit of the analytical method used, as a pure loaded strip liquor was produced in subsequent test work.

Strip Equilibrium Isotherm

The scrubbed organic phase (15 (v/v)% K2000 QN and 7.5 (v/v)% Isodecanol in Shellsol D70) was used for stripping test work. A strip equilibrium isotherm was done using 0.5 M ammonium sulphate at a pH value of 6. A concentration of 70 g/L ammonium hydroxide and 200 g/L sulphuric acid were used to adjust the pH of the solution. A pH value of 6 was chosen for the stripping equilibrium isotherm based on previous test work done[9]. The strip equilibrium isotherm presented in Figure 6, shows that molybdenum stripping was favourable.

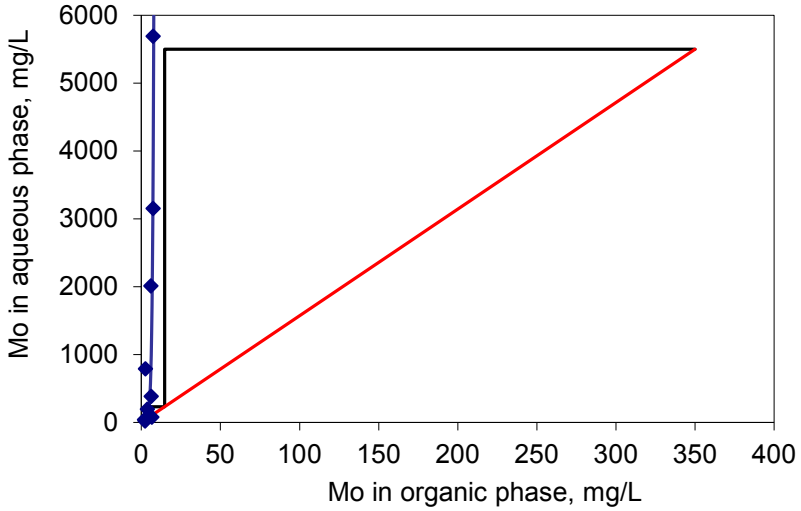

Figure 6: McCabe-Thiele construction for molybdenum stripping using 0.5 M ammonium sulphate at a pH value of 6 and at ambient temperature

McCabe-Thiele constructions done for the isotherm indicated that 2 counter-current stages at an O/A phase ratio of ~16 would be required for complete molybdenum stripping from the organic phase. A loaded strip liquor concentration of ~6 g/L molybdenum could be produced. Slow phase separation was observed at an O/A phase ratio of 2. Slight skin developments were observed at O/A phase ratios ≥5. A pilot plant run would help to determine if these physical problems would be major issues on a full scale plant.

The strip liquors contained molybdenum only; all the other elements were reported below the analytical detection limit of 2 mg/L. This indicates that a high purity molybdenum product can be produced and that the conditions applied during scrubbing were adequate.

Uranium Solvent Extraction

Uranium dissolves as UO_2^{2+} and forms two uranyl sulphate ion complexes in a sulphuric acid leach. The species formation is described by Equation 1 and Equation 2 below[2]:

$UO_2^{2+}(aq) + 2SO_4^{2-}(aq) \rightarrow UO_2(SO_4)_2^{2-}(aq)$ *Equation 1*

$UO_2(SO_4)_2^{2-}(aq) + (SO_4)^{2-}(aq) \rightarrow UO_2(SO_4)_3^{4-}(aq)$ *Equation 2*

Uranyl sulphate is typically extracted from a sulphuric acid medium using C8-C10 tertiary amines (Alamine®336). Equations 3 and 4 show the protonation of the tertiary amine and thereafter the extraction of the uranyl sulphate ions by means of ion pair formation[3].

$R_3N_{(org)} + H_2SO_4 \leftrightarrow [R_3NH^+]HSO_4^-{}_{(org)}$ *Equation 3*

$4[N(R)_3H^+(HSO_4)^-]_{(org)} + H_4UO_2(SO_4)_3 \rightarrow [N(R)_3H]_4UO_2(SO_4)_{3\,(org)} + 4H_2SO_4$ *Equation 4*

Extraction Equilibrium Isotherm

Molybdenum removal was required prior to uranium purification to prevent the contamination of the final uranium yellow cake. A single batch contact was done to remove molybdenum and to generate a feed solution for uranium recovery. An organic phase concentration of 15 (v/v) % K2000 QN and 7.5 (v/v) % Isodecanol in Shellsol D70 was used for a single batch extraction done at an O/A phase ratio of 6.8 and at a pH value of 1.5. The composition of the raffinate produced after the single contact, which was used for further uranium purification test work, is given in Table 12.

Table 12: Raffinate composition after molybdenum removal

Concentration (mg/L)			
Al	304	**Mn**	285
As	84	**Mo**	<2
Ca	649	**Ni**	8.5
Co	15	**Pb**	7.4
Cr	<2	**Si**	161
Cu	<2	**Ti**	2.4
Fe	2560	**V**	<2
Mg	106	**Zn**	14
U_3O_8	1915		

The raffinate solution produced was used to generate a uranium extraction equilibrium isotherm. The composition of the organic phase was 5 (v/v)% Alamine®336 and 2.5 (v/v)% Isodecanol in Shellsol D70. The extraction equilibrium isotherm was done at ambient temperature with no pH control. It should be noted that clear phases were present at all the O/A phase ratios that were tested. The McCabe-Thiele construction which was done for the extraction equilibrium isotherm is as shown in Figure 7.

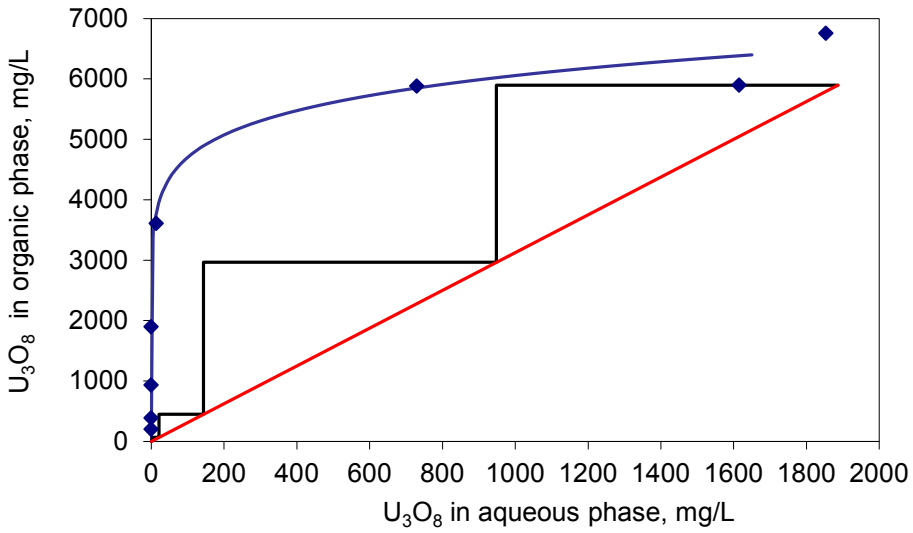

Figure 7: McCabe-Thiele construction for uranium extraction using 5 (v/v)% Alamine®336 and 2.5 (v/v)% Isodecanol in Shellsol D70 and feed solution (molybdenum raffinate solution) at 25ºC

The McCabe-Thiele construction indicated that at an O/A phase ratio of 0.3, three counter-current stages were required for uranium recovery. Bulk batch loading was done to generate a loaded organic phase for further scrubbing and stripping test work. Three batch contacts were done by contacting the organic phase (5 (v/v)% Alamine®336 plus 2.5 (v/v)% Isodecanol in Shellsol D70) with PLS at an O/A phase ratio of 0.3. The composition of the loaded organic phase after the three contacts is given in Table 13. The loaded organic phase which was generated contained relatively low concentrations of impurities such as Si, Ca, Ti and Mg.

Table 13: Composition of loaded organic phase after the bulk batch contacts using organic phase (5 (v/v)% Alamine®336 and 2.5 (v/v)% Isodecanol in Shellsol D70) and feed solution (i.e. raffinate produced from molybdenum SX)

Concentration (mg/L)			
Al	<2	**Fe**	<2
Si	77	**Co**	<2
Ca	21	**Ni**	<2
Ti	5.8	**Cu**	<2
V	<2	**Zn**	2.7
Cr	<2	**Pb**	<2
Mn	<2	**Mg**	30
As	<2	**Mo**	<2
U_3O_8	5558		

The loaded organic phase that was generated by bulk batch loading was scrubbed using the standard scrub solutions which are used in industry for uranium purification by Alamine®336 SX. Scrubbing was done at ambient temperature and at an O/A phase ratio of 30. Three scrub solutions were used, namely pH adjusted water (at a pH value of 1.8), 10 g/L sulphuric acid and 120 g/L ammonium sulphate solution. The scrub water at a pH value of 1.8 acted as a displacement wash. The 10 g/L sulphuric acid solution was used to scrub off the iron and the 120 g/L ammonium sulphate solution at a pH value of 2.3 was used to scrub off impurities such as silica, zirconium, arsenic and other metal anions. Efficient scrubbing of magnesium, silica and calcium were achieved. The uranium that scrubbed off the organic phase would be recycled back to the leach step and is not lost.

Strip Equilibrium Isotherm

The McCabe-Thiele construction for uranium stripping using 120 g/L ammonium sulphate as a strip liquor and the scrubbed organic phase is shown in Figure 8.

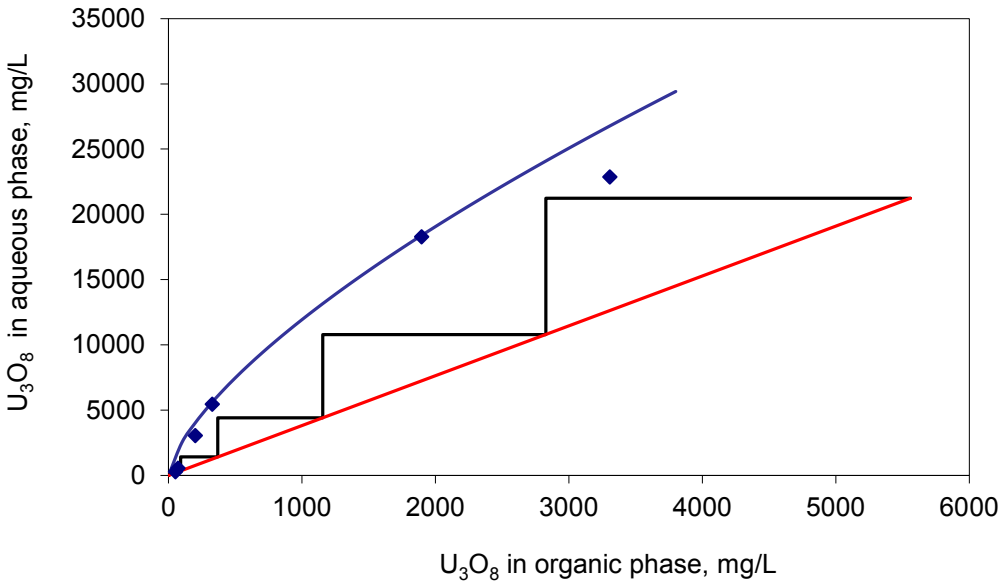

Figure 8: McCabe-Thiele construction for uranium stripping using scrubbed organic phase (5 (v/v) % Alamine®336 and 2.5 (v/v) % Isodecanol in Shellsol D70) and ammonium sulphate at a temperature of 25ºC

The stripping of uranium from the organic phase occurred via deprotonation of the organic phase as indicated in Equation 5[10]:

$$(N(R)_3H)_4UO_2(SO_4)_3 + 0.4(NH_4)2SO_4 + 3.2NH_3 \rightarrow 3.2N(R)_3 + 0.4[N(R)_3H]_2SO_4 + (NH_4)_4UO_2(SO_4)_3$$

Equation 5

Gradual pH adjustment is required for uranium stripping as a too sudden increase in the pH would result in uranium yellow cake formation which is undesirable for the operation of mixer-settler cells. A 200 g/L sulphuric acid solution and 70 g/L ammonium hydroxide solution were used to control pH between 5.54 and 3.41. Skin formation was observed at an O/A phase ratio of 0.05; all other O/A phase ratios that were tested resulted in clear phases. The McCabe-Thiele construction indicated that at an O/A phase ratio of 3.82, approximately four counter-current stages would be required for stripping of uranium off the organic phase.

The strip liquors contained uranium only, all the other elements analysed were reported below the analytical detection limit of 2 mg/L. The loaded strip liquor could therefore be used directly for the production of yellow cake (ammonium diuranate in this instance).

High Level Economic Valuation

The results obtained from the laboratory test work were used to estimate OPEX related to reagent flows while the revenue was calculated using current metal prices. The OPEX and revenue were compared for three process options, to determine the effect of including an upfront carbonate removal step via flotation and the recovery of molybdenum as a by-product. The sequence of the processing steps for Option A, Option B and Option C was as follows:

Leaching → *Mo SX* → *U SX* A

Carbonate flotation → *Leaching (pH = 1.5)* → *Mo SX* → *U SX* B

Carbonate flotation → *Leaching (pH = 1.2)* → *Mo SX* → *U SX* C

Option B targeted maximum uranium recovery in the leach step whilst Option C targeted uranium and molybdenum recovery. The efficiency of each process step was based on laboratory test work described above as summarised in Table 14.

Table 14: Molybdenum and uranium recoveries for process routes A and B

Unit operations	Recoveries	
	U_3O_8 (%)	Mo (%)
Route A		
Leaching	90	74
Solvent extraction	98	98
Overall recovery	**88**	**73**
Route B		
Flotation	84	82
Leaching	89	50
Solvent extraction	98	98
Overall recovery	**65**	**36**
Route C		
Flotation	84	82
Leaching	90	74
Solvent extraction	98	98
Overall recovery	**74**	**59**

A feed rate of 500 000 tonnes of ore per annum at a uranium and molybdenum content as listed in Table 15 was used as a basis for the high level OPEX and revenue estimates.

Table 15: Flow of feed material and composition

Feed	500 000	tonnes of ore/annum
U_3O_8 (%)	0.38	%
Mo (%)	0.04	%

The overall recovery for uranium and molybdenum was 88% and 73%, respectively (see Table 14), for process Option A. Some uranium and molybdenum losses occurred in the flotation step, hence, the overall recoveries for uranium and molybdenum for Option B and Option C were lower than that of Option A. OPEX and revenue estimations were based on the price of value metals and processing reagents as shown in Table 16.

Table 16: Price of chemicals used for OPEX estimations

Chemical	Price (USD/ton)	Reference source
U_3O_8	60 627	(11)
MoO_3	17 505	(12)
Dextrin	400	(13)
Soda Ash	215	(14)
Sodium silicate	500	(15)
Sulphuric acid	200	(16)
K2000	12 000	(17)
Shellsol D70	1 950	(18)
Isodecanol	1 000	(19)
Ammonium sulphate	200	(20)
Alamine® 336	12 500	(21)
Manganese dioxide	1 850	(22)

The total revenue and OPEX estimates for each option are summarized in Table 17. Organic losses in the solvent extraction circuit were assumed to be 5% per annum. The strip and scrub reagents would be recycled and it was assumed that losses for these streams were 10 % per annum. It should be noted that recycling of the residual sulphuric acid in the PLS was assumed to be not viable due to the relatively low tenors (~3 g/L free sulphuric acid).

Table 17: Total revenue and OPEX for Option A, Option B and Option C

Process circuits	Option A	Option B	Option C
	USD/tonne of ore		
Flotation circuit cost	0	0.20	0.20
Leaching circuit cost	29	10	16
Mo solvent extraction circuit cost	0.05	0.04	0.04
U solvent extraction circuit cost	0.03	0.02	0.02
Total OPEX	**29**	**11**	**16**
Total Revenue	**247**	**183**	**187**
OPEX/Revenue	11%	6%	9%

The percentage of OPEX/revenue for Option A and Option B as shown in Table 17, decreased from 11% to 6%, respectively. This was an indication that the introduction of a flotation step was favourable. However further optimisation of the flotation carbonate rejection step will most probably improve the attractiveness of processing the Karoo Sandstone deposit.

The costs associated with each unit operation and the total OPEX for Option A and B is illustrated in Figure 9.

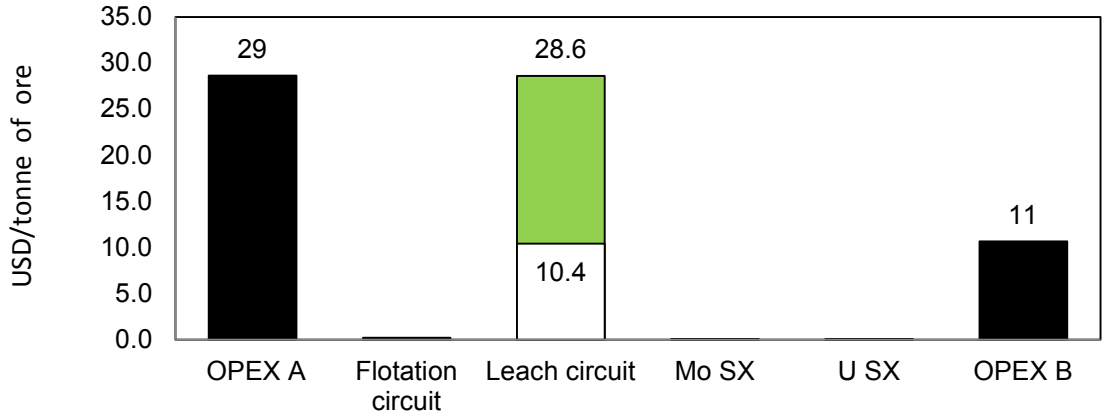

Figure 9: Costs of each unit operation and the overall OPEX for Option A and Option B

The main cost component of both options was the leach unit operation (see Table 17 and Figure 9). The introduction of the flotation step resulted in a drastic reduction in OPEX from 29 USD/tonne of ore to 11 USD/tonne of ore. The costs for the flotation, Mo SX and U SX circuits were relatively minute, when compared to the leach circuit. The profit estimates for Option A and Option B are shown in Figure 10.

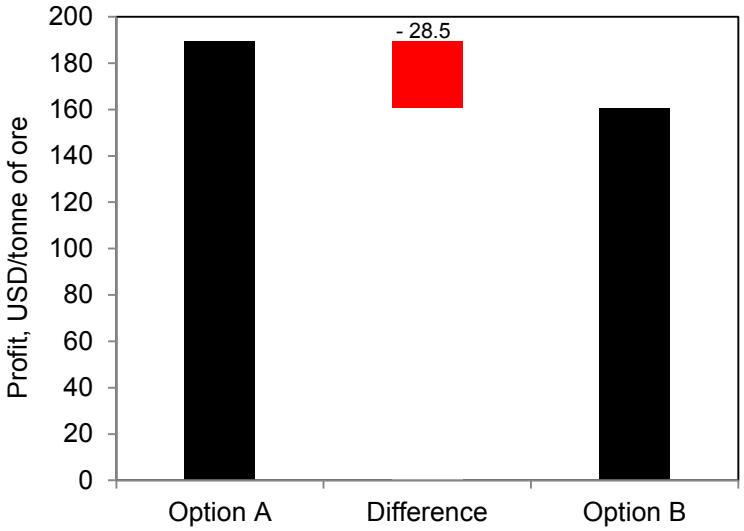

Figure 10: Profit estimates for Option A and Option B

It should be noted that Option A did have a substantially higher revenue estimate due to the higher overall uranium and molybdenum recoveries. The uranium losses in the flotation step resulted in a lower revenue estimate for Option B. There is a need to minimise the uranium loss to the flotation concentrate, however a balance between acid consumption and uranium recovery needs to be established.

Since molybdenum removal is required prior to uranium solvent extraction to prevent possible third phases and crud formations, the recovery of molybdenum as a by-product was evaluated. The revenue estimated for molybdenum recovery and the cost of molybdenum solvent extraction is shown in Figure 11.

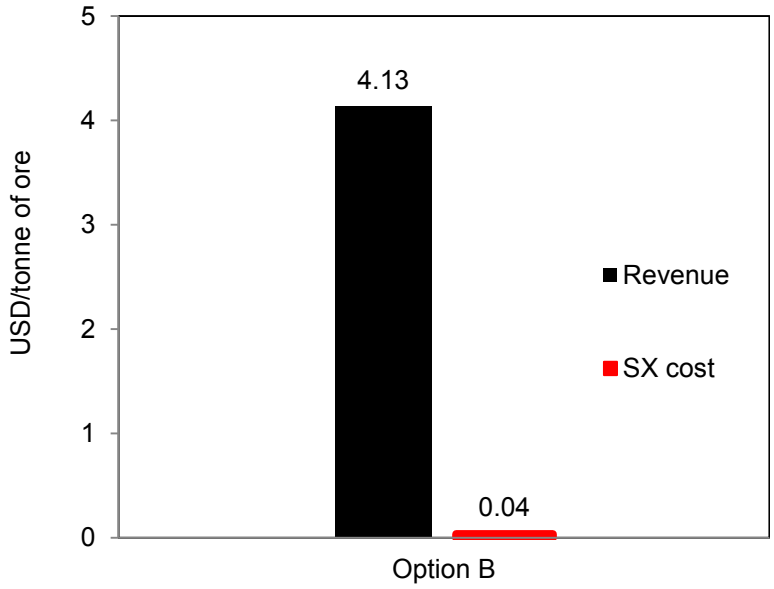

Figure 11: Molybdenum revenue and cost of molybdenum solvent extraction for Option B

The revenue estimated for molybdenum recovery was much higher than the cost of molybdenum solvent extraction for Option B. The recovery of molybdenum was thus viable for Option B. The potential profit calculated for molybdenum recovery for Option B and Option C, are illustrated in Figure 12.

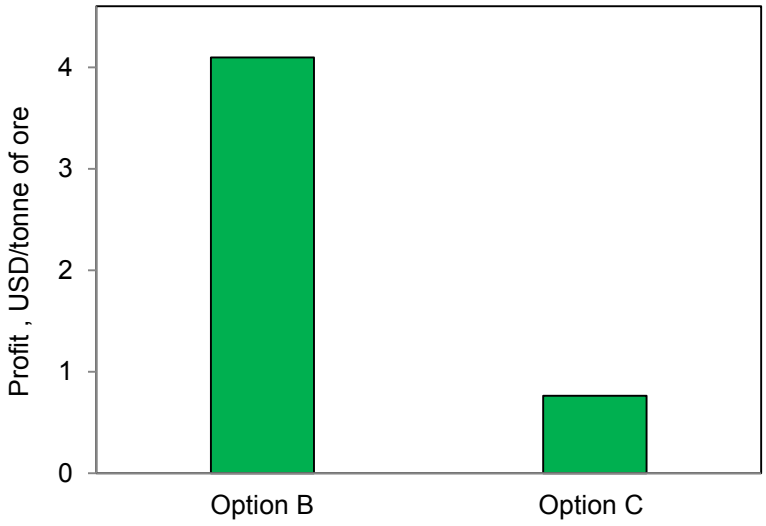

Figure 12: Potential profit for molybdenum recovery for Option B and Option C

The increased consumption of leach reagents for Option C was much higher than that of Option B. Thus the improved molybdenum recovery (74%) by leaching at a lower pH (1.2) for Option C was not as profitable when compared to Option B (i.e. leach at a pH value of 1.5). Uranium recovery is therefore the primary target for processing the Karoo Sandstone deposit.

CONCLUSIONS AND RECOMMENDATIONS

The Karoo Sandstone deposit up until now remains unlocked due to the high processing cost and unfavourable uranium market conditions. Research undertaken by Mintek resulted in the following improvements in the acid leach flowsheet for the recovery of uranium:

- Reverse flotation of carbonates combined with optimisation of leach conditions resulted in a decreased acid leach consumption from 143 to 52 kg/tonne;
- Results indicated that oxidant addition as well as an elevated leach temperature were not necessary for maximum uranium recovery;
- Solvent extraction test work indicated that uranium and molybdenum streams suitable for achieving high purity products could be obtained from the acid leach liquor.

An overall uranium and molybdenum recovery of 65% and 36%, respectively, was achieved after carbonate rejection, which was lower than the 88% U_3O_8 and 73% Mo extraction which was reported for the direct acid leaching route. However, the removal of acid consumers resulted in a drastic decrease in OPEX of 62%. The percentage of OPEX (associated with reagents only) over revenue generated for Option A and Option B decreased from 11% to 6%, respectively, indicating an improvement in the feasibility of the process.

The cost of molybdenum solvent extraction as a percentage of the total OPEX was in the range of 0.1-0.4%. This was an indication that the recovery of molybdenum as a by-product was favourable. The increase in molybdenum recovery by leaching at a lower pH for Option C was not beneficial as the profit for Option C was lower when compared to Option B, due to the higher reagent consumptions. Hydrometallurgical data and economic estimations have shown that the recovery of high purity uranium and molybdenum from the Karoo Sandstone deposit is promising.

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COMMISSIONING OF A MINI REE SX PILOT PLANT AT SGS MINERALS SERVICES – LAKEFIELD SITE

By

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ABSTRACT

SGS Minerals Services commissioned an internal R&D program to develop in-house expertise in the design, setup, and operation of a REE separation pilot-plant at its Lakefield, Canada site. A mini pilot scale SX circuit of 120 stages was designed, constructed and operated to separate Pr and Nd from La and Ce contained in a synthetic REE chloride stream simulating the raffinate from an initial La-Nd|Sm-Lu+Y separation.

Two pilot campaigns were run totalling 25 days of 24/7 operation with 99.4% plant availability in the final 20 day campaign. Purities of >99.9% in the PrNd strip liquor and >99% in the LaCe raffinate were achieved and simultaneously sustained for prolonged periods. Key to controlling and adjusting the circuit was the rapid assay turnaround (as low as 1-2 hours) provided by the on-site SGS analytical laboratory. This permitted the operating team to modify conditions and observe the effect of changes relatively quickly considering the large number of stages. A portable XRF analyser was also used to monitor progressive assay trends. A MS Excel-based model was developed to simulate the SX plant behaviour and allow future circuit design.

This paper discusses the design of the circuit, operating conditions, some of the key operating factors and controls, and results obtained.

Keywords: Rare Earth Elements, REE Separation, Solvent Extraction, Process Development, Pilot Plant, Hydrometallurgy

INTRODUCTION

REE ores are subjected to a combination of mineral processing, pyrometallurgical and hydrometallurgical process aiming to produce a purified mixed REE carbonates, oxalates, hydroxides or oxides. These mixed REE concentrates are leached in order to produce a REE-rich solution which is used for the production, mainly by solvent extraction, of purified individual REE or REO (rare earth oxides).

The separation of individual rare earth elements by solvent extraction is done by a sequence of binary separation steps (Yan et al. 2006). In each step, one group of mixed REE is separated into two subgroups of REE and so on until individual rare earth elements are produced. Figure 1 shows a simplified version of a REE separation flowsheet.

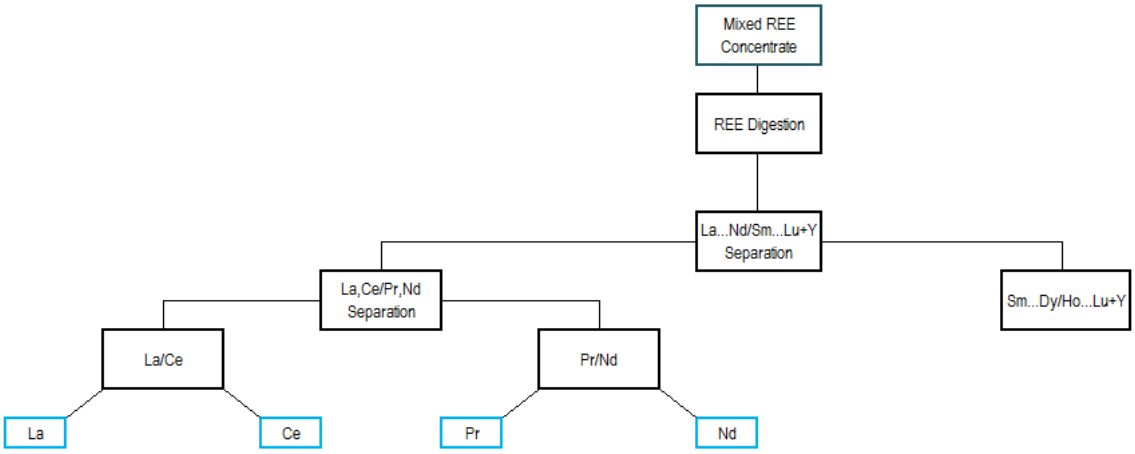

Figure 1: REE SX Separation (Simplified) Block Diagram

Among the different REE separation steps the separation of lanthanum and cerium from praseodymium and neodymium was selected as the process to study. Table 1 shows the average distribution of the light rare earths elements (LREE: La, Ce, Pr and Nd) in a survey of 58 deposits from around the world (Lifton & Hatch, 2015). The LREE account for more than 78% of the total rare earths for the majority of these deposits; within the lights group, the La+Ce content is roughly three times the Pr+Nd content, though in terms of value, Pr+Nd is worth more. It is then expected that in any REE separation scheme, a split between Pr+Nd from La+Ce, would be common.

Table 1: Percentage Distribution of the LREE

REE	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3
Average REO/TREO	21.0	39.0	4.3	14.6
Average REO/LREO	26.0	49.4	5.5	19.1

PLANT DESIGN, CONSTRUCTION, AND START-UP SET POINTS

SGS commissioned the design of a solvent extraction (SX) mini pilot plant for REE separation from MetNetH2O Inc. The pilot plant was built at SGS's Lakefield Canada site. Figure 2 shows a photograph of the circuit. The plant consists of a battery of 120 mixer-settlers readily adaptable to different configurations, set up in a dedicated and secured building. The mixer-settlers were made of clear PVC. Mixer and settler volumes were around 100 mL and 300 mL, respectively, with a settler interfacial area of 52 cm^2. Each cell was equipped with a polypropylene pump-mix impeller to both mix the two liquid phases and advance them from stage to stage. Each settler was connected to an exhaust manifold to control vapour emissions.

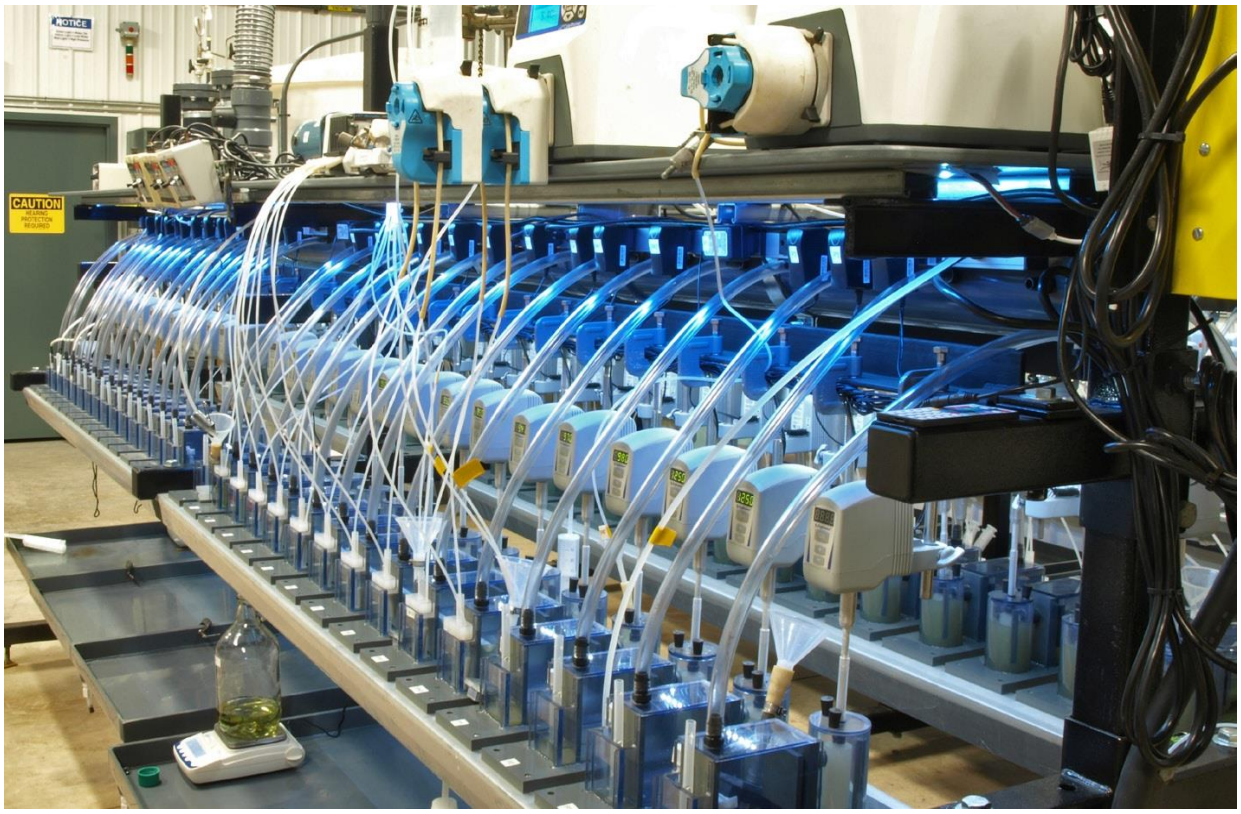

Figure 2: Photographs of REE SX Pilot Plant

A schematic of the flowsheet is shown in Figure 3. In the first of two pilot plant campaigns (identified as PP1) the circuit was set up with 30 extraction stages, 30 scrubbing stages, 8 stripping stages, 2 acid wash stages and 3 saponification stages. Organic and aqueous streams flowed counter-currently in all circuits with the exception of the saponification circuit where the sodium hydroxide flowed co-currently with the acid-washed organic. Cells were identified based on the circuit they were located in and numbered following the organic flow path, that is, the recycled organic entered the extraction section in cell E1 and left the extraction section after cell E30, and so on.

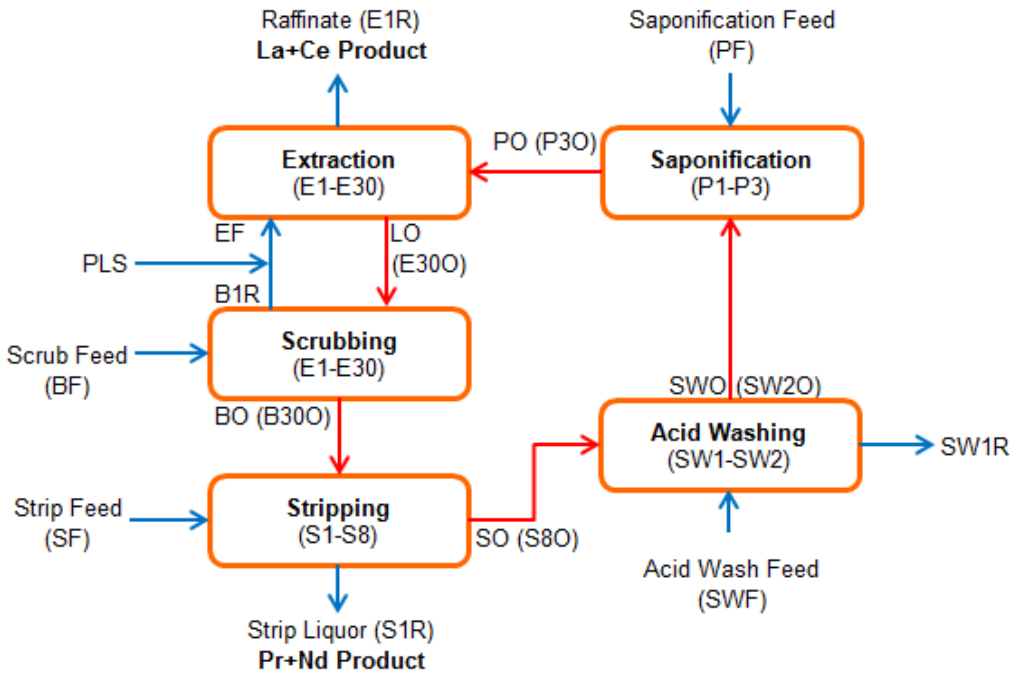

Figure 3: Simplified Schematic of the SX Circuit as Operated in PP1

Acid-washed organic was saponified using a precisely metered flow of sodium hydroxide. The feed solution (PLS) was mixed with spent scrub liquor in a separate mixing stage in order to provide a uniform composition feed to the extraction circuit. The acidity profile of the extraction section was maintained solely by controlling the degree of saponification via the NaOH flowrate.

A hydrochloric acid solution (scrub feed, BF) was introduced at scrubbing stage B30 to scrub any lanthanum and cerium off the loaded organic. There was no other pH control in the scrubbing stages. Scrubbed organic advanced to the stripping circuit. A hydrochloric acid solution (SF) was used to strip the scrubbed organic. Loaded strip liquor (Nd/Pr product) was collected in batches from the S1 stage discharge.

The aqueous feed for the extraction circuit consisted of a blend of the PLS (described below) and the scrub liquor (B1R). PLS flowrate was controlled but B1R flowrate set the scrub feed rate and could surge with small upsets or level changes in the scrub stages. Scrub (BF), strip (SF), organic wash (SWF), and saponification feeds (PF) were all pumped with metering pumps. The only pumped organic flow was the saponified organic (P3O) going to the extraction section in order to control the extraction O/A ratio.

Feed Streams

The aqueous feed for the SX circuit was a synthetic solution simulating the raffinate from an Nd|Sm separation step. Table 2 gives the composition of the solution prepared; traces of other REEs as well as other elements were below detection limit. This synthetic solution was prepared by dissolving reagent-grade (>99%) $CeCl_3$, La_2O_3, Pr_6O_{11}, Nd_2O_3, all purchased from American Elements, in hydrochloric acid to obtain a total REE concentration of about 150 g/L. In order to simulate a typical rare earth process solution, the elemental mixture target was 23% La, 50% Ce, 6% Pr and 21% Nd, corresponding to a typical mix of elements within the light rare earths group as can be seen in Table 1. The pH of the solution was adjusted to 1.0 using sodium hydroxide.

Table 2: Composition of Feed Solution (PLS)

LREE & Major Elements	
Element	**mg/L**
La	35800
Ce	81400
Pr	9520
Nd	34000
Na	4870
Zn	7.2

The extractant chosen for this separation was 2-ethylhexyl 2-ethylhexylphosphonic acid (EHEHPA) sourced from Solvay Group (USA) under the name Ionquest® 801; the extractant was prepared at 50% v/v (1.5 M) using Exxol D80 (Exxon aliphatic solvent) as diluent. The prepared organic was pre-treated by washing with 2 M HCl followed by pH 2 water. A number of studies have confirmed that the extractant exists as a dimer in the diluent and the generally agreed chemistry for extraction of rare earth elements is:

$$REE^{3+} + \overline{3(HA)_2} \rightleftharpoons \overline{REE(A)_3(HA)_3} + 3H^+$$

where the overline denotes species in the organic phase (Kao et al.,, 2006; Xie et al.,2014). The dimerisation effect should be taken into account when calculating maximum loading. To control pH, the organic can be partially saponified, whereby some of the HA is converted to NaA and then Na^+, rather than H^+, is released into the raffinate during extraction of rare earth cations.

Start-Up Set Points

Flowrates were set to give mixer residence times of about 3 minutes in all stages of the circuit. O/A ratio for the extraction circuit was set at 2.5 and the saponification target was 40%. PLS flowrate was set at 7.0 mL/min while the B1R flowrate was monitored but not controlled. Scrubbing circuit advance O/A ratio was set at 10 while the mixer O/A ratio was controlled at 2.3 by recycling aqueous solution from each cell settler to its mixer. Scrubbing feed was made up as 3.5 M HCl.

Scrubbing circuit advance O/A ratio was set at while the mixer O/A ratio was controlled at 2.3 by recycling aqueous solution from each cell settler to its mixer. Stripping feed was made up as 2.9 M HCl. Acid Wash circuit advance O/A ratio was set at 20 while the mixer O/A ratio was controlled at 2.3 by recycling aqueous solution from each cell settler to its mixer. The circuit operated at ambient temperature, averaging around 20ºC.

PLANT OPERATION AND PERFORMANCE

The REE SX pilot plant operation was split in two campaigns; a commissioning campaign (PP1) and a 21-day campaign (PP2). The PP1 campaign was operated to learn how to run the circuit and less emphasis was placed on the results while the overall objective of the PP2 campaign was to produce and sustain a strip liquor with >99% (Nd+Pr)/TREE purity, and to produce and sustain a raffinate with >99% (La+Ce)/TREE purity.

PP1 - Commissioning Campaign

The REE SX pilot plant was operated in continuous mode for 109 hours processing 47 L of feed solution and producing approximately 66 L of raffinate (La+Ce product) and 22 L of strip solution (Nd+Pr product). Equipment availability was better than 99% with less than 50 minutes of downtime. The key equipment, including: agitators, pumps and mixer-settlers, operated well with sufficient flexibility to deal with adjustments.

Raffinate purity reached a maximum purity of 98.9%. Maximum strip liquor purity of 99.2% was achieved during the second day of the campaign, though in view of the time estimated to reach steady state, not much weight was placed on the Nd+Pr purity obtained in those first two days.

PP2 - 21-day Campaign

Based on the PP1 campaign results some changes were made to the circuit for the PP2 campaign. Mainly:

- The extraction circuit was increased to 35 stages in order to improve Pr extraction;
- Washed organic flowrate to saponification was controlled in order to accurately control the degree of saponification and make it immune to organic flow fluctuations;
- A portion of the strip liquor was recycled to make up the scrub feed in order to achieve better scrubbing;
- The impellers were changed, from a slotted cylinder design to semi-open type with four radial blades mounted on the hub plate, in order to increase the pumping suction.

The REE SX pilot plant operated in continuous mode for 474 hours with 99.5% availability (only 2.4 hours of total downtime to address minor mechanical issues). Approximately 150 L of feed solution was processed making about 240 L of raffinate (La+Ce product) and 100 L of strip solution (Nd+Pr product). Saponification was well controlled during this campaign and there was no emulsion and no pH excursions in any of extraction cells. It was noticed early in the run that the circuit suffered some instability right after sampling. The sampling procedures were optimized to avoid upsetting the circuit.

Recovery and Purity

Lanthanum extraction was kept below 10% and La scrubbing was >99%. Cerium extraction was kept to 34-40% after a few adjustments made to the rate of saponification. Praseodymium extraction was >99% during the first 10 days of the campaign, but decreased considerably (to a minimum of 40%) after that due to more aggressive scrubbing; changes in the extent of saponification as well as the organic flowrate (in order to increase extraction capacity) resulted in Pr extraction increasing to 99%. Neodymium extraction was 100% throughout the campaign.

Raffinate purity (expressed as (La+Ce)/TREE) was over 99% for the first 12 days of the campaign. At that point the excessive Pr scrubbing started affecting the extraction performance (i.e. Pr extraction). As noted above, both the extent of saponification as well as the recycled organic flowrate were increased with the aim of maximizing Pr extraction. These measures were effective, with raffinate purity climbing steadily to >99%.

The scrub feed composition was not adjusted until the circuit had settled down and the improved sampling protocol had been put into practice. After approximately 115 hours a series of changes in Nd+Pr concentration and acidity in the scrub feed were implemented in order to increase the strip liquor purity (expressed as (Nd+Pr)/TREE). Strip liquor purity reached 99% after these changes (at approximately 180 h) and continue to rise to >99.9%. That level of purity was maintained for the rest of the campaign.

The strip circuit performance indicated near complete stripping of Nd and Pr, averaging over 99.6% throughout the PP2 campaign. Most of the Ce was stripped in the scrubbing circuit; leading to tolerably low Ce levels in the Nd+Pr product. However, accumulation of cerium in the scrubbed and stripped organic was observed. This was thought to be due to the presence of Ce(IV) in the feed liquor originated from the $CeCl_3$ reagent used to prepare the synthetic PLS. This was controlled by replacing a percent of the total organic inventory with fresh organic once a day. This Ce accumulation would not be expected in a real operation. Nonetheless, Ce buildup is worth monitoring and methods to strip Ce(IV) off should be developed if required.

Distribution Coefficients and Separation Factors

The distribution coefficient for element x, D_x is defined as $[X]_e/(X)_e$ where $[X]_e$ is the equilibrium concentration of the solute in the organic phase and $(X)_e$ is the equilibrium concentration of that solute in the aqueous phase. The separation factor between two elements, X and Y, is then calculated as $SF_{x/y} = D_x/D_y$. Distribution coefficients and separation factors were calculated based on the full profile samples from the extraction circuit taken at the end of each campaign. A summary of values obtained for both pilot plant campaigns is given in Table 3.

As can be seen, the separation factors calculated are in fairly good agreement with values obtained by other workers (Balint, 1975). Since the pilot plant was run to split La+Ce from Pr+Nd the more critical SF was Pr/Ce and these values were more consistent across the two campaigns and in good agreement with the reference value.

Table 3 – Distribution Coefficients and Separation Factors in Extraction

		La	Ce	Pr	Nd
Distribution Coefficient	PP1	0.03	0.23	0.45	0.66
	PP2	0.03	0.23	0.42	0.64

		Ce/La	Pr/Ce	Nd/Pr
Separation Factor	PP1	6.97	1.98	1.47
	PP2	8.81	1.80	1.52
	Reference 5	6.83	2.03	1.55

CONCLUSIONS

The successful commissioning and operation of the REE SX separation facility at the SGS Lakefield site was accomplished. The key equipment including mixer-settlers, agitators and pumps performed well with adequate capacity and flexibility to deal with required adjustments. The SX pilot plant is very robust and has a flexible set-up, capable of handling different configurations/systems. There were no major physical issues observed relating to crud formation or phase disengagement. Successful operating and sampling procedures were established; analytical methods including direct analysis of metals in the organic phase were validated.

Due to the long retention time of the circuits, they should be run in very steady conditions keeping changes in operational parameters to a minimum. Circuits should also operate sufficiently long to reach steady state at optimized operating conditions. Feed availability for piloting is typically limited and producing large volumes of real feed for downstream separation work is expensive. Therefore, it is advantageous to use the smallest mixer-settlers that can be reliably operated in order to achieve longer campaign running times with the feed available, the SGS circuit has demonstrated that this can be done.

The operation of the two campaigns led to the development of a fully trained crew of REE SX operators, metallurgists and chemists. The participation and advice of outside consultants experienced in rare earth separation circuits acting as an advisory group allowed the SGS team to gain valuable knowledge on how to operate and control these circuits. The presence of the on-site

analytical laboratory proved invaluable in its ability to quickly (1–2 h turnaround) deliver reliable accurate and precise aqueous and organic assays. Analytical methods including direct analysis of metals in the organic phase were validated.

It was demonstrated during the PP2 campaign that the production of a NdPr product with over 99.9% purity and a LaCe product with over 99% purity is achievable with the SX pilot plant at SGS Lakefield site. Low extraction (averaged 6%) and maximum scrubbing of La (over 99%) were achieved. Pr extraction was close to 100% for most of the PP2 campaign, though Pr scrubbing still needed further optimization. Nd extraction was over 99% throughout all the campaign. Some Ce accumulated in the stripped organic, though this is not an ongoing concern. Nevertheless, Ce in the stripped organic needs to be monitored and if there is buildup, measures to control Ce accumulation will need to be developed.

ACKNOWLEDGMENTS

The authors of this paper would like to thank John Goode, Michael Nees and Jerry Tabor for their support and expertise.

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Uranium-REE Proceedings

Membranes in Uranium Ore Processing Forum

PROCESS MEMBRANES APPLIED IN THE MINING INDUSTRY

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ABSTRACT

With the growing demand for water and increasing water scarcity the mining industry is challenged to reuse water and recover process streams to meet environmental regulations. Using reclaimed treated effluents in the mining industry has enormous potential. Crossflow Membrane Filtration economically addresses the challenges facing the mining industry. The membranes provide separation from 2 microns (Microfiltratoin) to < 5 angstroms (Reverse Osmosis). The most common technologies used in the mining industry are Nanofiltration (NF) and Reverse Osmosis (RO). This presentation will address the fundamentals of how membranes work with a brief overview of the various commercial applications including ultra-low energy RO membranes to address reclaim and meet environmental discharge limits and acid stable NF membrane to recover valuable metals from process streams.

Keywords: Water reuse, Reverse Osmosis, Nanofiltration, Process Recovery

Agenda

- How Do Cross-Flow Membranes Work?
- Which Mining Applications Use Membranes?
- Case Studies
  - Copper Mine (low pH application)
  - Uranium Mine (tailings pond remediation)

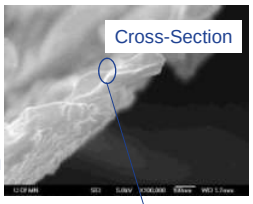
How Do Cross Flow Membranes Work?

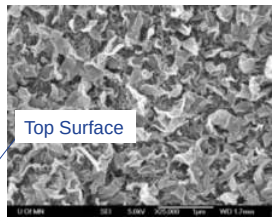
What is a Membrane?

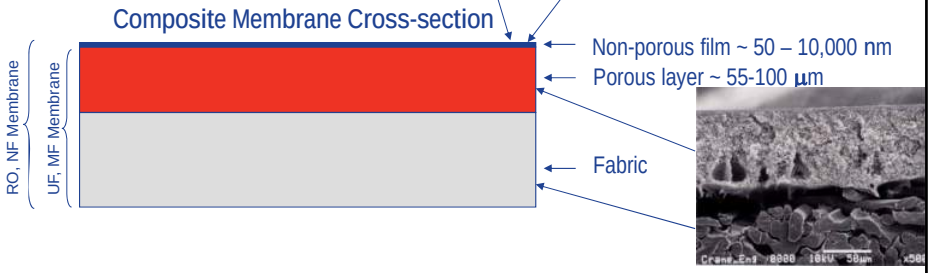
Two classes of membranes:

- Porous (UF, MF)
- Non-porous (RO, NF)

Non-porous membranes typically comprise a thin film on a support

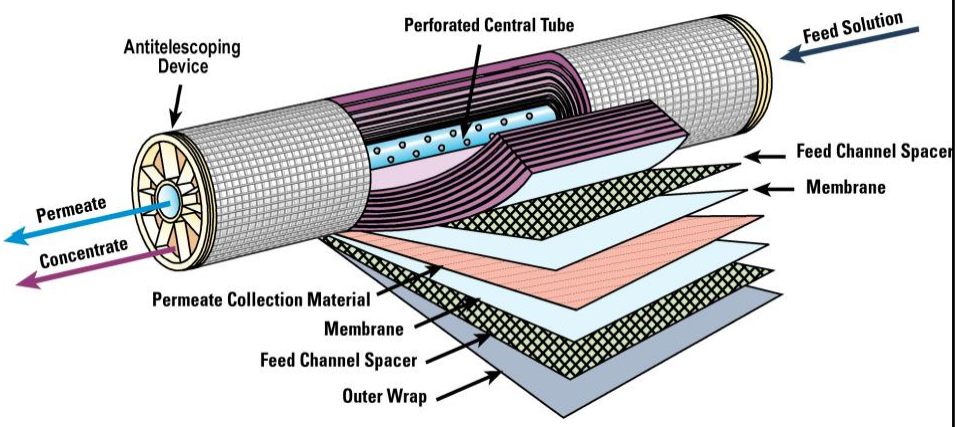




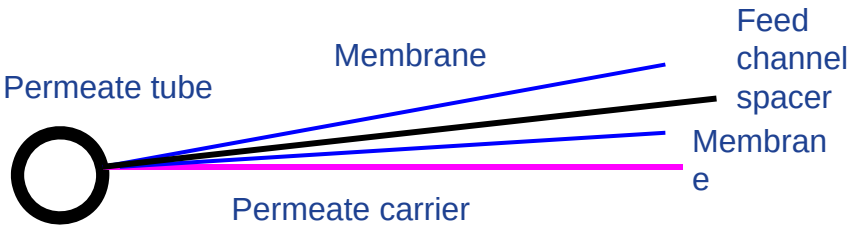


Membrane Element Detail

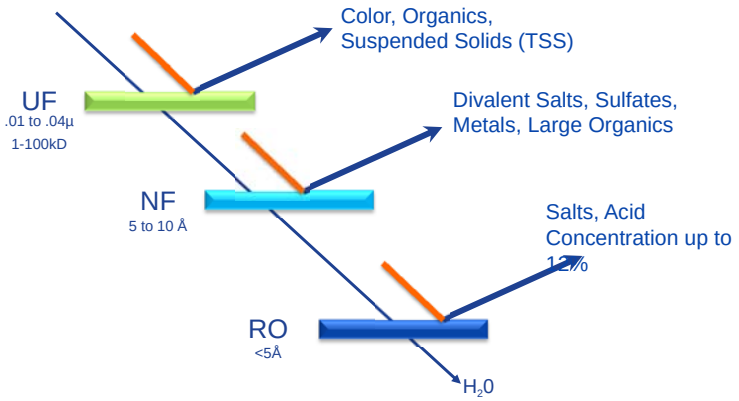
spiralwound_fl5.exe



Elements are built with multiple leafs of membranes rolled around a tube



What is Rejected by Different Membrane Element Types?



Which Mining Applications use Membrane Elements?

Environmental and Remediation Applications

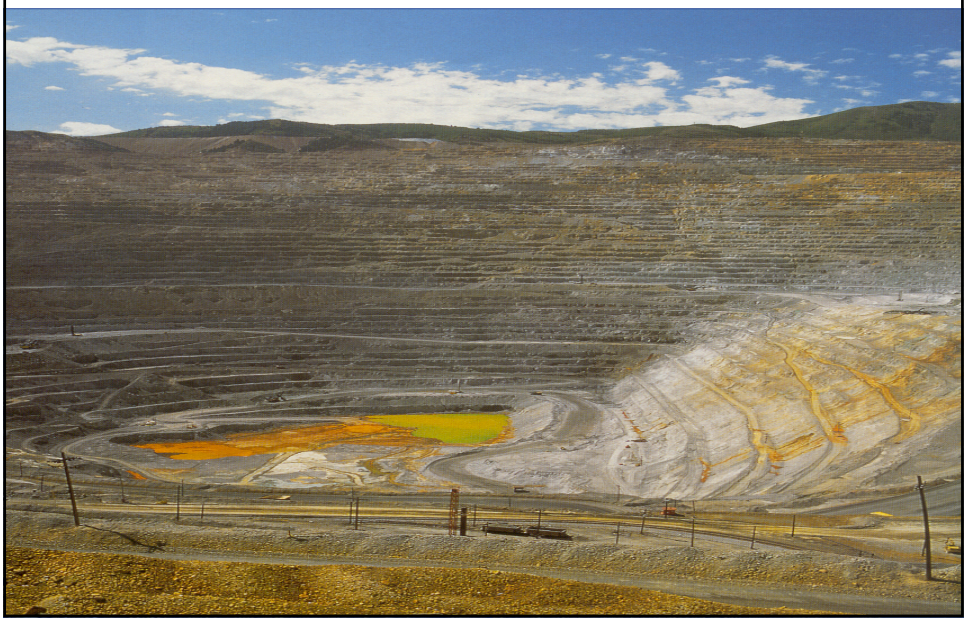
- Tailing pond management
- Acid mine drainage (AMD)

Concentration or Recovery of Minerals

- Pregnant Leaching solutions (PLS)
- Acid purification and reuse
- Raffinate streams

Case Studies

Mexico Copper Mine Case Study



Mexico Copper Mine Case Study

Application Details

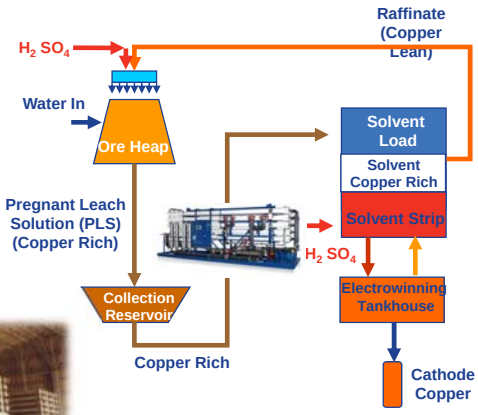
- Copper Mine located in Mexico
- 775 ppm Cu in collection reservoir at pH of 2-3
- Applying Nanofiltration to concentrate copper rich PLS stream (~900 m3/h) prior to metal extraction
- Using four separate NF trains for operations flexibility
- Recovering acid for reuse in process (390 m3/h)

Process Flow for Pregnant Leach Solution Concentration

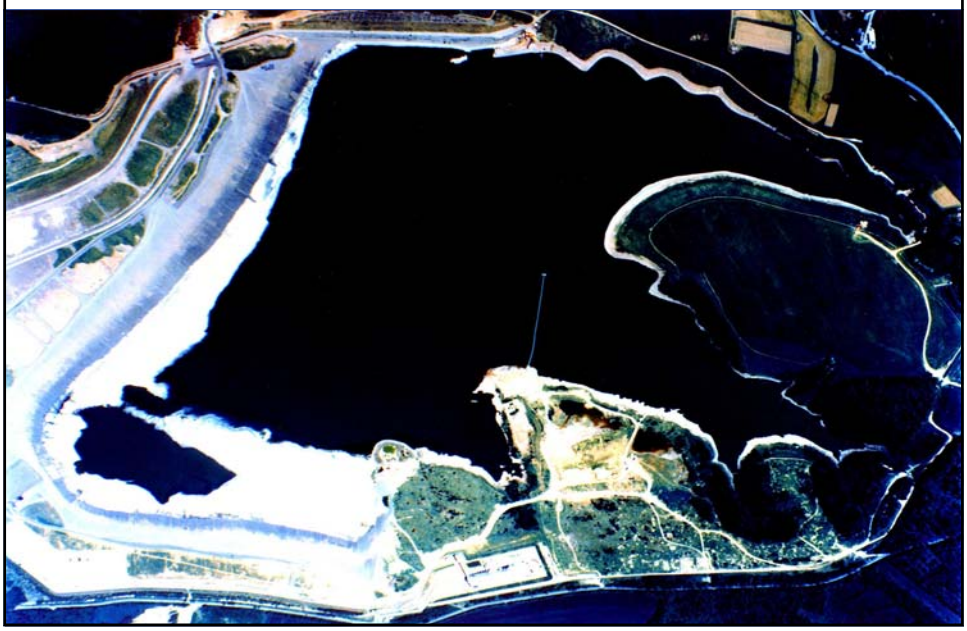
PLS Concentration

Background

- Patented pH stable (1-14) NF membrane
- Purification/concentrate metals from acid streams
- Pre-concentrate PLS, fractionate metals
- Multiple benefits of membrane separations in PLS
  - Concentrate Low pH copper leach solution 2x
  - 99% copper rejection
  - Acid water as permeate
- Proven stability in 20% H_2SO_4 and 25% H_3PO_4



German Uranium Mine Case Study



German Uranium Mine Case Study

Application Details

- Uranium Mine located in Germany
- Tailing pond remediation
- Pond contained Uranium, Radium, and Arsenic
- Pond effluent is pretreated (including chemistry/anti-scalant)
- Followed by NF for 10X metal concentration

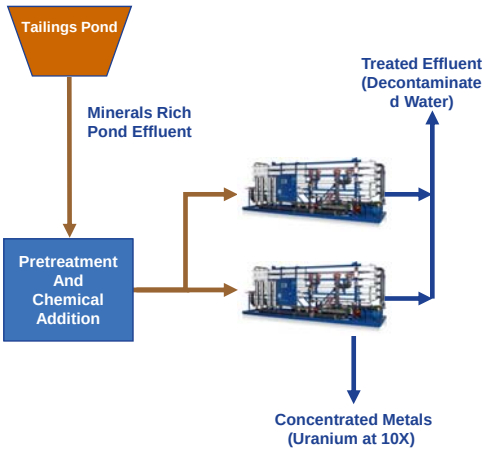
Signifant Reduction to Tailings Pond in 3 Years, Eliminated in 10 Years

1995: Prior to NF System Commissioning

1998: Much Smaller Pond 3 years later

NF System Installation

Process Flow for Tailings Pond Remediation with Low Energy RO



Application Detail

- Energy typically is biggest driven in determining remediation method
- RO membrane elements most effective at separating metals from tailings ponds
- Low energy (10 bar) and Ultra Low energy (6-7 bar) membranes improving ROIs

Pond Composition

Uranium	5-7 mg/l
Radium	800-1,200 mBq/l
Arsenic	60-120 mg/l
SO42-	6,000 mg/l
Cl -	1,500 mg/l
CO32-	2,000 mg/l
HCO3-	3,000 mg/l
Na+	7,000 mg/l

PALADIN ENERGY LTD – NANO-FILTRATION TECHNOLOGY FOR REAGENT RECOVERY

By

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ABSTRACT

A membrane-based acid recovery plant has been successfully installed and commissioned at Paladin Energy's Kayelekera Uranium Mine in northern Malawi. This Acid Recovery Plant (ARP) is believed to be the first commercial-scale operation of its kind in the world. The design has successfully demonstrated that a uranium-containing acid stream can be separated into a clean, uranium-depleted acid stream containing the majority of the acid and a low-volume, concentrated uranium stream. Apart from the significant acid savings (circa 40 t/day 98% sulfuric acid), the ARP also resulted in significant savings in neutralising chemical requirements downstream of the ARP.

Continuous operation over a six month period has demonstrated the success of the design and the long-term sustainability of membrane performance and cost savings. At a capital cost of US$5M, the net operating cost savings of approximately US$3 per lb U_3O_8 resulted in a simple payback period of 7 months. The project has been successful from both a technical and financial perspective. Despite the success of the ARP in reducing operating costs, Kayelekera Uranium Mine has since been placed on care and maintenance due to sustained low uranium prices.

Uranium can be stripped from ion exchange resins using a variety of acid and alkaline eluants. At Kayelekera, the eluant is sulfuric acid, while at Paladin's flagship operation, Langer Heinrich in Namibia, the eluant is sodium bicarbonate. Both eluants strip adsorbed uranium from ion exchange resins to produce Concentrated Eluate (CE). The acid or alkali component of the CE can be recovered using the nano-filtration technology developed by Paladin Energy and BMS Engineers. Paladin Energy has recently been granted a patent for this technology. Based on the success of the first membrane plant at Kayelekera, a second plant has been designed, installed and commissioned at Langer Heinrich. This plant, designed to recover sodium bicarbonate from the CE stream, was successfully commissioned in March 2015 and continues to perform above design expectation.

The Bicarbonate Recovery Plant (BRP) at Langer Heinrich recovers sodium bicarbonate from the CE and produces a clean, uranium-depleted sodium bicarbonate stream and a low-volume, uranium-rich stream. The sodium bicarbonate stream is recycled and fortified with fresh sodium bicarbonate to be reused as fresh eluant for further resin stripping in the ion exchange circuit, resulting in significant sodium bicarbonate and fresh water savings. At a capital cost of US$7M and net operating cost savings of circa US$6 per lb U_3O_8, this project has demonstrated a simple payback period of 3 months.

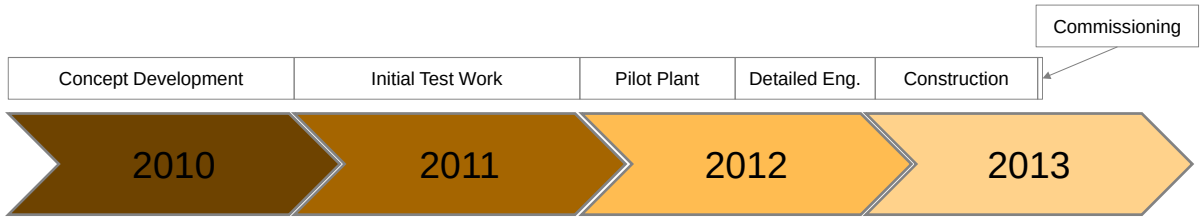
Keywords: acid recovery, membranes, nano filtration, Kayelekera, BMS Engineers, Paladin Energy

Kayelekera Uranium Mine

- **Kayelekera** is located in northern Malawi.
- Kayelekera Mine is owned 100% by **Paladin (Africa) Limited (PAL)**, a subsidiary of **Paladin Energy Limited**.
  - The mine design capacity is 3.3Mlb U_3O_8 per annum
  - Acid leach process utilising high pulp density Resin In Pulp (hdRIP) technology.
  - Plant on Care & Maintenance since April 2014 due to market conditions (price)
  - Uranium is precipitated from acidic Concentrated Eluate (CE) which requires the acid to be neutralised at significant cost.

Kayelekera's Nano-Filtration Acid Recovery Plant (ARP)

- **Concept developed in 2010**
- **Initial testwork in 2011 was encouraging using synthetic liquors**
- **Pilot plant operated at site in 2012 and provided confirmation of concept as well as design data**
- **Detailed engineering commenced October 2012 and capital commitment December 2012**
- **Hot commissioning commenced 21st October 2013 and design criteria achieved 25th October 2013**



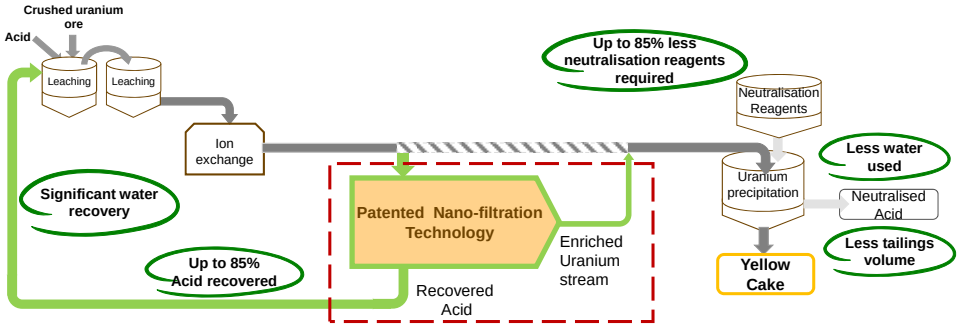
CONCEPT TO COMPLETION IN 3½ YEARS

Kayelekera's Nano-Filtration Acid Recovery Plant (ARP)

- **Recovery of over 40 t/day (equivalent) of 98% sulphuric acid**
  - **Typical feed flow of 30 m^3/hr @ 1M sulphuric acid**
- **Equivalent stoichiometric saving of neutralisation reagents.**
- **Uranium concentration to precipitation circuit increased from ~10 g/l to ~40 g/l**
  - **Improved refinery performance due to longer residence times**
  - **Improved final product contaminant removal.**
- **Project cost of US$5 M**
  - **Project on time and within budget**
  - **Net operating cost savings of over US$3 per lb U_3O_8.**
  - **Cash payback period (including all operating costs) of 7 months on reagent savings alone.**
  - **Significant other consequential benefits.**
- **Process now subject to patent and BMS hold commercial rights**

Patented Technology – Reagent Recovery from Uranium Process

One Application – Sulfuric Acid recovery



1 Elution Acid

- Up to 85% of elution acid recovered and reusable
- Significant acid cost reduction
- Acid supply logistics reduced significantly
- Site becomes acid self-sufficient

2 Neutralisation

- Neutralisation reagent proportionate to recovered acid
- Significant neutralisation cost savings

3 Water balance & Tailings

- Elution acid make-up water reduced by up to 85%
- Reduced tailings volume due to reduced acid, other reagents and water addition to circuit

Project Piloting

- Three pilot campaigns were undertaken to generate design data, identify membrane life and assess main plant design,
- Current BMS Personnel undertook all site testwork.

Project Membranes

- **Multiple membrane types tested:**
  - **Acid "resistant" membranes**
    - **Shorter life**
    - **Excellent uranium rejection**
    - **Low membrane cost**
  - **Acid "proof" membranes**
    - **Longer life**
    - **Lower uranium rejection**
    - **High membrane cost (~*6x acid resistant cost*)**
- **Test housing on main plant**
  - **Enables continuous membrane testing and ongoing optimisation.**

Modified Membranes

- **Improvements based on operational performance and process requirements,**
  - **Greater than 10% flux improvement achieved with modified membranes.**

Project Delivery – remote site

- **Plant fabricated in Johannesburg**
- **ARP was built to be fully transportable**
  - 3 containerised skids
  - 5 separate 316SS tanks
- **Complete FAT and Wet Commissioning prior to dispatch**
  - PLC programming fully tested during FAT,
  - All pumps operated,
  - All lines leak tested,
  - CIP skid fully tested.

Project Delivery – remote site application

Tanks and skids transported by truck from South Africa to Kayelekera Mine in Malawi

Project Delivery – remote site application

Pad installed while Skids being fabricated

Skid installation completed within weeks

Project Delivery – remote site application

Full operational performance within 5 days from first plant feed

Plant Performance

Inputs:

- **Feed stream**: Concentrated Eluant (CE) from RIP
- **Design Flowrate**: 30 m^3/hr
- **Composition**: 100 g/l H_2SO_4, 10 g/l U_3O_8

Objectives:

- Recover acid from CE for re-use

Design Outputs:

ARP Produced two streams

- Permeate (*recovered acid*) – 75% of CE volume
- Concentrate (*uranium rich*) – 25% of CE volume

Plant Output Streams:

- Permeate (*recovered acid*) re-used in leach process,
- Concentrate (*uranium rich*) progressed to CE neutralisation and Uranium Precipitation.

Project Findings

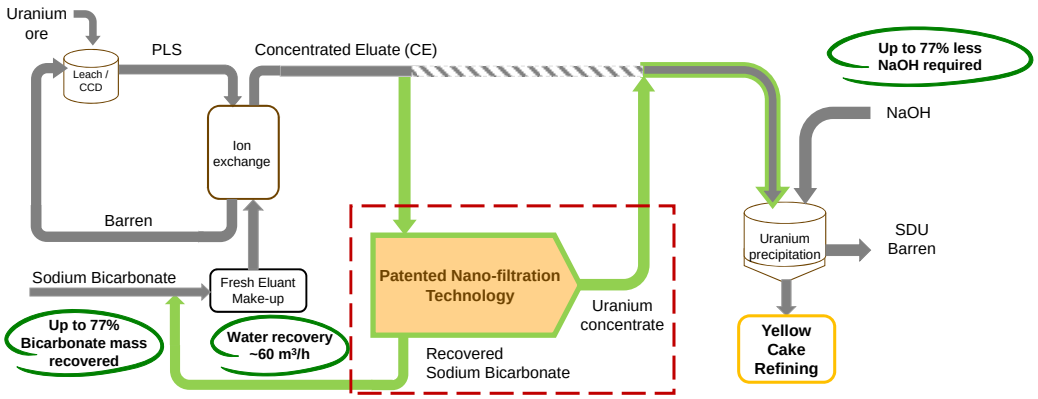
- **Uranium concentrations increased 4 fold in concentrate**
  - Can achieve 5 fold
- **Average membrane life**,
  - dependent on acid concentration
  - Achieved significantly longer life than used for project justification
- **No cleaning on NF membranes required**
- **Minimal NF scaling observed**

Langer Heinrich Uranium mine – Another Membrane application

Paladin Energy and **BMS Engineers** designed, installed and commissioned a second Nano-filtration plant for the recovery of Sodium Bicarbonate at Langer Heinrich, Namibia

Patented Technology – Reagent Recovery from Uranium Process

A Further Application – Bicarbonate Recovery (BRP)



1 Fresh Eluant

- **Up to 77% of sodium bicarbonate recovered and recycled to Fresh Eluant make-up**
- **Significant sodium bicarbonate savings**

2 Precipitation

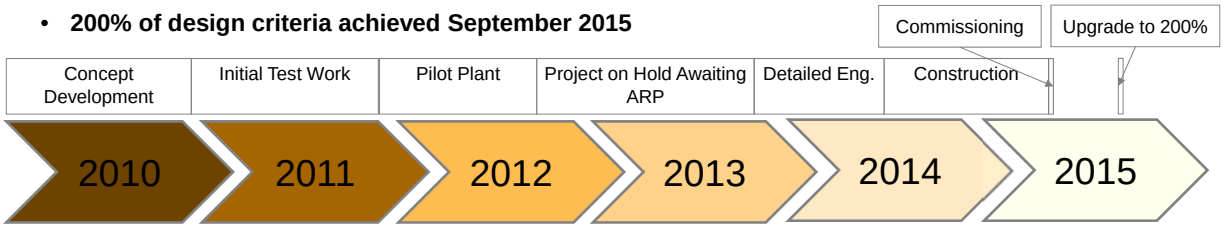
- **Neutralisation reagent savings proportional to recovered sodium bicarbonate**
- **Significant neutralisation reagent cost saving**

3 Fresh Water Input

- **Fresh Eluant make-up water addition reduced by up to 87% (60 m^3/h)**

Bicarbonate Recovery Plant (BRP)

- **Concept developed in 2010**
- **Initial testwork in 2011 was encouraging using plant liquors**
- **Pilot plant operated at site in 2012 and provided confirmation of concept as well as design data**
- **Engineering commenced November 2013 and capital commitment May 2014**
- **Hot commissioning commenced 11th March 2015 and design criteria achieved 12th March 2015**
- **200% of design criteria achieved September 2015**



APPROVAL TO COMPLETION IN 2 YEARS

Bicarbonate Recovery Plant (BRP)

Patented nano-filtration technology applied to the alkali uranium process

BMS and Paladin commissioned the BRP at Langer Heinrich in March 2015

- **BMS Engineers and Paladin** have designed and commissioned the world's first Bicarbonate Recovery Plant (BRP), recovering sodium bicarbonate from a uranium concentrated eluate stream using NF membranes.
- The membrane plant was commissioned in March 2015. The plant has exceeded its design bicarbonate recovery and has resulted in a significant reduction in reagent demand.
- The BRP has also significantly altered the circuit water balance and facilitated improved process recovery.
- Other consequential benefits have been significant.

Bicarbonate Recovery Plant (BRP)

BMS Engineers/Paladin have successfully undertaken:

- **Pilot plant trials for BRP concept**
- **Detailed design**
- **Commissioning**
- **Training of site personnel in BRP operations and maintenance**
- **Ongoing remote technical support**

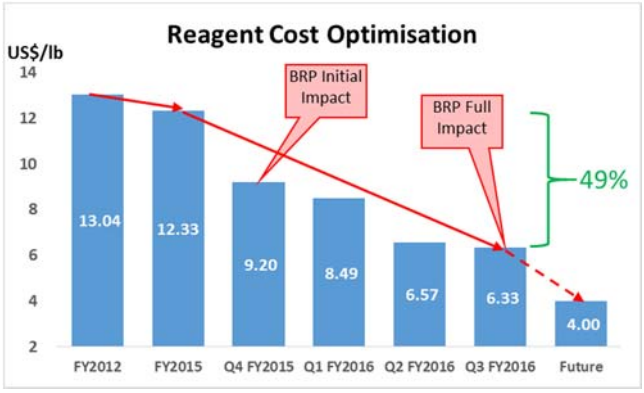
"...**BRP successfully commissioned in March and operating above design. The extent of this project's success has far-reaching implications for the Langer Heinrich operation now and into the future. BRP is expected to exceed design benefit by up to 100% and establish a new paradigm in carbonate uranium processing..." **

*Paladin website Q1 2015 ASX report

Bicarbonate Recovery Plant (BRP)

Based on plant performance, operational improvement (Enhancement 4) was undertaken and improved plant bicarbonate recovery to 200% of nameplate at minimal cost*.

- BRP Enhancement 4 now operational
  - ✓ Capital Cost of additional <US$100k of our original capital cost of US$6.8M
  - ✓ Recovery of sodium bicarbonate now exceeds 200% of design
  - ✓ Total operating cost saving now >US$6/lb (>US$30Mpa)
  - ✓ Additional secondary benefits



*Paladin 2015 AGM Report

Conclusions

- **Paladin has completed the development of a truly innovative uranium processing change**
  - **The process is broadly applicable in both acid and alkali environments**
  - **We have been able to patent the process involved**
  - **The impact on processing costs has been dramatic and creates a new paradigm for uranium hydrometallurgy**
- **This could not have been achieved without the engineering expertise of BMS who must now be considered world leaders in membrane applications within hydrometallurgical processes**
  - **The commissioning periods achieved here (days only) are testament to the level of engineering expertise involved**
  - **BMS hold the commercial exploitation rights to the process and have developed proprietary membranes – knowhow is the key**
- **THERE IS MORE TO COME FROM THIS TECHNOLOGY**

Acknowledgements

- **A number of people have been critical to the very successful development of this process and need to be acknowledged:**
- **Paladin Employees:**
  - **Darryl Butcher,** EGM – Technical, Project Development
  - **Dr Merrill Ford,** Metallurgy Manager
  - **Paul Boshoff, GM –** Technical, Project Development
  - **Simon Donegan,** Principal Process Engineer
  - **Harry Russell,** Principal Chemist
  - **Deogratias Bukunkwe,** Superintendent – Process Development
- **BMS Employees:**
  - **Mark Peacock,** Principle Engineer
  - **Shana McDougall,** Principle Process Engineer
  - **Paul James,** Field Technician

APPLICATIONS OF NANOFILTRATION IN HYDROMETALLURGY

By

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ANSTO Minerals, Australia

Presenter and Corresponding Author

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ABSTRACT

Due to its ability to separate mono-valent and multi-valent ions, nanofiltration has potential to improve the main metallurgical recovery process in a number of commodity areas. Thus far, however, only a few such applications have been commercialized. Most nanofiltration applications in hydrometallurgy are related to waste water treatment where the concentrations of metals and acid are low.

This presentation reviews commercial and potential applications of nanofiltration that are central to the metallurgical recovery process and considers the issues that impact the suitability of nanofiltration in this field. Issues include the chemical resistance of the membranes and the potential for scale (esp. gypsum) formation and fouling.

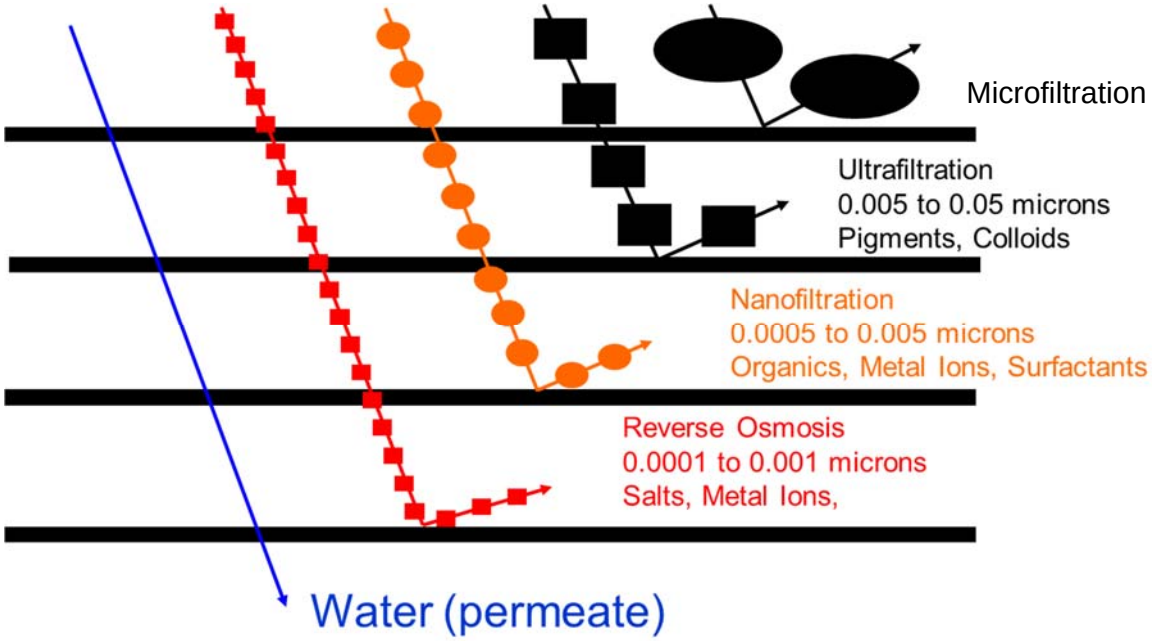
Applications will be presented from a range of commodity areas, including uranium, zinc, lithium, gold, vanadium and nickel. Examples include reagent purification and recovery (esp. acid), the concentrating of target metals and the removal of impurities from target metals.

Keywords: Nanofiltration, hydrometallurgy, acid recovery

Presentation Outline

- Uranium – stripping/elution options
- Lithium – brines
- Nickel – EW electrolyte bleed
- Zinc – Waelz oxides
- Other

Membrane Filtration



Drivers for Nanofiltration

- Reagent recovery
- Downstream benefits:
  - Less acid to neutralise (eg lime after acid recovery)
  - Concentrate up a liquor prior to precipitation
  - Decrease in water usage, sludge disposal

Why so Few Applications?

Review found few commercial applications.
Economics often positive, so why few applications?:

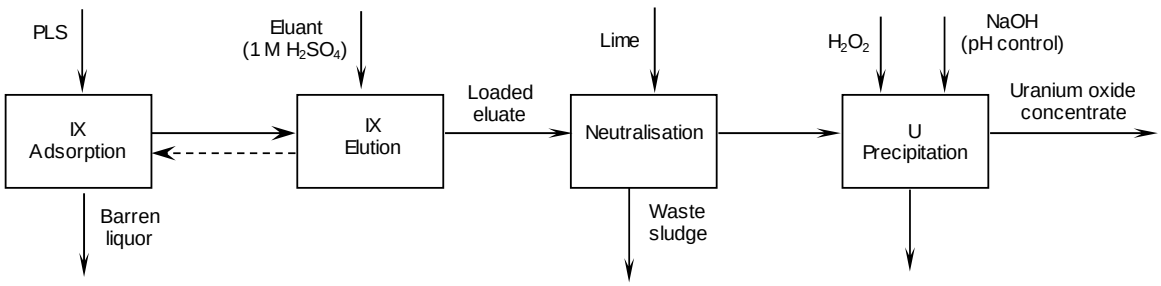
- NF still relatively new in hydromet
- Fouling via scale formation (esp. gypsum)
- Membrane performance/lifespan in acid
- Demonstrate long term flux/rejection (piloting)

NF Options in Uranium Elution/Stripping

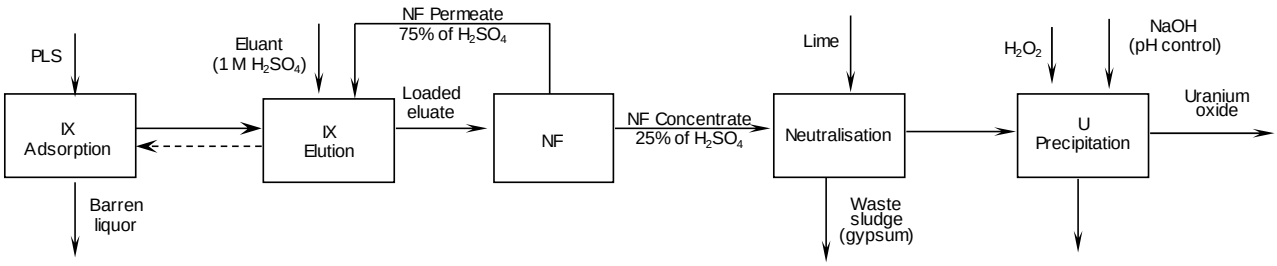
- Acid leach flowsheets where NF is an option:
  - IX: SB elution with 1 M H_2SO_4 (Kayelekera[1], Mkuju River[2], Michelin[3])
  - SX: 4 M H_2SO_4 strip with Alamine (avoids NH_3) (Rabbit Lake[4])
  - Options for high chloride in PLS:
    - SX: 4.5 M H_2SO_4 in loaded strip with DEPHA/Alamine (proposed by ANSTO Minerals[5])
    - IX: 1 M NaCl strip (proposed by ANSTO Minerals[6])
- Alkaline leach flowsheets where NF is an option:
  - IX: $NaHCO_3$ elution (Langer Heinrich[1])

[1] Peacock et al, Paladin Nanofiltration for Reagent Recovery, ALTA U Conf., 2016; [2] Naidoo et al, Recovery of Acid from IX Eluate using Nanofiltration, AATM Conf., 2015; [3] Goode and Brown, Michelin U project, Labrador Testwork, Uranium 2010 Conf.; [4] van Tonder and Edwards, Uranium SX strip options, CIM Journal, 4(4), 2013; [5] Soldenhoff et al, ISEC 2005; [6] Wilson et al, Options for IX for Uranium from Saline Liquors, ALTA U Conf., 2011

Acid Leach Flowsheet: Elution with 1 M H_2SO_4



Acid Leach Flowsheet: Elution with 1 M H_2SO_4 with NF for H_2SO_4 Recovery



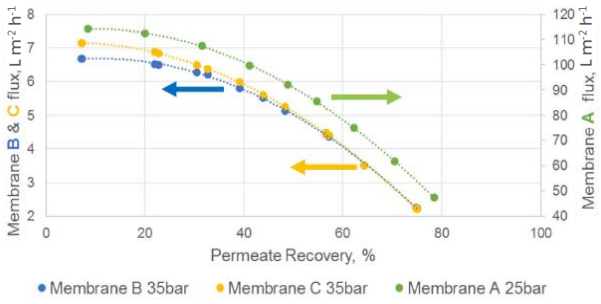
- Permeate recycle to elution and/or leach

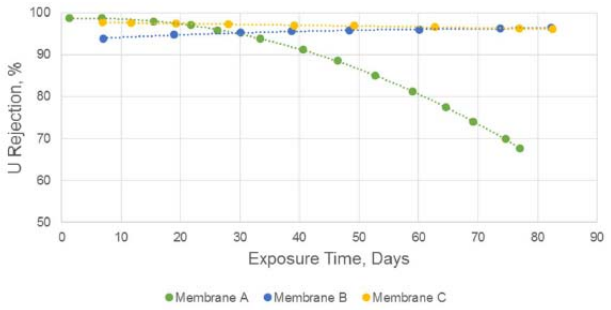
Uranium Eluate – 1 M H_2SO_4 (Mkuju River Pilot)

Rig used at ANSTO Minerals

Acid Recovery from 1 M H_2SO_4 Uranium Eluate

- Flux v membrane life trade-off at 1 M H_2SO_4

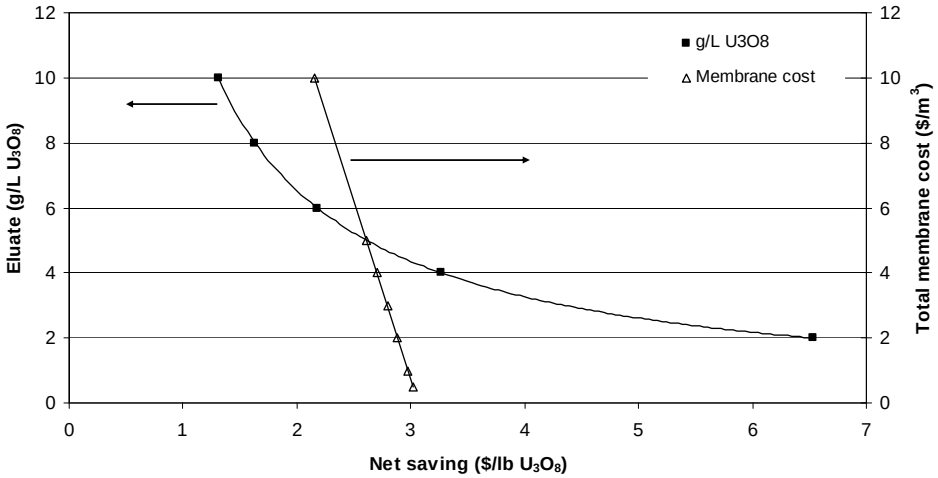




Data from DRA:

A. Naidoo, S.J. Archer, and V.E. Coetzee, The recovery of acid from a uranium ion exchange eluate using nano-filtration technology, Africa Australia Technical Mining Conference 2015, 11-12 June 2015, 2015, Adelaide, Australia, The Australasian Institute of Mining and Metallurgy.

Uranium Eluate – 1 M H_2SO_4 Process Economics



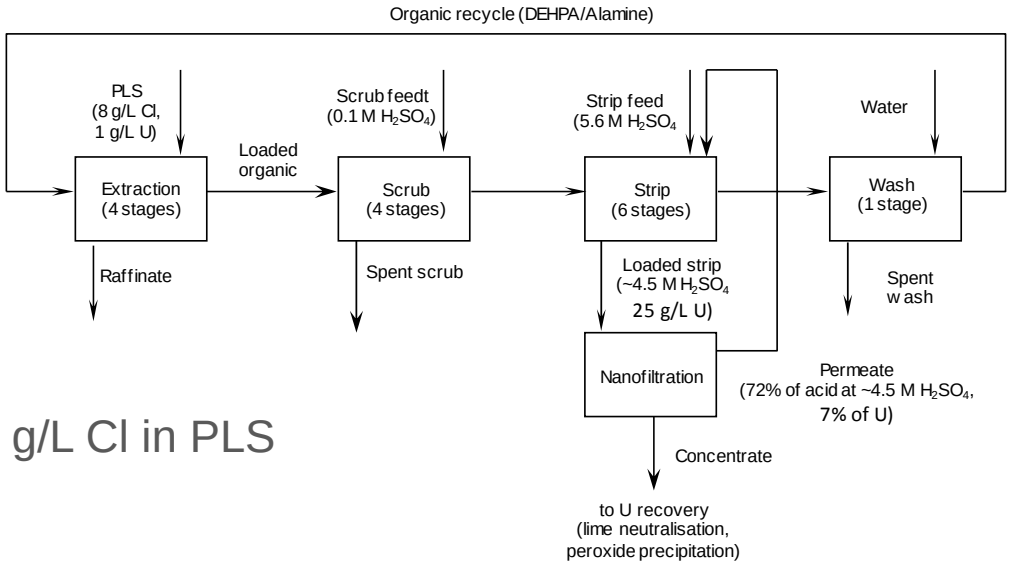
Savings depend on :

- eluate loading (reagent:U ratio), flux, [U], reagent:U ratio, MOC, membrane life

Data from ANSTO:

A. Manis, K. Soldenhoff, and M. Ovinis, Membranes in uranium processing, The AusIMM International Uranium Conference 2011, 8-9 June 2011 Perth Western Australia, 2011, AusIMM.

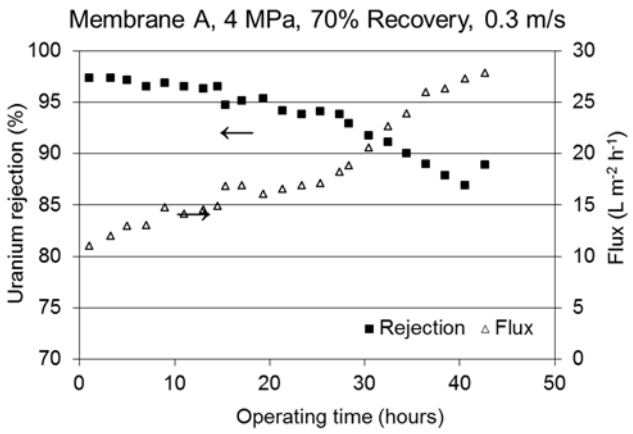
Acid Leach Flowsheet: Uranium Strong Acid Strip

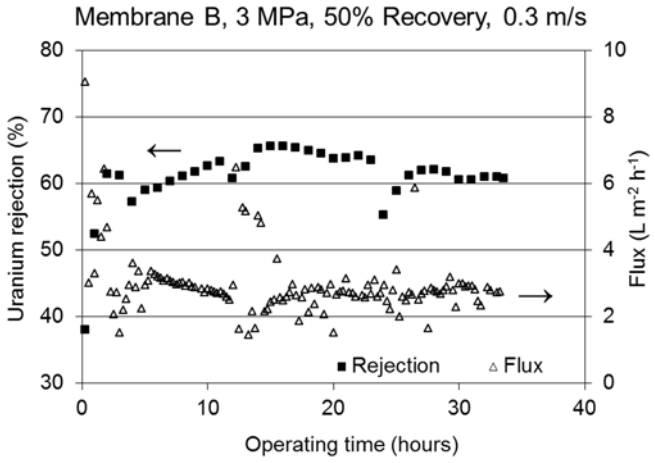


- 8 g/L Cl in PLS

Data from ANSTO (2005): K. Soldenhoff, D. Wilkins, M. Shamieh, and A. Manis, Mini-plant testing of uranium solvent extraction process for acid leach liquors containing chloride, ISEC 2005, 17th International Solvent Extraction Conference 19-23 September, 2005, Beijing, China.

Acid Leach Flowsheet: Uranium Strong Acid Strip

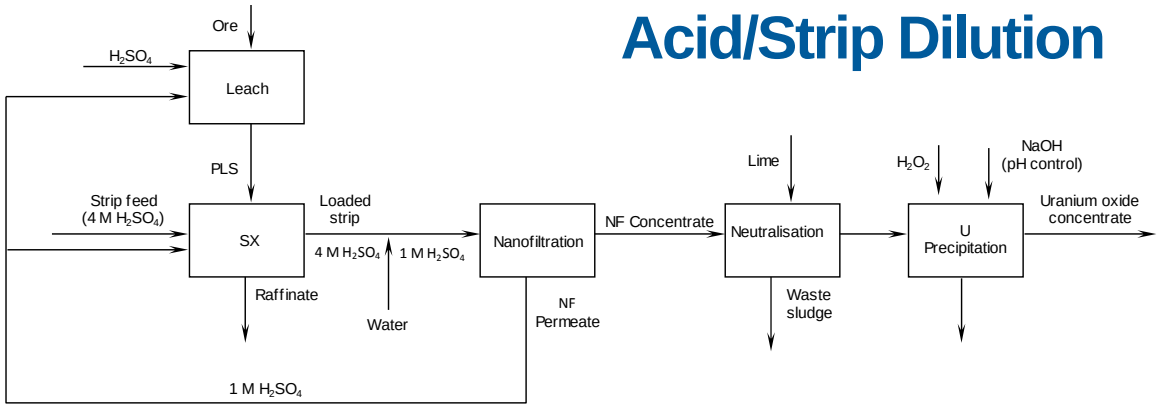




ANSTO Minerals data (2002) – 3 day flat sheet trials

Uranium Strong Acid Strip (4 M H_2SO_4)

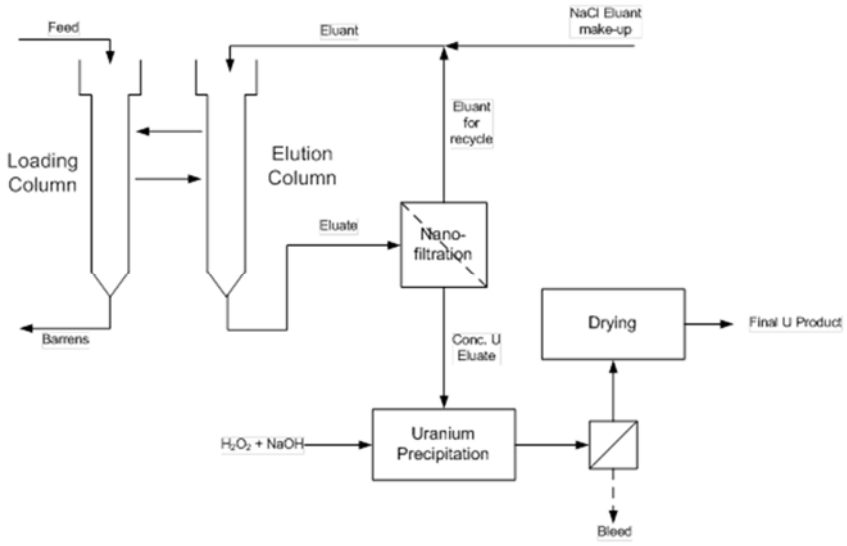
Acid/Strip Dilution



- Dilution prior to NF (proposed by DRA[7])
- Decrease in acidity – improves membrane life, U rejection and flux
- Impact on water balance / PLS flow depends on PLS and eluate U tenors

[7] S.J. Archer, V. Coetzee, E.L. Forner, N. Morgan, and M.H. Kotze, Solvent extraction versus nano-filtration for upgrading uranium and recovery of acid from ion exchange eluate, ISEC 2014, International Solvent Extraction Conference, September 7-11, 2014, 2014, Wurzburg, Germany.

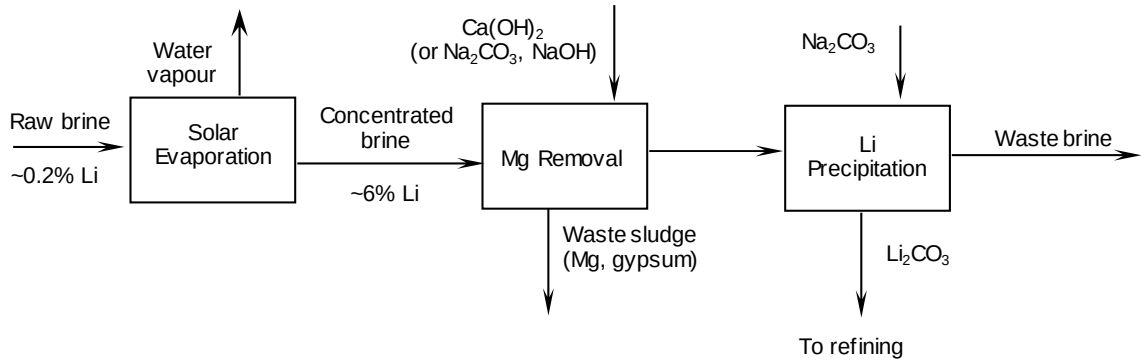
Uranium: NaCl Strip (1 M NaCl)



- Weak base resin for saline leach liquors (5-12 g/L Cl)
- At 72% permeate recovery:
  - 93% U recovery to concentrate
  - 58% NaCl recovery to permeate
- Flowsheet for hypersaline liquors (>12 g/L Cl) with chelating resin, elution with 4 M H_2SO_4 + acid recovery via NF

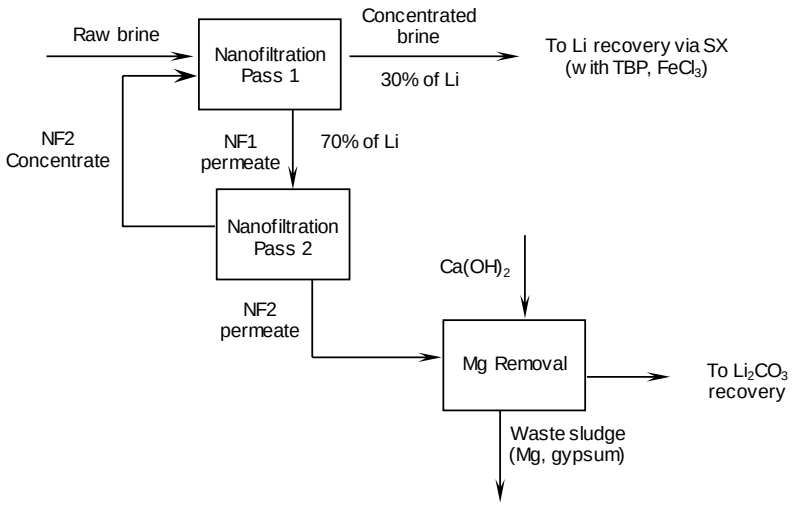
Data from ANSTO: A. Wilson, M. Fainerman-Melnikova, and K. Soldenhoff, What are the options for an integrated IX process to recover uranium from saline and hypersaline liquors?, ALTA 2011 Uranium Conference May 26-27 2011, Perth, 2011, ALTA Metallurgical Services, Australia.

Lithium from Brines



- Brines (mainly NaCl) – largest Li source
- Elevated Mg = ↑ alkali costs

Lithium from Brines

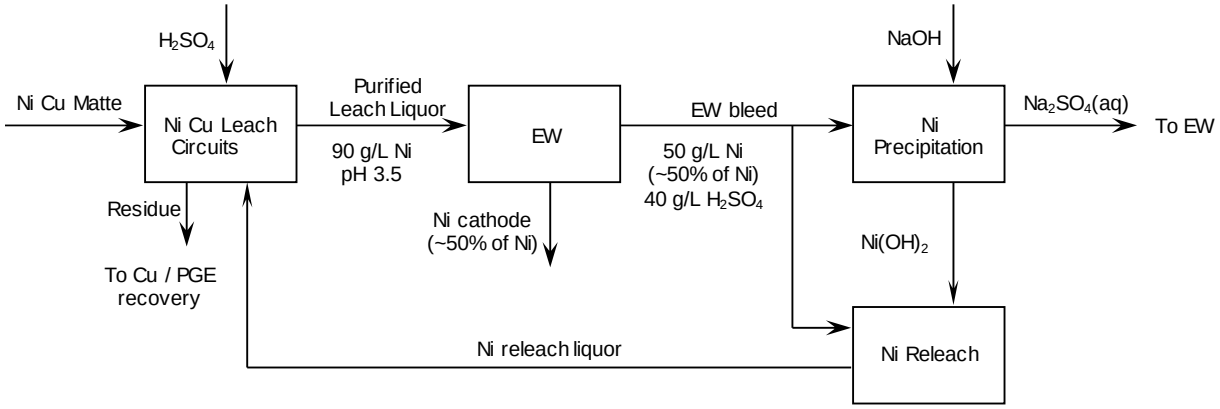


- Low Li tenor would impact recovery to CO_3
- Decrease in Li losses during evap
- Mg rejection (decrease in lime costs)
- Li concentrates in permeate (-ve rejection)
- NaCl, Li not rejected
- $CaSO_4$ formation
  - Dilution, anti-scalant

Data from Wang:

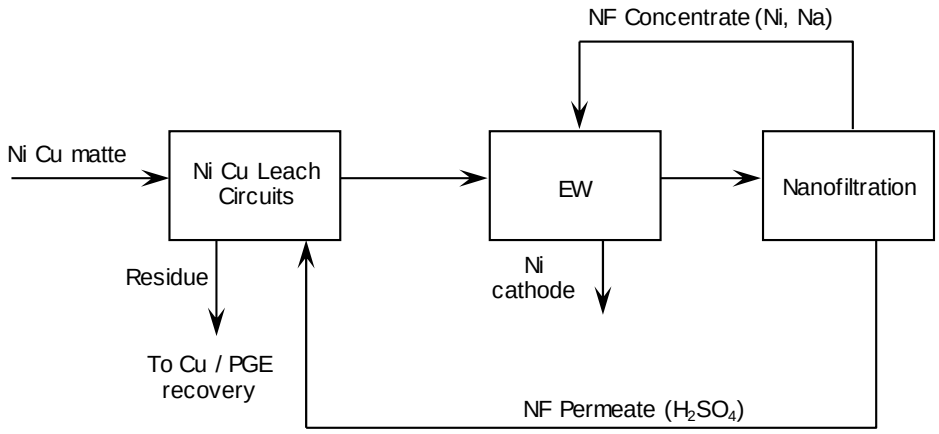
H. Wang and G. Chen, Method for Increasing Lithium Recovery from Brine by Combined Membrane Filtration and Solvent Extraction, Chinese Patent No. CN 102249267, 2011

Nickel Electrolyte Bleed



- Rustenburg Base Metals Refinery (Sherritt Gordon process)
- 50% Ni bleed from EW

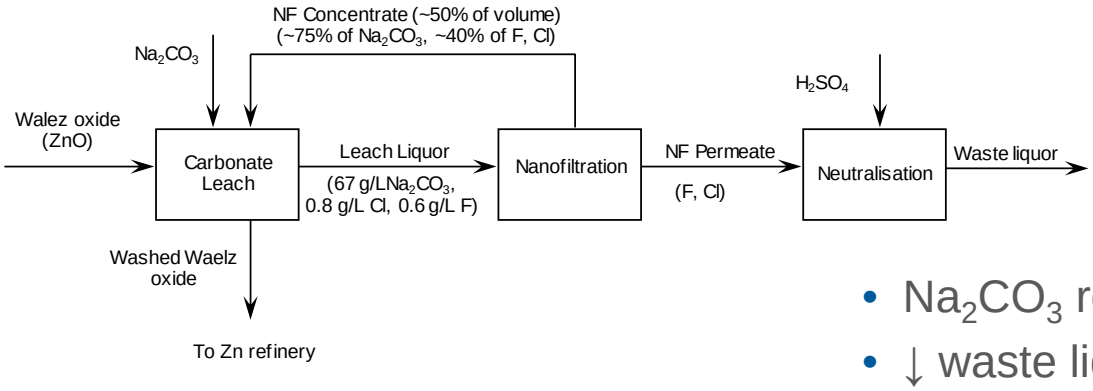
Nickel Electrolyte Bleed



- ↓NaOH costs
- Relatively low fluxes (osmotic pressure difference)
- Bleed to control impurities, recycle Na_2SO_4?

Data from Nel: D.W. Nel, P. van der Gryp, H. Neomagus, and D. Bessarabov, Application of membrane technology in a base metal refinery, Journal of the Southern African Institute of Mining and Metallurgy, 113(4) (2013) 363-374.

Zinc from Waelz Oxides



- Na_2CO_3 recovery
- ↓ waste liquor

- Waelz oxides are from steel EAF dust
- Accounts for ~7% of global Zn production (ICZ, ILZSG, 2015)

Data from Mishina: O. Mishina, M. Stelter, H. Bombach, and E. Niederschlag, Separation of halogenides from alkaline solutions generated during hydrometallurgical zinc winning Part 2: Separation by means of nanofiltration, Erzmetall (in German), 59(1) (2006) 19-25.

Other applications

- Purification of phosphoric acid
- Recovery of vanadium from stone coal (in China)
- Separation of $Cu(CN)_3^{2-}$ from $Au(CN)_2^-$ in gold recovery

Summary

- Growing adoption of membranes in hydrometallurgical flowsheets
- Acid stable membranes are commercial but challenges remain at higher acidities
- Scaling is an issue with gypsum saturated liquors (eg, U acid leach).
- Downstream (cleaner) streams (eg eluate/loaded strip, electrolytes) good candidates for NF
- Suitability of NF to alkaline systems (easier to remove Ca to avoid scale).

Thank you!

Examples of ANSTO Minerals' Facilities:

SX mini-rig

Heap leach columns

Hydromet demonstration plant - 2014

Uranium-REE Proceedings

Not Presented

Not Presented

NANO-FILTRATION TECHNOLOGY IN OPTIMIZING URANIUM PROCESS EFFICIENCY

By

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ABSTRACT

Following the fall of uranium prices after the Fukushima Daiichi nuclear disaster and the volatility of acid prices, uranium mining companies are facing strong incentives to increase extraction efficiency and optimize reagents consumption. Nanofiltration membrane separation, which is based on the difference in rejections of solution components, is gaining attention from uranium miners to resolve the issues. This paper aims to provide support for potential of using polymer nanofiltration membranes, which, given minor capital and low operational costs, allow to increase uranium extraction and decrease eluant consumption.

In cooperation with a top uranium mining company, a series of tests with nanofiltration membranes was conducted to treat *1)* productive leach stream from sulphuric acid heap leaching process, U = 810 mg/L, *2)* raffinate stream after ion exchange resin extraction U = 4.6 mg/L and *3)* uranium mine drainage waters, U = 14.6 mg/L. Aim of the tests was to concentrate uranium in retentate and recover sulphuric acid in permeate, which can be re-used. Research has proven that the rejection of uranium reaches 99%. Due to the high concentration of dissolved solids in streams 1 and 2, the volumetric concentration factor was 1.5, which allowed increasing the uranium concentration in the retentate up to 1.5 times for the productive leach stream and raffinate stream. Mine drainage solution, which is poorer in total dissolved solids, exhibits 99.9% rejection and 20 times concentration increase.

Further, the separation process confirmed low sulphuric acid rejection of up to 10%. This rejection value allows to recover acid in the metal-poor permeate that can be reused at the prior stage of the process.

The ability to effectively separate solution into uranium-rich retentate and metal-poor permeate brings an opportunity to reduce mine operating costs and increase extraction efficiency.

Keywords: nanofiltration, membranes, uranium, acid recovery, productive leach solution, extraction raffinate, mine drain waters

MEMBRANE FILTRATION

In filtration processes membrane acts as a selective barrier allowing certain components of the solution to pass through and rejecting the others. Membranes can be classified by their nature: natural or synthetic; by their structure: porous or continuous; by their morphological structure; by phase separation: gas-gas, gas-liquid etc.; by working principle: absorption, diffusion, ion-exchange, osmotic and so on. Molecular weight cut-off is one of the principal characteristics of the membranes, usually defined as molecular weight of the component of which at least 80% passes through the membrane.

Membrane is selected based on the separation requirements of the components in the stream and the nature of the stream. Characteristics of basic membrane processes are presented in Table 1.

Table 1: Characteristics of basic membrane processes

Process	Working Force	Retentate	Permeate
Osmosis	Chemical Potential	Solutes, Water	Water
Dialysis	Concentration Potential	Large Molecules, Water	Small Molecules, Water
Microfiltration	Pressure	Suspended Particles, Water	Dissolved Solutes, Water
Ultrafiltration	Pressure	Large Molecules, Water	Small Molecules, Water
Nanofiltration	Pressure	Small Molecules, Divalent Salts, Dissociated Acids, Water	Monovalent Ions, Undissociated Acids, Water
Reverse Osmosis	Pressure	All solutes, Water	Water
Electrodialysis	Voltage, Current	Nonionic Solutes, Water	Ionized Solutes, Water
Pervaporation	Pressure	Nonvolatile Molecules, Water	Volatile Small Molecules, Water

For industrial usage flat-sheet membranes are assembled into membrane elements. Spiral-wound elements are commonly employed in the mining and natural resources industries. Such an element has the form of a cylinder composed of sets of sheets (feed spacer, membrane, permeate spacer) rolled around a permeate tube. During the filtration process feed solution is fed with the pressure on the element from its side entering the feed spacer. Membrane faces the feed spacer with its selective side, so that allowed components can pass through the membrane on the permeate spacer. Allowed components pass through the permeate spacer to be collected in the permeate tube, while the rejected components remain in the feed spacer and move to the other end of the element to be collected as retentate. The spiral structure of the element, given its small geometrical dimensions, produces large membrane area and, hence, high production capacity of the element.

In order for the allowed components to pass through the membrane, they have to overcome the osmotic pressure of the solution. This requires the working pressure to be higher than the osmotic pressure of the solution. By altering the working pressure one can control the speed at which permeate is generated, so called the permeate flux. Permeate flux is defined as the volume of permeate produced from unit area of membrane in unit time, and is measured commonly in LMH (liter per meter-squared per hour) or GFD (gallon per foot-squared per day). As filtration proceeds retentate gets more concentrated and its osmotic pressure increases. To indicate the volumetric state of filtration the volumetric concentration factor (VCF) is used. It is defined as the current ratio of initial feed volume to the current retentate volume:

$$\mathrm{VCF} = \frac{\text{Initial Feed Volume}}{\text{Current Retentate Volume}}.$$

The difference in throughput capacity of the membrane for a particular component, leads to mass redistribution of the component between permeate and retentate, and hence concentration change, which is a primary goal of membrane filtration. Rejection is commonly employed to define the ability of the membrane to retain or allow through a particular component. It is defined as one minus the ratio of concentrations of component X in permeate and retentate:

$$R(X) = 1 - \frac{C(X)_{Permeate}}{C(X)_{Retentate}}.$$

If the rejection is equal to one, component X will be completely rejected by the membrane and remain in retentate. If the rejection is equal to zero, component X is fully allowed through the membrane and its concentration will be equal in the feed, permeate and retentate.

NANOFILTRATION MEMBRANES IN URANIUM INDUSTRY

AMS Technologies was contracted by a global uranium producing company to conduct a series of tests to evaluate the feasibility of membrane filtration for uranium concentration and acid recovery in production solutions from mining units. Tests were conducted at the customer's production site using recently collected samples. Three solutions were the subject of the experiment: *1)* productive leach solution, *2)* extraction raffinate, and *3)* mine drainage water stream. The purpose of filtration was to collect and concentrate uranium for later extraction and to recover acid for re-use in earlier process stages. The successful completion of the experiments led to the design of a commercial nanofiltration membrane system.

Tests were performed using NanoPro™ A–3012[1] membrane with 180 Dalton cut-off weight, stable in high acid environment (pH 1–14) and compliant with elevated working pressure (up to 80 bar, 1160 psi) and temperature (up to 80°C, 176°F).

Because the molecular weight cut-off for nanofiltration membranes does not exceed 500 Da in general and 180 Da in particular for A–3012, an appropriate pre-treatment stage must be in place to clean the solution from suspended solids that pose risk to the membrane, causing fouling. All the streams in the test-set were pre-treated with a 5 μ polypropylene filter to reduce fouling risk.

Stream 1 is a productive leach solution (PLS) from a heap leaching unit that was treated mainly to concentrate uranium leading to increased extraction efficiency. Table 2 summarizes the obtained separation results. It can be inferred that the vast majority, 99.0%, of the uranium mass was collected in retentate, and given volumetric the concentration factor of 1.67; the concentration increase was 1.65 times from 0.8 g/L to 1.3 g/L. Around 40% of the sulfuric acid mass was recovered in permeate. Given the substantial decrease in the concentration of impurities (iron, aluminium, molybdenum, vanadium, etc.), recovered acid can be partially re-used in the leaching stage.

The limiting factor in this treatment was the high osmotic pressure of the feed solution generated by high concentrations of iron (19.9 g/L) and aluminium (16.7 g/L). Despite high osmotic pressure, an economical flux figure of 6 LMH, that justifies commercial system installation, was obtained at a VCF of 1.67.

Table 2: Treatment parameters for Stream 1 (PLS solution): working pressure 70 bar

Component		Feed	Permeate	Retentate	Rejection, %	Mass Recovery, %
Volume, m^3		100	40	60		
U,	[mg/L]	809.6	20.0	1'336.0	98.5	99.0
Ca,	[mg/L]	629.2	13.9	1'039.4	98.7	99.1
Mg,	[mg/L]	8'437.0	103.0	13'993.0	99.3	99.5
Fe,	[mg/L]	19'910.0	210.2	33'043.2	99.4	99.6
Na,	[mg/L]	301.4	132.1	414.3	68.1	82.5
Al,	[mg/L]	16'720.0	82.9	27'811.4	99.7	99.8
Mn,	[mg/L]	610.5	9.9	1'010.9	99.0	99.4
Mo,	[mg/L]	90.8	2.7	149.4	98.2	98.8
V,	[mg/L]	210.1	4.5	347.1	98.7	99.1
Si,	[mg/L]	77.2	56.7	90.9	37.6	70.6
SO_4^{2-},	[mg/L]	169'510.0	7'986.0	277'192.7	97.1	98.1
H^+,	mol	0.1	0.1	0.1	2.7	39.3

[1] Detailed data-sheet for NanoPro™ A-3012 membrane can be found at http://www.amsmembrane.com/index.php/en/products/data-sheets

Stream 2 is a raffinate solution after uranium solvent extraction from the productive leach stream. The treatment posed the same goals as with stream 1: concentrate uranium and recover acid. The raffinate stream is depleted in uranium content after extraction. Nanofiltration treatment allowed concentrating the major part of the uranium (97.6%) in retentate and increasing its concentration 1.5 times. At the same time, 30% of the sulphuric acid was collected in permeate for re-use. The treatment proved a high rejection of uranium components (95.2%) even at low concentrations of several mg per liter. The presence of iron and aluminium caused high osmotic pressure of the solution, again, limiting the volumetric recovery.

Table 3: Treatment parameters for Stream 2 (extraction raffinate): working pressure 70 bar

Component		Feed	Permeate	Retentate	Rejection, %	Mass Recovery, %
Volume, m^3		100	34	66		
U,	[mg/L]	4.6	0.3	6.8	95.2	97.6
Ca,	[mg/L]	646.8	22.2	968.6	97.7	98.8
Mg,	[mg/L]	8’591.0	63.9	12’983.7	99.5	99.7
Fe,	[mg/L]	17’160.0	231.0	25’881.0	99.1	99.5
Al,	[mg/L]	16’830.0	26.2	25’486.5	99.9	99.9
Mn,	[mg/L]	617.1	10.0	929.8	98.9	99.4
V,	[mg/L]	212.3	4.6	319.3	98.5	99.3
Si,	[mg/L]	76.5	67.9	80.9	16.1	69.8
SO_4^{2-},	[mg/L]	162’800.0	8250.0	242’416.7	96.6	98.3
H^+,	[mol]	0.2	0.2	0.2	9.9	31.7

Stream 3 was mine-drainage water with low uranium concentration coming from a carbonate leaching plant. The filtration purpose was to collect uranium from the solution. A summary of the treatment is shown in Tab. 4. Low total dissolved solids content, compared to streams 1 and 2, made possible a volumetric concertation to the high VCF figure of 20. Average flux obtained reached 55 LMH.

As in the previous case, the low uranium content did not have significant impact on uranium rejection, which reached 99.9% and brought a concentration increase of almost 20 times.

Table 4: Treatment parameters for Stream 3 (mine drainage): working pressure 70 bar

Component		Feed	Permeate	Retentate	Rejection, %	Mass Recovery, %
Volume, m^3		100	95	5		
U,	[mg/L]	14.63	0.11	290.6	99.9	99.3
Ca,	[mg/L]	82.17	1.10	1’622.5	99.9	98.7
Mg,	[mg/L]	63.25	0.66	1’252.4	99.9	99.0
SO_4^{2-},	[mg/L]	759.00	3.96	15’104.8	99.9	99.5
Cl^-,	[mg/L]	35.20	20.90	306.9	93.2	43.6
HCO^{3-},	[mg/L]	409.20	109.56	6’102.4	98.2	74.6

CONCLUSION

Nanofiltration membranes are a relatively new technology employed by the mining sector, but gain strong and constant attention. They allow separating and concentrating solution components. The uranium industry has high improvement potential and incentives to optimize production.

All three cases illustrate high rejection (> 98%) to uranium and volumetric concentration and flux driven primarily by osmotic pressure of the solution. This result can be highly leveraged in uranium production by concentrating uranium before the extraction stage to increase extraction efficiency and, potentially, to decrease transportation cost if extraction takes place at a different location. Another profitable application lays in treating strip solution to increase uranium concentration before yellow cake production.

Not Presented

EGYPTIAN MONAZITE DIGESTION BY SULPHURIC ACID PROCESS; SEPARATION OF THORIUM

By

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ABSTRACT

The major factors that affect the digestion the monazite mineral obtained from the Egyptian black sand deposits on Rosetta area and the along Mediterranean coast using sulfuric acid were investigated experimentally. The results reveal that digestion temperature of 220^{o}C, acid/monazite ratio of 1.6/1, digestion time of 2.5 hrs and acid concentration of 93% verifies the maximum digestion efficiency for the studied monazite sand, which reached to 93.7%. Precipitation of thorium, rare earths and uranium from the filtrate sulfate solution was carried out using ammonium hydroxide, as a neutralizing agent. The precipitation efficiency of thorium at pH 1.1 was 99.1 % with only 1% of the rare earths co-precipitated. Further precipitation of uranium at pH of 6.5 verifies almost complete precipitation.

Keywords: Thorium Recovery, Leaching, Sulfate Digestion, Monazite, Process Development

INTRODUCTION

Recently, the Chinese government has begun imposing strict export quotas on the rare earth, RE, industry thereby driving RE exploration and mine development in many other regions of the world. The three most common RE minerals that can be mined are bastnäsite, monazite and xenotime. Monazite can be found in Egypt within the black sands. The Egyptian black sands deposits occur along the north Mediterranean coast of the Egyptian Nile delta starting from the west of Rosetta to Damietta and extending to Rafah through 400 km and contain up to 15% of its weight valuable materials[1][2][3][4][5][6].The monazite mineral was separated as a by-product during the concentration and recovery of the more abundant minerals e.g. magnetite, ilmenite, rutile and zircon. Monazite is generally forming about 0.4 – 0.6 % of the highly concentrated black sands, and is essentially an orthophosphate of rare earth elements and thorium with low content of uranium.

Many processes have been suggested for monazite sand digestion, some of them are based on pure alkali digestion using sodium hydroxide followed by mineral acid and/or solvent extraction[5][7][8][9], while others adapted the mechanical chemical alkali digestion process using autoclaved ball mill[3][10]. In spite of the fact that the sulphuric acid process has been introduced a long time ago[11], it is still preferred by many researchers. The main advantage of the sulfuric acid process is its ability to digest all types and grades of monazite, bastnasite or xentotime ores without prior fine grinding[12][13][14][15][16][17][18][19]. Besides, it is a simple and relatively fast process. This process will reduce the hazardous effects and the cost arising from monazite radioactivity in the concentration or separation plant needed to obtain high grade monazite concentrate (> 99%). In addition, this procedure will raise the overall recovery of the crude monazite due to the reduction of the separation steps. The acid solutions obtained from this process contain the valuable elements, while the other gangues are left as un-dissolved residue. It allows for the recovery of thorium, rare earths and uranium elements from the acid solutions with minimum co-precipitation of each one with the others through sequential fractional precipitation by gradually increasing the pH.

The main objective of this study is oriented towards the establishment of a simple and inexpensive process for digestion the low grade Egyptian monazite sand (assaying 48.5% purity), which obtained as a by-product during the physical separation of black sands to separate the more abundant high economic minerals.

EXPERIMENTAL

Materials and Reagents

The chemical materials and reagents used during this study are all laboratory grade produced by ADWIC except for Arsenazo III, sodium salt of 2,2-[1,8- dihydroxy-3,6-disulpho-2,7 naphthalene-bis (azo)] dibenzenearsonic acid, and Arsenazo I, Trisodium salt of 2-[4,5- dihydroxy-2,7-disulpho-3-naphthylazo] benzenearsonic acid were obtained from SIGMA.

Instruments

1) Laser-Fluorometer "UA-3" Uranium Analyzer (Scintrex, Canada) is used for uranium determination. An intense excitation source, N_2-Laser, at 337 nm is applied for exciting uranium. All measurements are carried out in nitrate solutions.

2) UV-Double Beam Spectrophotometer (UNICAM) with 1 cm cells. The optical system is checked automatically and the instrument is periodically calibrated.

3) PH-meter (SCHOTT GERATE, Germany), is used for all experiments in the present work. Calibration of the pH-meter is carried out before each experiment by using two successive buffer solutions (pH 4 and 7, or pH 7 and 10).

Monazite Sand Digestion

The experimental work was conducted upon low-grade monazite sand (about 48.5 % monazite) produced during physical beneficiation of Rashid black sand, Egypt. The bench scale experimental work involves mainly two steps, the first involves studying the digestion of monazite sand, while the second step involves studying precipitation of thorium, rare earths and uranium from the produced solutions. However, a large sample weighing 2 kilograms was also tested to verify the bench scale results.

The sulfuric acid process was applied in this work; in this regards the conditions of maximum digestion of thorium and rare earths were investigated. These conditions involve mainly acid to ore weight ratio, the digestion temperature, agitation time and acid concentration. During the digestion conditions study, one factor is varied while the others were kept constant as was mentioned at each case. For all tests the concentrated acid, proportional with initial monazite sand weight, was firstly heated to about 100°C in a 250 ml Pyrex beaker before beginning the digestion test. For each experiment 50 gram of monazite sand, of -100 mesh, was added gradually to the hot concentrated acid with continuous stirring at 450 r.p.m using a mechanical stirrer, then the temperature was thoroughly increased to the required testing temperature or as mentioned. At the end of each experiment, the reactants paste was cooled to 70°C then transferred to a beaker of one liter using ice water to prevent the temperature increasing above 17°C during leaching for 4 hours, where the quantity of ice water added was equivalent to ten times the monazite sand weight except when the optimum dilution ratio was studied. The leach slurry was then decanted, filtered using filter paper then the residual was washed three times using dilute sulfuric acid. The filtrate and wash was up to a total volume of one liter.

Effect of Digestion Temperature

Effect of temperature on monazite sand digestion was studied at temperature ranges from 160°C to 300°C at intervals of 20°C between each test, while the acid (100%) to ore weight ratio was kept constant at 1.6/1. The required testing temperature was controlled during further heating using an adjustable hot plate and external temperature sensor measurement. The agitation was continued for 2.5 hours from beginning of the monazite sand addition and through the controlled temperature testing.

Effect of Acid to Monazite Sand Ratio on the Digestion

The effect of the acid to monazite sand ratio on the digestion efficiency was studied using ratios from 0.6/1 to 2/1. The required ratio of sulfuric acid was firstly heated to 100°C then the monazite sand gradually added as previously mentioned then the temperature was increased to 220°C and kept constant during agitation each test for 2.5 hours.

Effect of the Digestion Time

To determine the effective digestion time required for reaction completion, several experiments were conducted at constant temperature of 220°C and acid to monazite sand ratio of 1.6/1. The digestion time varies between 0.5-4 hrs.

Sequential Precipitation

The precipitation tests were carried out on a 25 ml sample of clear solution, where the pH value was adjusted using 17.5% ammonia solution. The effect of initial dilution ratio on the precipitation efficiency was tested using dilution ratios ranging from 1:5 to 1:20 through 2.5 incremental increases. The quantities of consumed ammonia were determined during the test to know the effective final dilution for accurate concentration calculations. After precipitation, the slurry was left to settle and samples of clear solutions were withdrawn for analysis against rare earths and uranium to calculate their precipitation efficiency.

The thorium precipitation was investigated in the pH range of 0.5-1.9, rare earths precipitation was investigated in the pH range of 2.1 to 4.1 while uranium precipitation was investigated in the pH range of 4.3 to 6.5.

Analytical Determination Procedures

Analytical determination procedures for thorium and rare earths were carried out utilizing two main procedures; gravimetric in the case of high concentration samples or spectrophotometrically using UV-Double Beam Spectrophotometer (UNICAM) in the case of low concentration samples. In the gravimetric case, thorium was analyzed by the oxalic acid hexamine precipitation method, while rear earths were analyzed by the oxalate precipitation method[20]. The lower concentration samples of thorium and rare earths were analyzed spectrophotometrically using arsenazo III.

Uranium concentration was always analyzed by UB – 3 uranium analyzer utilizing arsenazo I[20][21].

RESULTS AND DISCUSSION

Digestion of Monazite Sand

The raw monazite sand utilized in this research has an effective monazite mineral of 48.5 %. Besides it has other economic minerals such as zircon, rutile and ilmenite, which in total, represent about 33.5%. The latter minerals cannot be attacked during processing of the raw monazite with sulfuric acid and remain as residue, which could be further treated. The composition of the raw monazite sand that was used in this work is indicated in Table 1.

Table 1: The composition of the raw monazite sand

Constituent	Monazite	Zircon	Rutile	Ilmenite	Silicates and others
%	48.5	21.5	6.5	5.5	18

Moreover, the results of the chemical analysis of the main constituents as oxides, in the 48.5 % monazite are illustrated in table 2.

Table 2: The chemical analysis of the main constituents as oxides, in the 48.5 % monazite

Metal Oxide	(REE)2O3	ThO2	U3O8	P2O5
%	30.5	2.97	0.22	13.37

The liquor produced through digestion of monazite with sulfuric acid contains different useful elements such as rare earths, U, Th and Fe. The high commercial value of rare earth elements depends on their purity and the quality of their compounds. In order to purify the liquor, the rare elements are usually precipitated either in the form of rare earth and sodium double sulfate through added amounts of NaOH and sodium sulfate[16] or simply by the addition of ammonia solution[1][18]. The rare earth recovery could be approximately > 98% when the stoichiometric amount of the reagent was two times as high.

Effect of Temperature on Digestion Efficiency of Monazite Sand

The effect of temperature on digestion efficiency of monazite sand was investigated in the temperature range of 160°C to 300°C. The digestion efficiency was calculated as percentage of weight loss of the residuals as compared with the original sample weight. The results of these investigations are illustrated in Figure 1. It is noticeable that the digestion efficiency of monazite sand increased from 63.1% at 160°C to a maximum value of 93.7 at 220°C before it was reduced to 77.9 % at 300ºC respectively.

Finally we can conclude that the optimum digestion operating temperature is 220ºC, which verifies 93.7% digestion efficiency for the monazite sand. This optimum temperature is close to the case of xenotime digestion by sulfuric, which was reported by Vijayalakshmi et al to be 250°C[14] .

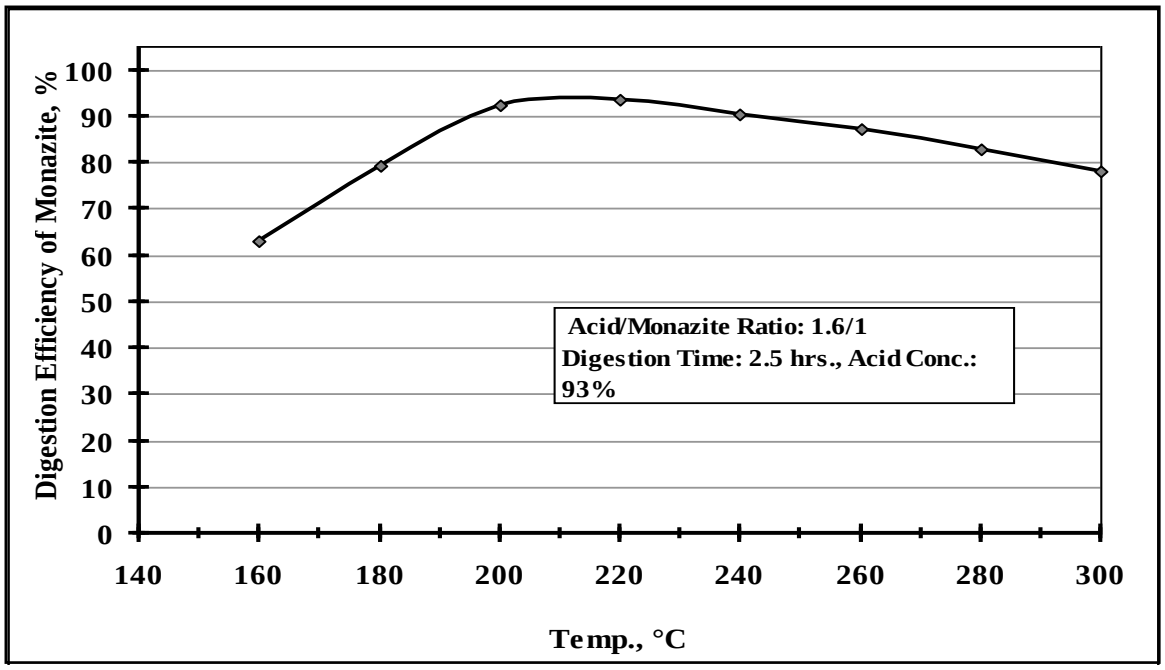

Figure 1: Effect of temperature on the digestion efficiency of monazite.

Effect of Acid to Monazite Ratio on the Digestion Efficiency

The results of studying the effect of acid to monazite sand ratio, in the range of 0.6/1 to 2/1, on digestion efficiency are presented in Figure 2. It can be noticed that increasing the acid/monazite sand ratio increased the extraction efficiency of rare earths. This efficiency increased from 66.6 % at a ratio of 0.6/1 to 92.5% at a ratio of 1.2/1, while there is a slightly increase at the higher ratios where at a ratio of 1.6/1 it was 93.3% and 94.4 % at a ratio of 2/1.

The slight increase in the digestion efficiency after a ratio of 1.6, does not justify the extra huge amount of acid and neutralizing chemicals needed at higher acid to monazite ratios.

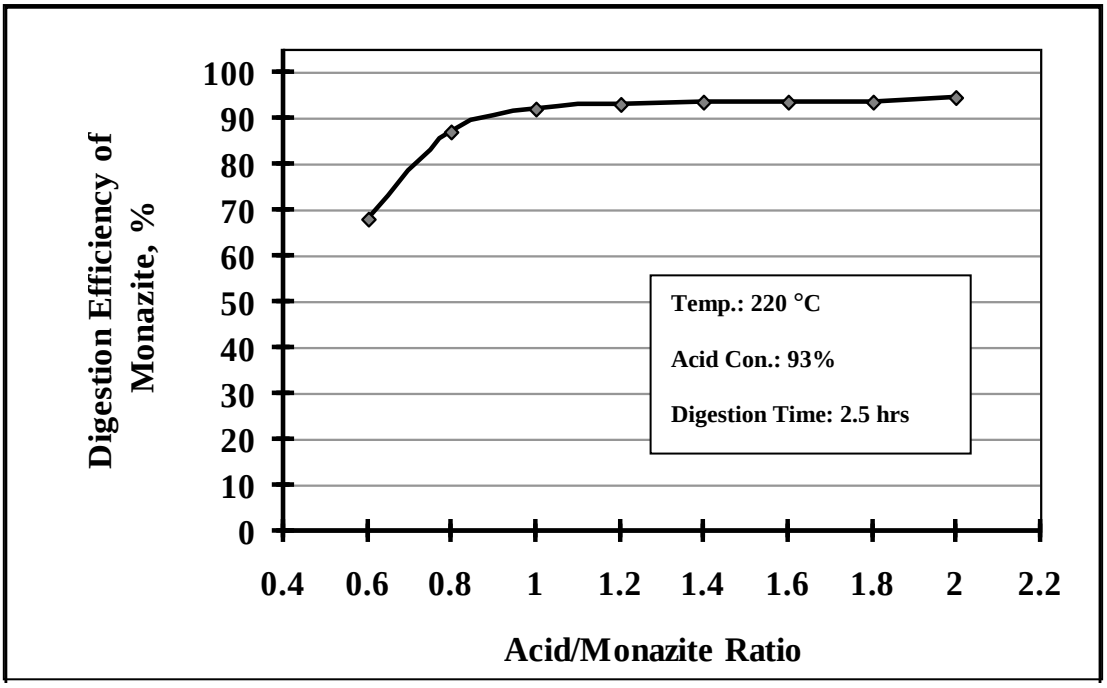

Figure 2: Effect of acid/monazite ratio on the digestion efficiency of monazite.

Effect of Reaction Time on the Digestion Efficiency of Monazite Sand

Figure 3 shows the effect of reaction time on the digestion efficiency in the reaction time range of 0.5 hr to 4 hrs. From this figure it can concluded that the best reaction time is 2.5 hrs. The reduction in digestion efficiency after 2.5 hrs may be attributed to the deposition of some sulfate products on the residuals solid particle surface.

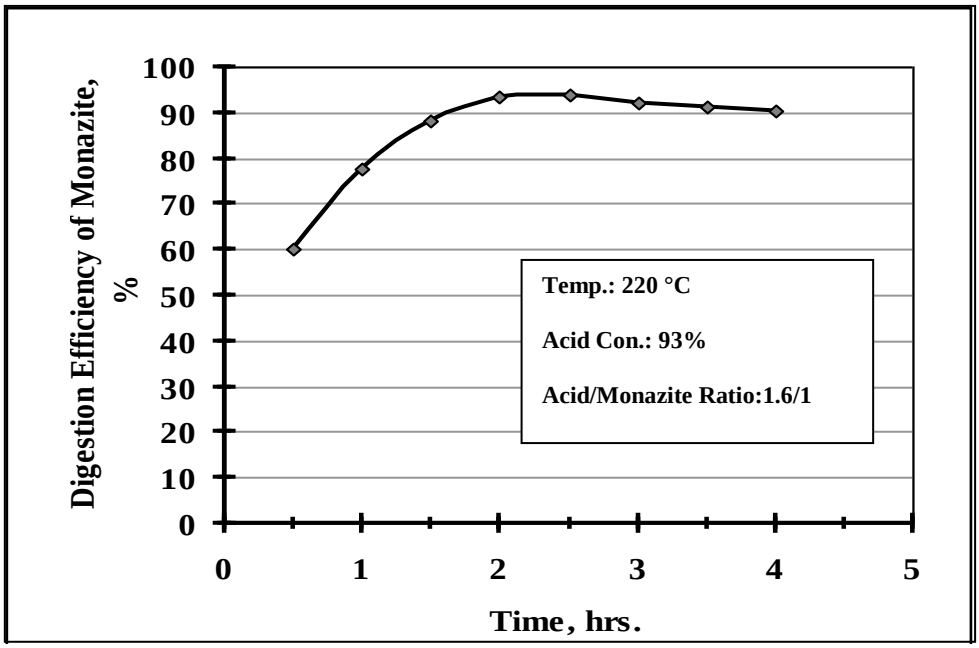

Figure 3: Effect of time on the digestion efficiency of monazite.

Sequential Precipitation

The different main constituents of the clear liquor, obtained after digestion, dilution and filtration, namely thorium, rare earths and uranium, were sequentially precipitated by increasing the pH using NH_4OH. The detailed results of rare earths were published elsewhere[1], while those of uranium will be published later on. We shall mainly discuss the detailed study results for thorium in this article.

The precipitation efficiency of thorium from the clear liquor was calculated according to following equation:

$$\text{Precipitation Efficiency of Th} = \frac{[\text{Initial Th Conc.} - \text{Final Th Conc.}]}{\text{Initial Th Conc.}} X\,100 \qquad (1)$$

While the extraction efficiency of Th was calculated according to Eq. 2:

$$\%\ \text{Extraction efficiency of Th} = \frac{Extracted\ Wt.Th}{Original\ Wt.Th} X\,100 \qquad (2)$$

Effect of pH on Precipitation

The effect of pH and dilution ratio on the precipitation of thorium, rare earths and uranium were studied in the pH range of 0.5 up to 6.5 as can be noticed from Figure 4. It was found that by increasing the pH of the sulphate clear liquor thorium starts to precipitate at pH of 0.7 and is completely precipitated at 1.9, more than 98 % precipitation efficiency, at a dilution ration of 5/1.

At this relatively high pH value the quantity of rare earths co-precipitated with thorium reaches up to 15 %. By increasing the dilution ratio, the precipitation efficiency of 99 % can be reached at lower pH values which in turn decreases the co-precipitated rare earths. The rare earths started to precipitate at pH of 1.8 and were completely precipitated at 4.2.

The precipitation of uranium started at pH > 4 and was almost completely precipitated (more than 99%) at pH value of 6.5. These pH values were utilized through the rest of experimental work during the study of other parameters effect on the precipitation of different components.

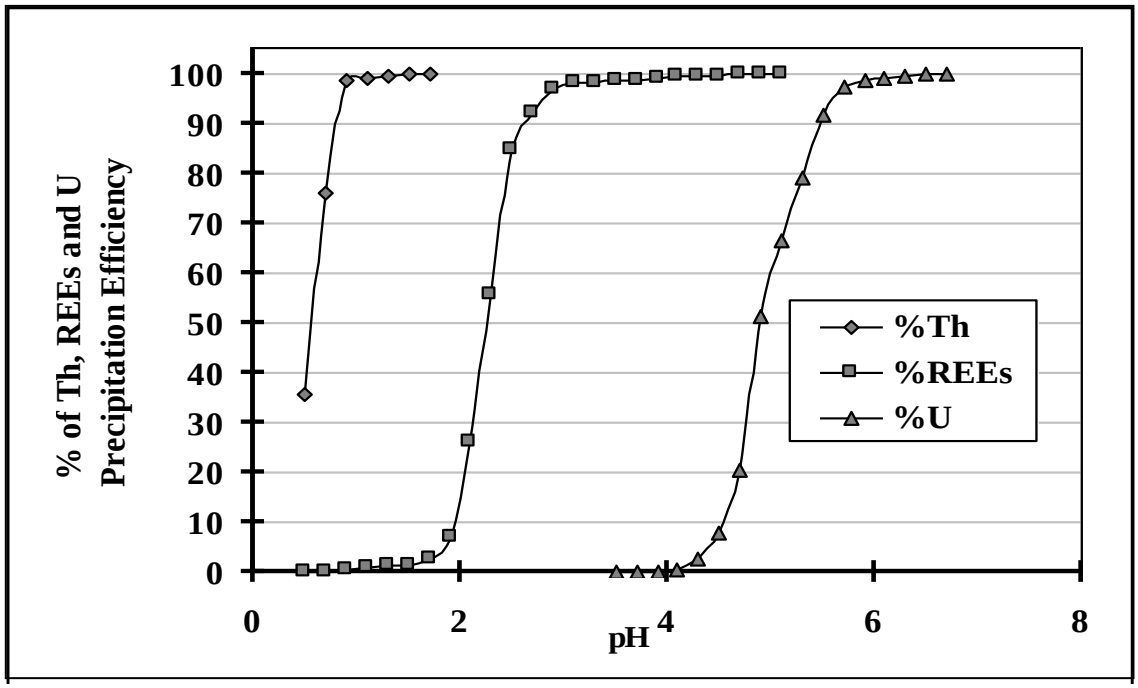

Figure 4: Effect of pH on the recovery of thorium, rare earths and uranium at dilution ratio of 17.5.

Effect of Acid/Monazite Ratio of Thorium Precipitation

The thorium precipitation efficiency was found to be equivalent to 80.7 % at a ratio of 0.6/1 and increased to its maximum value of 99.2 % at a ratio 1.2/1. However, the slight decrease in the extraction efficiency of thorium at the higher ratios as was shown in Figure 5 is not relevant and can be considered to be within experimental error. From these results, it was found that the ratio of 1.6/1 could be considered as the suitable reactant ratio because this ratio is really necessary to maintain the reactants fluidity enough to proceed the reaction. On the other hand, excessive quantities of free sulphuric acid would suppress the fractional precipitation of rare earths and thorium as well as interfere with the later purification step.

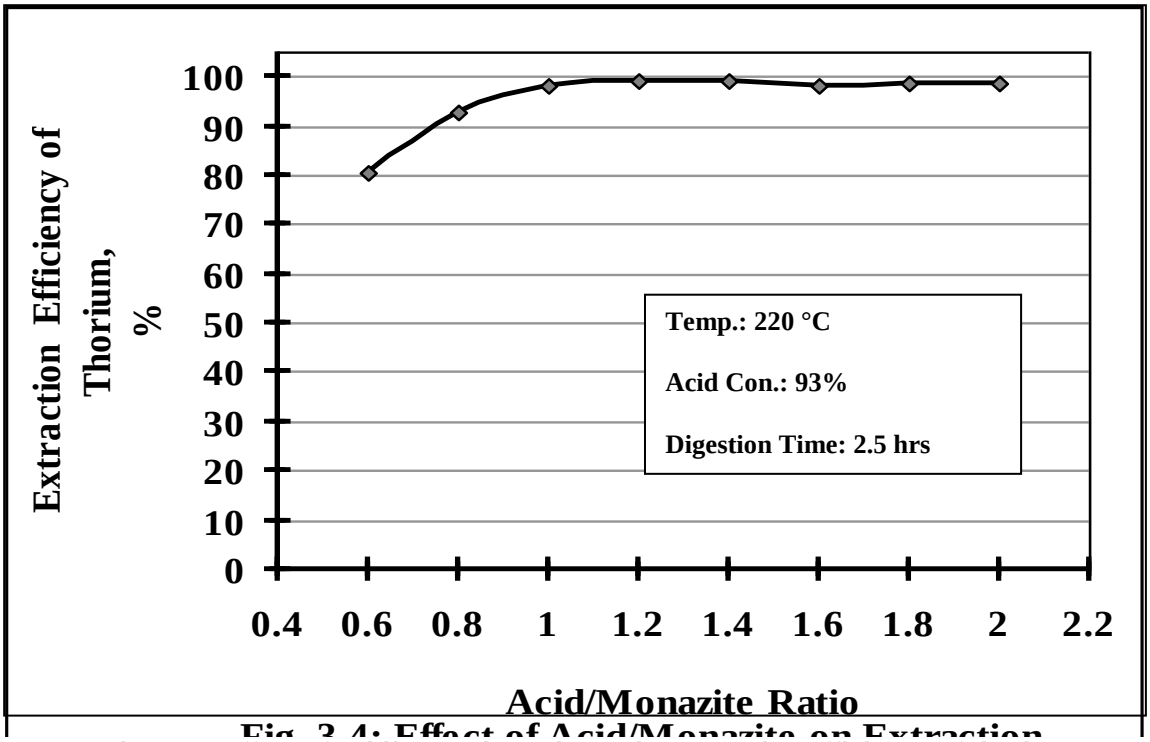

Figure 5: Effect of acid/monazite ratio on the extraction efficiency of thorium.

Effect of Temperature of Digestion on Thorium Extraction Efficiency

Figure 6 shows the effect of digestion temperature on the extraction efficiency of thorium. It is obvious that efficiency increases with temperature up to maximum at 220°C. This is in good agreement with the previously discussed results of effect of temperature on monazite digestions. It is expected that the reduction in monazite digestion efficiency at temperature higher than 220°C is due to the decrease in thorium extraction at higher temperature. This decrease may be also attributed to the formation of thorium pyrophosphate at higher temperatures.

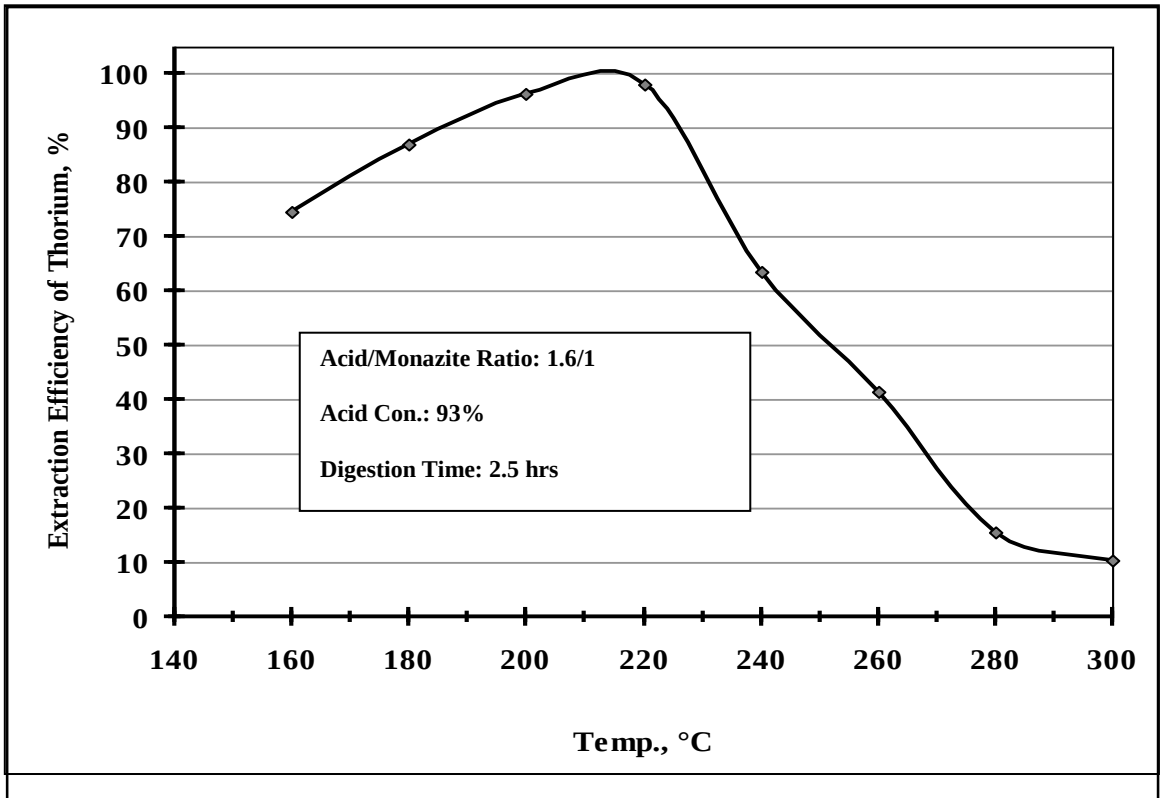

Figure 6: Effect of temperature on the extraction efficiency of thorium.

Effect of Digestion Time on Thorium Extraction Efficiency

Figure 7 illustrates the effect of digestion time on the extraction efficiency of thorium, which was found to be equivalent to 54.8 % at a reaction time 0.5 hr. and to increase to its maximum value of 99.4 % at a reaction time of 2 hr. This efficiency began also to slightly decrease to 98.1 % at a reaction time 2.5 hr. When the reaction time increases to more than 2.5 hr, the extraction efficiency sharply decreases from 85 % to 75.7% at times 3 hr and 4 hr respectively. However, this tendency is similar to that of monazite digestion efficiency and may be also attributed to the formation of thorium pyrophosphate. Based on these results, it was suggested that a digestion time of 2.5 hrs is the suitable digestion time.

It is worth noting that an alternative technique is to extract U & Th from monazite via alkaline decomposition followed by leaching with alkaline carbonate solutions preferentially extracted by Aliquat-336 from 4 M HNO_3 solutions. Hydrochloric acid is considered a good selective stripping agent for Th from U. The extraction efficiency is 80% whereas the stripping efficiency is 82%[8].

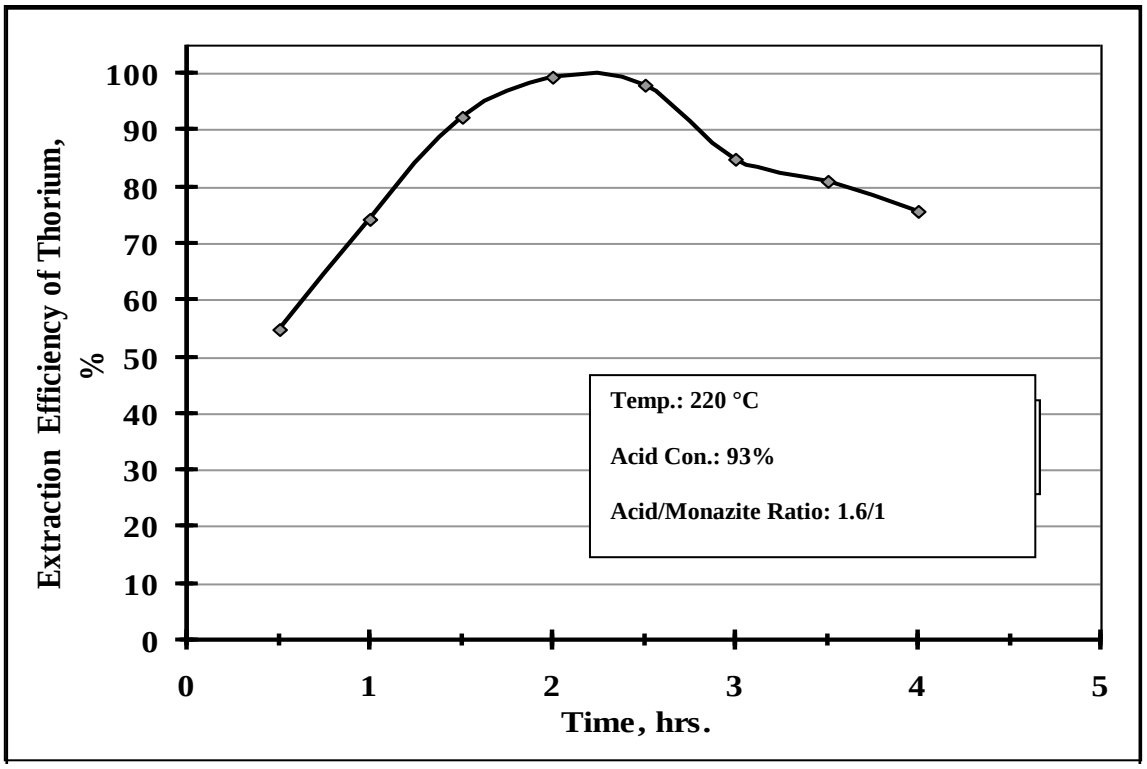

Figure 7: Effect of time on the extraction efficiency of thorium.

CONCLUSION

Egyptian monazite was digested using the sulphuric acid process aiming to separate its valuable components. The major factors that affect the digestion using sulphuric acid such as digestion temperature, acid to monazite sand ratio, the digestion time as well as the acid concentration were examined. The results of these experiments reveal that a digestion temperature of 220 ^{o}C, acid/monazite ratio of 1.6/1, digestion time of 2.5 hrs and acid concentration of 93% verifies the maximum digestion efficiency for the studied monazite sand which reached to 93.7%. The optimum conditions for precipitation and extraction of thorium, rare earth and uranium were investigated.

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