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2023
27 YEARS
30 April - 6 May | Perth, Australia

27TH Annual Conference Proceedings

Uranium Rare Earths Conference

Organised in cooperation with International Atomic Agency (IAEA)

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Purolite

ALTA Metallurgical Services, Melbourne, Australia

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PROCEEDINGS OF
ALTA 2023 URANIUM-RARE EARTHS SESSIONS

4 May 2023

Perth, Australia

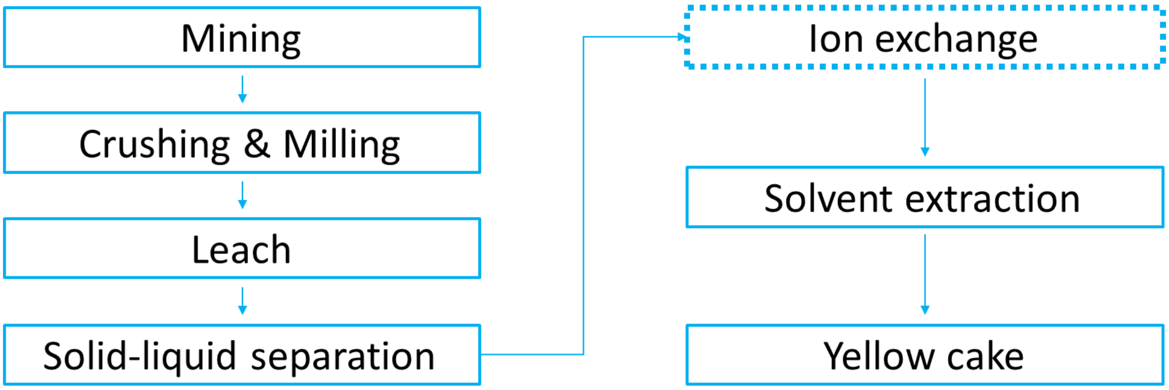
978-0-6458390-1-2

ALTA Metallurgical Services Publications

Uranium Recovery using Purolite Ion Exchange resins

Ion exchange plays an integral role in the economic recovery of uranium. Our innovative product development and strong technical sales support have made Purolite a market leader for uranium extraction around the world.

A typical flowsheet for uranium recovery showing the position of the ion exchange unit operation:



Dissolution of the uranium can be done via an acidic or alkaline leach, depending on the nature of the ore. This process releases the uranium from the ore, generating a pregnant leach liquor containing uranium as an anionic uranyl-sulfate (H_2SO_4 leach) or uranyl-carbonate (alkaline leach) complex. Strong base anion exchange resins readily take up these anionic uranyl-complexes. The ion exchange (IX) resin selectively targets the uranium only, leaving behind most impurities (such as calcium and iron) to report to the barren liquor. The reaction is reversed during the elution step, when the uranium is stripped from the resin into a smaller volume of liquor with a high concentration of uranium.

Ion exchange resins can withstand multiple cycles of loading and elution and typically last for several years.

Please speak with your nearest Purolite office for product recommendations for your specific application. Find us at www.purolite.com.

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URANIUM-RARE EARTHS OPENING

IAEA SUPPORT TO MEMBER STATES FOR SUSTAINABILIY OF NUCLEAR FUEL FOR NUCLEAR POWER PLANTS

By

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ABSTRACT

In January 2023, a total of 422 commercial nuclear reactors were connected to the electrical grid in 32 countries and globally an additional 57 reactors were under construction. Uranium demand is based on both the number of installed nuclear power plants as well as fuel cycle duration, enrichment level, burn-up and advanced fuel technologies.

The IAEA provides support to 175 Member States through a number of programmatic areas. To help ensure sustainability of uranium for the current and future fleet of nuclear power plants, the IAEA currently provides direct support to 52 Member States that are actively involved in development of the uranium production cycle. This includes prospecting, exploration, mine and processing facility development and finally decommissioning and remediation. To enhance support to Member States across all phases of the uranium production cycle, the IAEA published in January 2023 a Nuclear Energy Series Guidance publication titled “Milestones in the Development of National Infrastructure for the Uranium Production Cycle”. This publication can be used by Member States to assess their own status of uranium production development against each of the milestones. This publication also sets the foundation for IAEA integrated uranium production cycle review missions, which upon request from a Member State, will review a Member State’s progress in developing their national uranium production programme. The output of such missions will be a comprehensive final report outlining recommendations, suggestions and identification of areas of good practice. In addition, the results of such a review mission will form the basis for an integrated work plan, which the Member State may use a guidance in their development of national infrastructure for the uranium production cycle.

The OECD-NEA in collaboration with the IAEA is publishing the 2022 edition of “Uranium Resources, Production and Demand”, also commonly known as the “Red Book”. This government-sponsored publication, published biannually since 1965, provides an overview of global trends and developments in uranium resources, production and demand.

This presentation will provide detail on supply and demand forecasts for uranium based on the joint OECD-NEA/IAEA Uranium Resources, Production and Demand (Red Book) 2022 publication as well as provide a more detailed overview of IAEA global support to ensure a sustainable supply of uranium for nuclear power that meets social, environmental and economic requirements.

Keywords: Uranium, Mining, Supply, Demand, Sustainability, Nuclear Fuel, Nuclear Power

Talking Points…

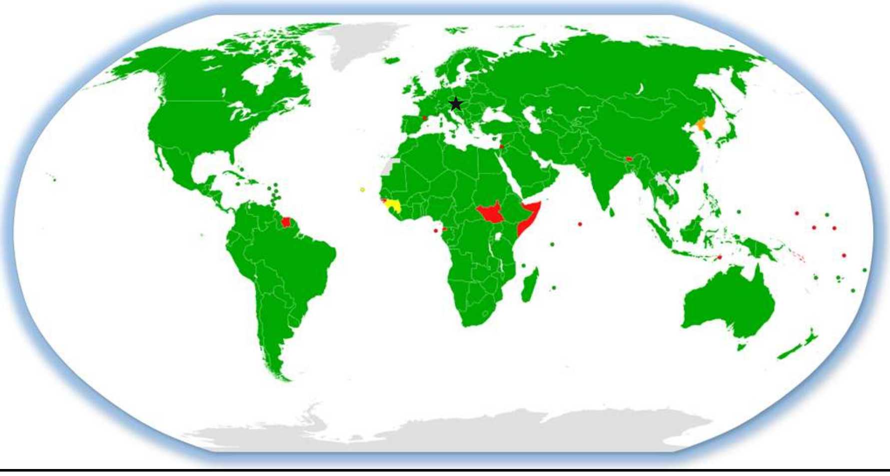
- International Atomic Energy Agency (IAEA)
- IAEA Nuclear Fuel Cycle & Materials Section (NFCMS), Uranium Production Cycle (UPC) Team
- NFCMS UPC Team support to Member States
- NFCMS UPC Team outputs
- Joint OECD-NEA / IAEA Uranium Group
- The “Red Book”… World uranium exploration, resources, and production

International Atomic Energy Agency (IAEA)

- 1953 – Eisenhower’s “Atoms for Peace” speech, UN General Assembly
- 1957 – Established as autonomous agency
  - Although established independent of UN, reports to UN General Assembly and Security Council
- Promotes the peaceful use of nuclear technology and nuclear power worldwide
- Intergovernmental forum for scientific and technical cooperation

IAEA Member States… 176 As of 3 January 2023

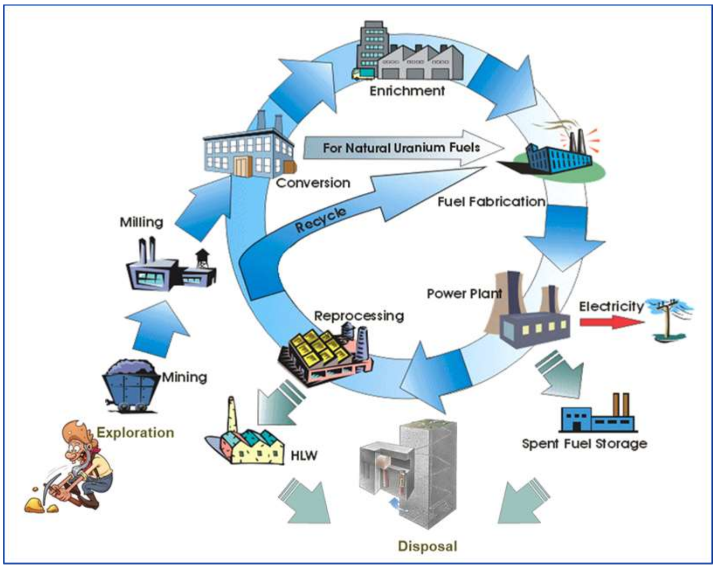
- IAEA provides direct support to 52 Member States actively involved in the development of the uranium production cycle…



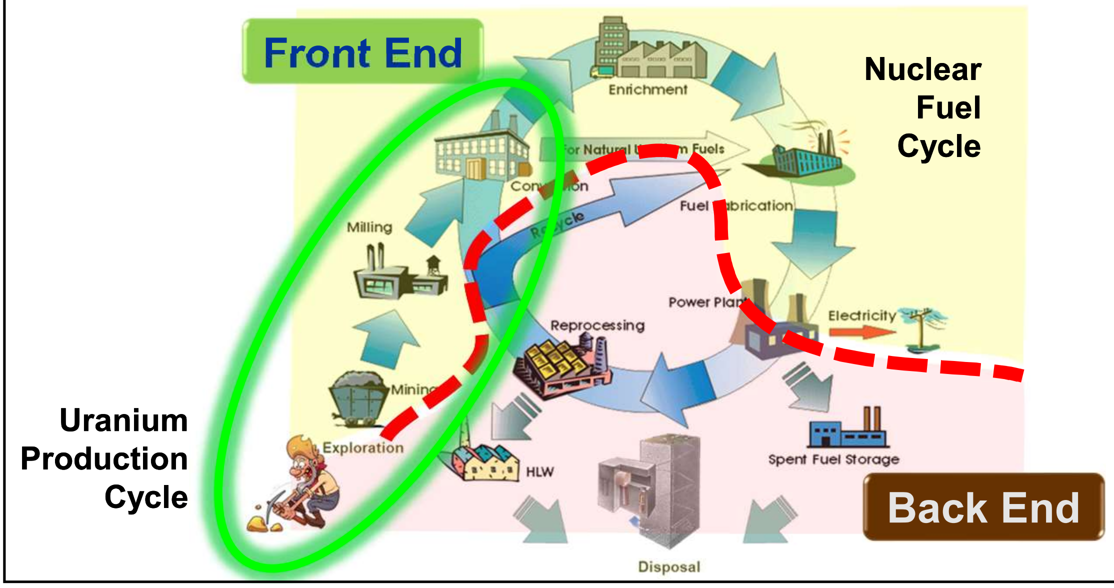
🟩 Member states
🟨 Membership approved
🟧 Withdrew membership
🟥 Non-members

IAEA Provides Support for the Nuclear Fuel Cycle

- Prospecting and exploration
- Mine and processing facility development
- Decommissioning and remediation
- Fuel enrichment and fabrication
- Nuclear power plants
- Spent fuel management



IAEA Nuclear Fuel Cycle & Materials Section (NFCMS), Uranium Production Cycle (UPC) Team…



IAEA NFCMS UPC Team… International Technical Cooperation Projects Support

- Technical training
- Workshops
- Expert missions
- IUPCR missions
- Fellowships
- Scientific visits
- Procurements

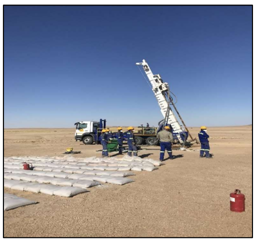
Some 40-60 international experts provided training for 400-600 participants during 2018-2023…

Over 450 lectures on specific topics; Q & A sessions, discussions

During 2016-2023, the UPC Team provided technical advice and support to 27 Inter-Regional, Regional, and National projects

IAEA NFCMS UPC Team… Development of National Infrastructure for the UPC

Development of national infrastructure to support and regulate the uranium production cycle is a significant and complex task



Uranium Exploration

Uranium Mine and Processing Facility Construction

Uranium Mine and Processing Facility Operation

Uranium Mine and Processing Facility Decommissioning and Remediation

The IAEA has developed a Milestones approach to support Member States in developing national infrastructure in a systematic and manageable way

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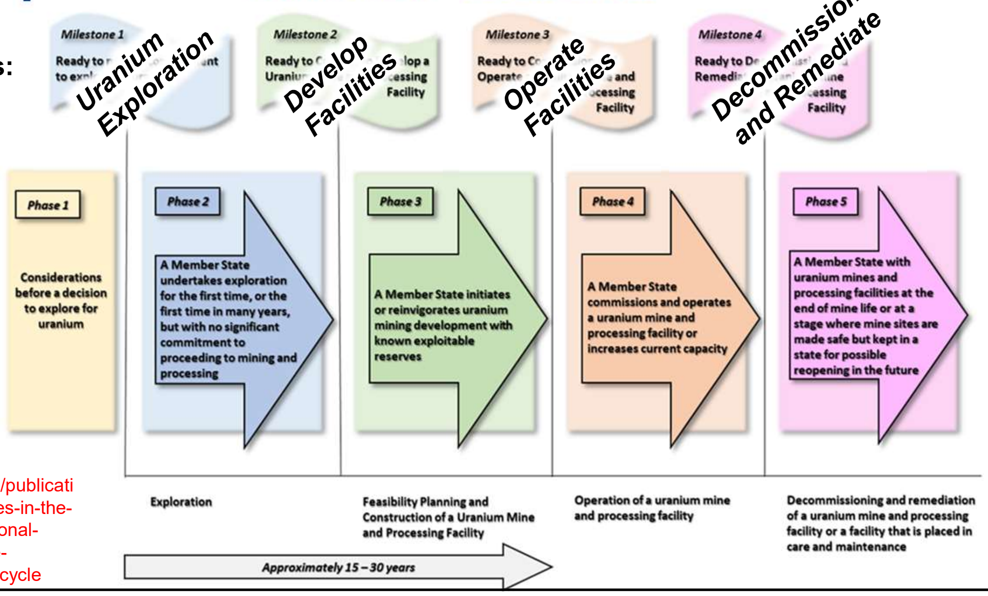
IAEA NFCMS UPC Team… Milestones Approach to Development of National Infrastructure for UPC

Milestones:



Uranium Exploration

Develop Facilities

Operate Facilities

Decommission and Remediate

Considerations before a decision to explore for uranium

A Member State undertakes exploration for the first time, or the first time in many years, but with no significant commitment to proceeding to mining and processing

A Member State initiates or reinvigorates uranium mining development with known exploitable reserves

A Member State commissions and operates a uranium mine and processing facility or increases current capacity

A Member State with uranium mines and processing facilities at the end of mine life or at a stage where mine sites are made safe but kept in a state for possible reopening in the future

Exploration

Feasibility Planning and Construction of a Uranium Mine and Processing Facility

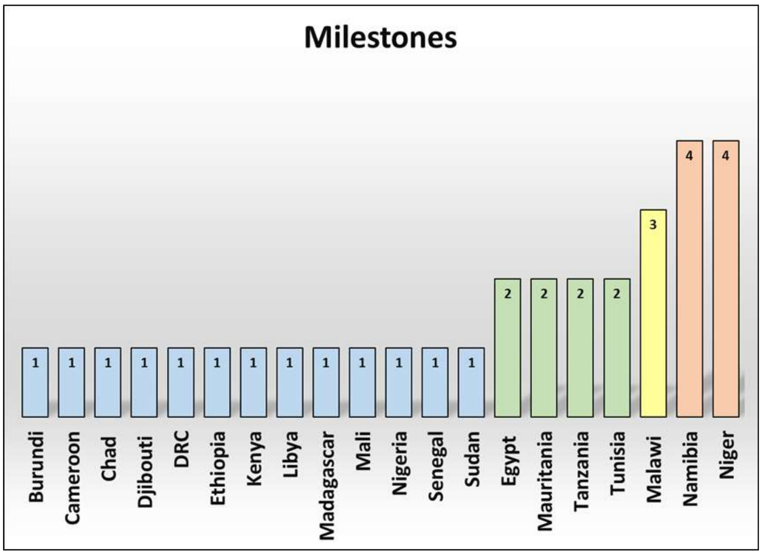
Operation of a uranium mine and processing facility

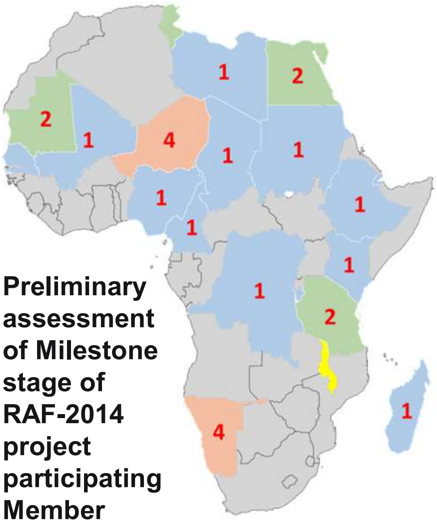
Decommissioning and remediation of a uranium mine and processing facility or a facility that is placed in care and maintenance

https://www.iaea.org/publications/15010/milestones-in-the-development-of-national-infrastructure-for-the-uranium-production-cycle

IAEA NFCMS UPC Team… Milestones Application

Regional Africa IAEA Technical Cooperation Project…





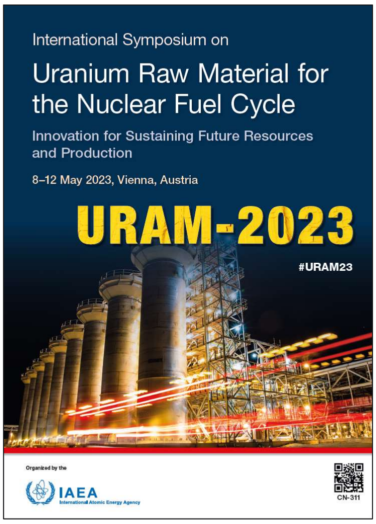
Preliminary assessment of Milestone stage of RAF-2014 project participating Member States…

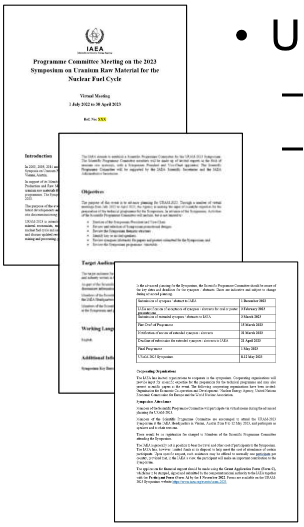
IAEA NFCMS UPC Team Outputs (Resources-Related)

- Authoritative, objective, and reliable information to support member states with characterization and evaluation of uranium resources…
  - Statistical databases
  - Geology
  - Deposit types
  - Deposit distribution
  - Undiscovered resource assessment and mineral potential
  - Best practices guides

https://nucleus.iaea.org/sites/connect/UPCpublic/SitePages/Home.aspx

Meetings… Uranium Raw Material for the Nuclear Fuel Cycle




Programme Committee Meeting on the 2023 Symposium on Uranium Raw Material for the Nuclear Fuel Cycle

Virtual Meeting
1 July 2022 to 30 April 2023

Ref. No: XXX

In the advanced planning for the Symposium, the Scientific Programme Committee should be aware of the key dates and deadlines for the synopses / abstracts. Dates are indicative and subject to change during advanced planning.

Submission of synopses / abstract to IAEA	**1 December 2022**
IAEA notification of acceptance of synopses / abstracts for oral or poster presentations	**3 February 2023**
Submission of extended synopses / abstracts to IAEA	**3 March 2023**
First Draft of Programme	**15 March 2023**
Notification of review of extended synopses / abstracts	**31 March 2023**
Deadline of submission for extended synopses / abstracts to IAEA	**21 April 2023**
Final Programme	**1 May 2023**
URAM-2023 Symposium	**8-12 May 2023**

Cooperating Organizations

The IAEA has invited organizations to cooperate in the symposium. Cooperating organisations will provide input for scientific expertise for the preparation for the technical programme and may also present scientific papers at the event. The following cooperating organizations have been invited: Organisation for Economic Co-operation and Development / Nuclear Energy Agency, United Nations Economic Commission for Europe and the World Nuclear Association.

Symposium Attendance

Members of the Scientific Programme Committee will participate via virtual means during the advanced planning for URAM-2023.

Members of the Scientific Programme Committee are encouraged to attend the URAM-2023 Symposium at the IAEA Headquarters in Vienna, Austria from 8 to 12 May 2023, and participate as speakers and to chair sessions.

There would be no registration fee charged to Members of the Scientific Programme Committee attending the Symposium.

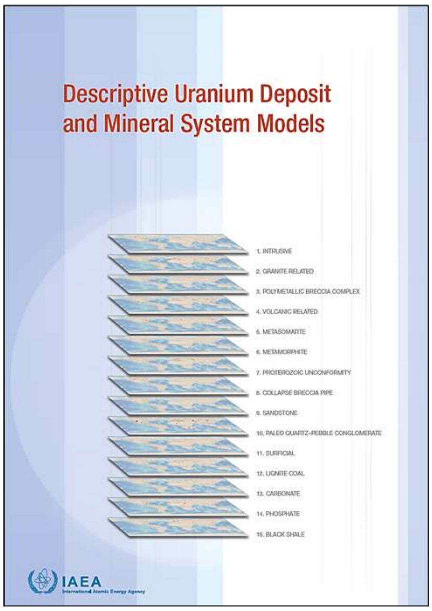
The IAEA is generally not in position to bear the travel and other cost of participants to the Symposium. The IAEA has, however, limited funds at its disposal to help meet the cost of attendance of certain participants. Upon specific request, such assistance may be offered to normally one participate per country, provided that, in the IAEA's view, the participant will make an important contribution to the Symposium.

The application for financial support should be made using the **Grant Application Form (Form C)**, which has to be stamped, signed and submitted by the competent national authority to the IAEA together with the **Participant Form (Form A)** by the **1 November 2022**. Forms are available on the URAM-2023 Symposium website https://www.iaea.org/events/uram-2023.

- URAM Series…
  - 2000, 2005, 2009, 2014, 2018
  - Sessions on…
    - Nuclear power and modern energy markets
    - Uranium markets
    - Uranium geology and resources
    - Advances in exploration
    - Uranium deposit evaluation
    - ISL and other U mining & processing
    - Unconventional U resources, Th
    - Health, safety and environment
    - Tailings and waste management

https://www.iaea.org/events/uram-2023

Publications… Uranium Deposit Types and Models



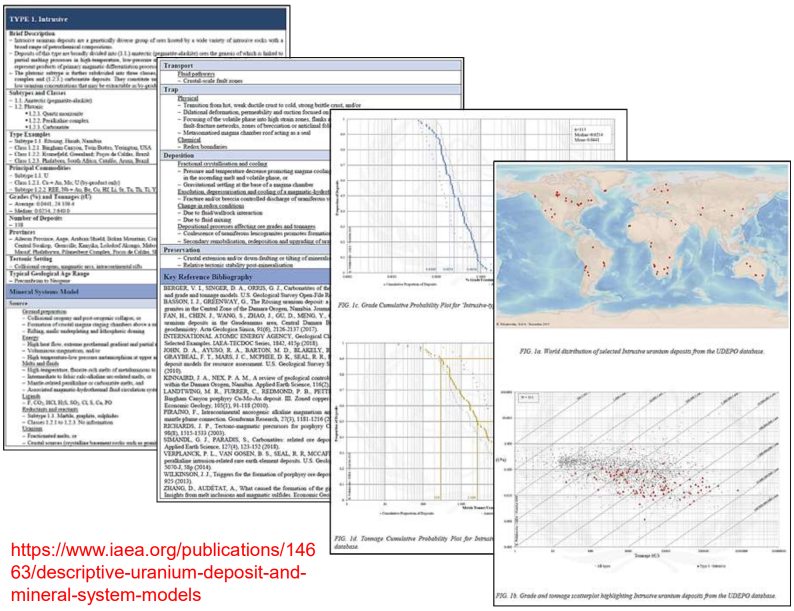


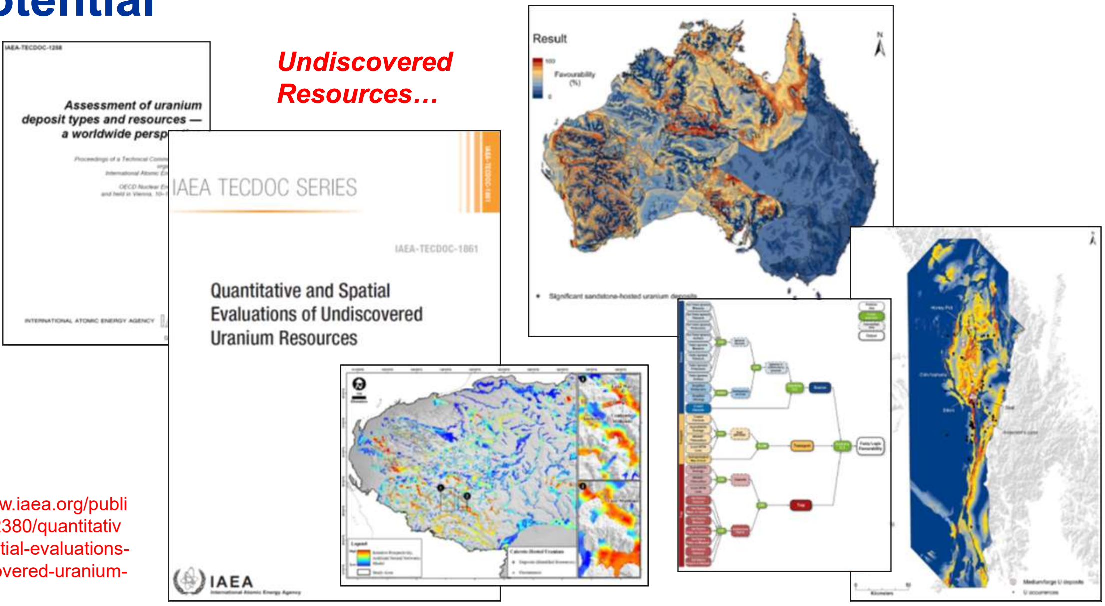
FIG. 1a. World distribution of selected Intrusive uranium deposits from the UDEPO database.

FIG. 1b. Grade and tonnage scatterplot highlighting Intrusive uranium deposits from the UDEPO database.

https://www.iaea.org/publications/14663/descriptive-uranium-deposit-and-mineral-system-models

Publications… Resource Assessment & Mineral Potential

Undiscovered Resources…



IAEA-TECDOC-1258

Assessment of uranium deposit types and resources — a worldwide persp

INTERNATIONAL ATOMIC ENERGY AGENCY

IAEA TECDOC SERIES

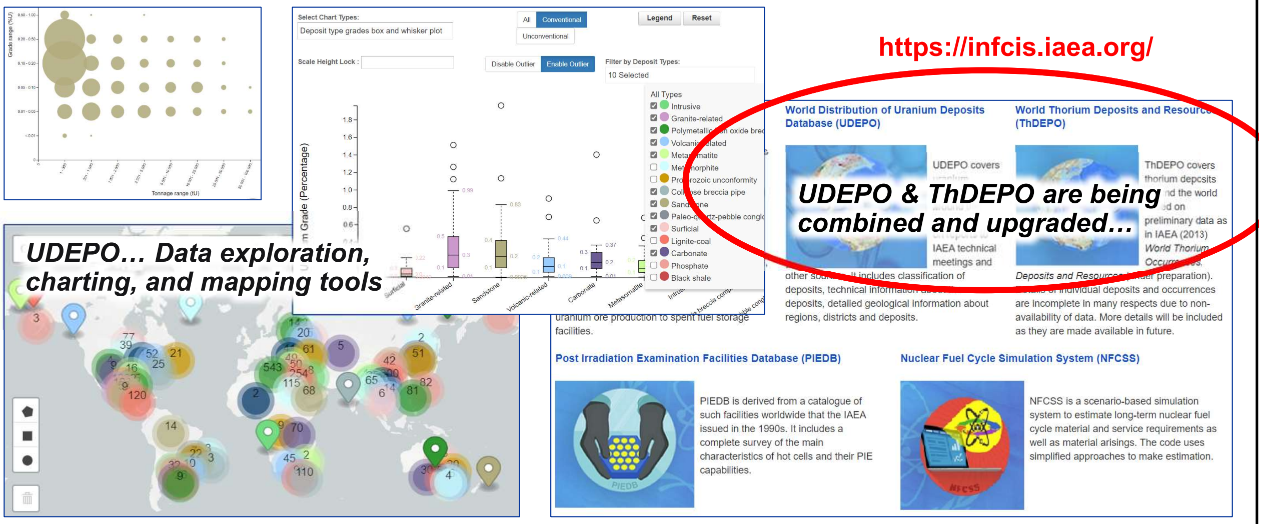
IAEA-TECDOC-1861

Quantitative and Spatial Evaluations of Undiscovered Uranium Resources

IAEA International Atomic Energy Agency

https://www.iaea.org/publications/12380/quantitative-and-spatial-evaluations-of-undiscovered-uranium-resources

Databases & Data Explorers… Integrated Nuclear Fuel Cycle Information Systems, UDEPO & ThDEPO



UDEPO… Data exploration, charting, and mapping tools

https://infcis.iaea.org/

UDEPO & ThDEPO are being combined and upgraded…

Select Chart Types: Deposit type grades box and whisker plot

Filter by Deposit Types: 10 Selected

World Distribution of Uranium Deposits Database (UDEPO)

UDEPO covers … IAEA technical meetings and other sou… It includes classification of deposits, technical information about … deposits, detailed geological information about regions, districts and deposits.

World Thorium Deposits and Resource (ThDEPO)

ThDEPO covers thorium deposits …nd the world …d on preliminary data as in IAEA (2013) *World Thorium Occurrences, Deposits and Resources* (under preparation). … are incomplete in many respects due to non-availability of data. More details will be included as they are made available in future.

… uranium ore production to spent fuel storage facilities.

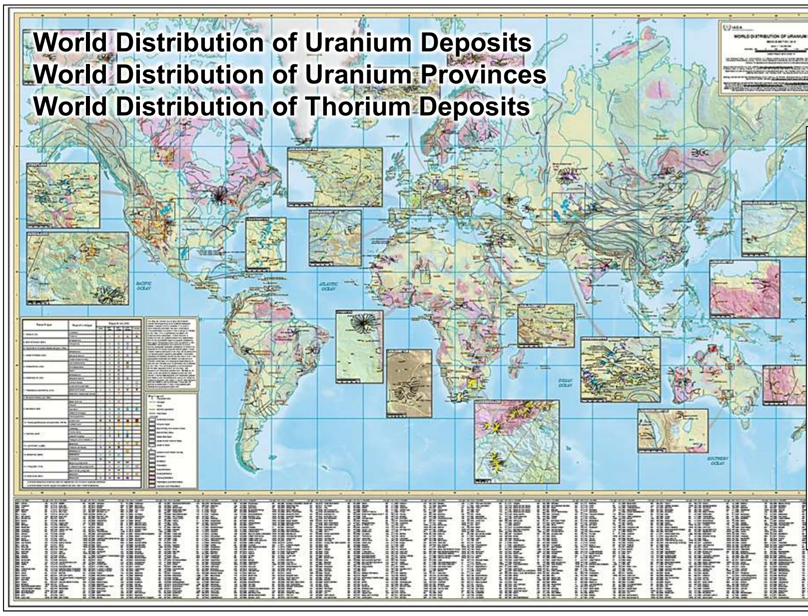
Post Irradiation Examination Facilities Database (PIEDB)

PIEDB is derived from a catalogue of such facilities worldwide that the IAEA issued in the 1990s. It includes a complete survey of the main characteristics of hot cells and their PIE capabilities.

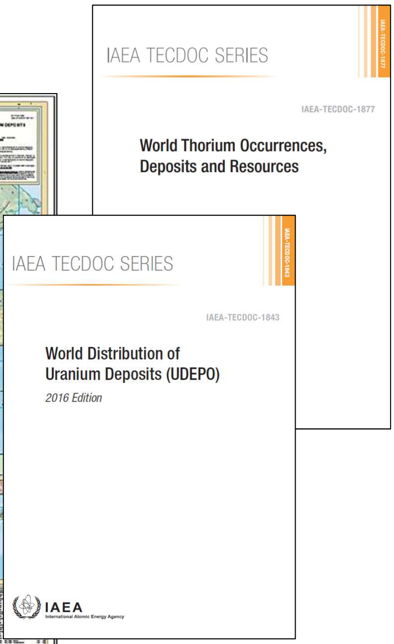
Nuclear Fuel Cycle Simulation System (NFCSS)

NFCSS is a scenario-based simulation system to estimate long-term nuclear fuel cycle material and service requirements as well as material arisings. The code uses simplified approaches to make estimation.

Databases… Interactive PDF Maps



World Distribution of Uranium Deposits
World Distribution of Uranium Provinces
World Distribution of Thorium Deposits



IAEA TECDOC SERIES

IAEA-TECDOC-1877

World Thorium Occurrences, Deposits and Resources

IAEA TECDOC SERIES

IAEA-TECDOC-1843

World Distribution of Uranium Deposits (UDEPO)

2016 Edition

IAEA
International Atomic Energy Agency

https://www.iaea.org/publications/12314/world-distribution-of-uranium-deposits

Joint OECD-NEA / IAEA Uranium Group

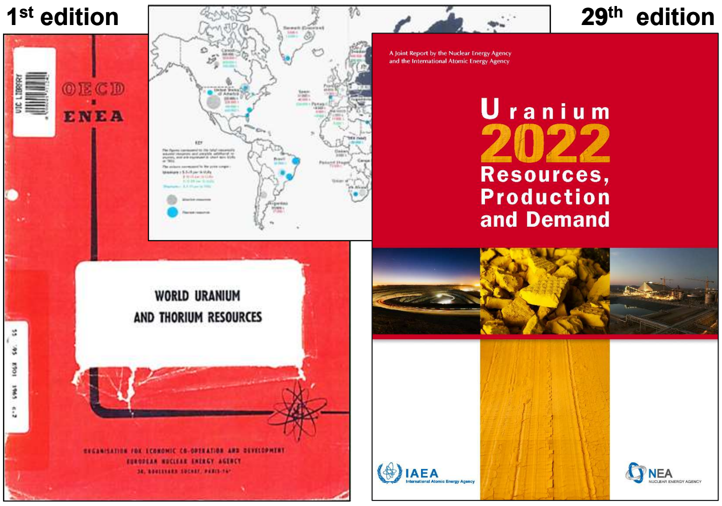
- Collaborative effort between the Nuclear Energy Agency (NEA) of the Organisation for Economic Cooperation and Development (OECD) and the International Atomic Energy Agency (IAEA)…
  - – Forum for the exchange of information, analysis, and guidance on the uranium market and its role and relationship with respect to the global nuclear fuel cycle
  - – Platform for dialogue and cooperation among governments, industry, and other stakeholders on issues related to the uranium market and the nuclear fuel cycle
  - – Activities are based on the principles of transparency, objectivity, and impartiality

https://www.oecd-nea.org/jcms/pl_28567/the-joint-nea/iaea-group-on-uranium-ug

Joint OECD-NEA / IAEA Uranium Group… Red Book

- Responsible for preparation and publication of the "**Red Book**"
- Tracks world and country trends and developments in uranium resources, production & demand…
  - Derived from government information officially reported to the IAEA
  - Aims to obtain a uniform, worldwide acceptable classification of uranium resources

1st edition **29th edition**



1965
OECD / ENEA

2023
OECD-NEA / IAEA

https://www.oecd-nea.org/jcms/pl_79960/uranium-2022-resources-production-and-demand

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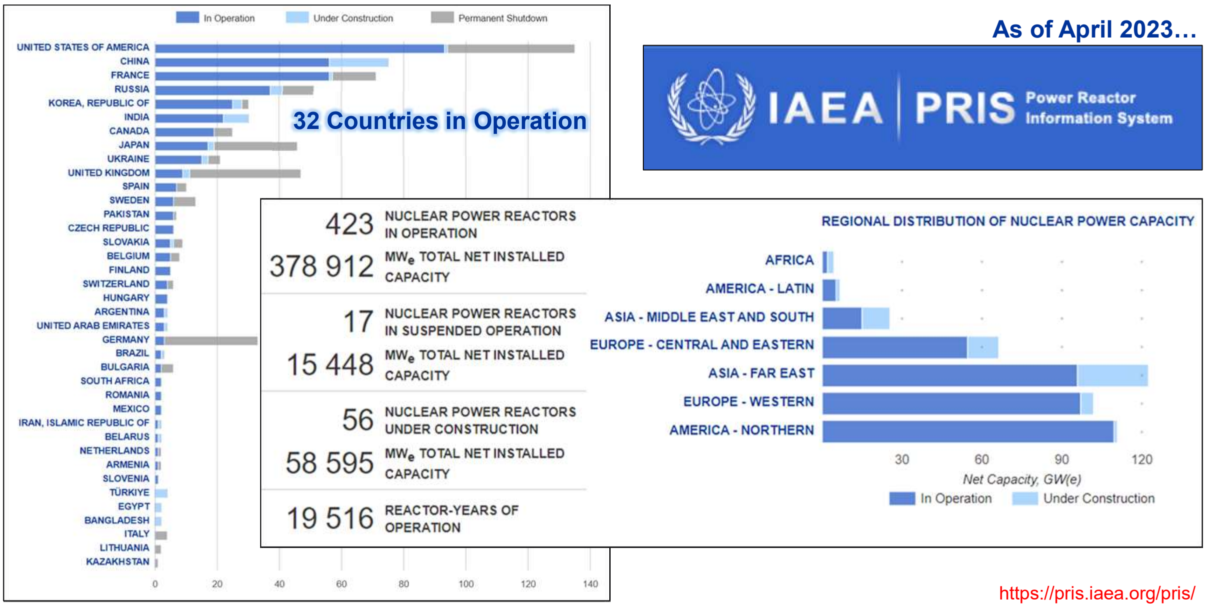
Red Book… Uranium Demand, Commercial NPPs…

As of April 2023…



423 NUCLEAR POWER REACTORS IN OPERATION

378 912 MW_e TOTAL NET INSTALLED CAPACITY

17 NUCLEAR POWER REACTORS IN SUSPENDED OPERATION

15 448 MW_e TOTAL NET INSTALLED CAPACITY

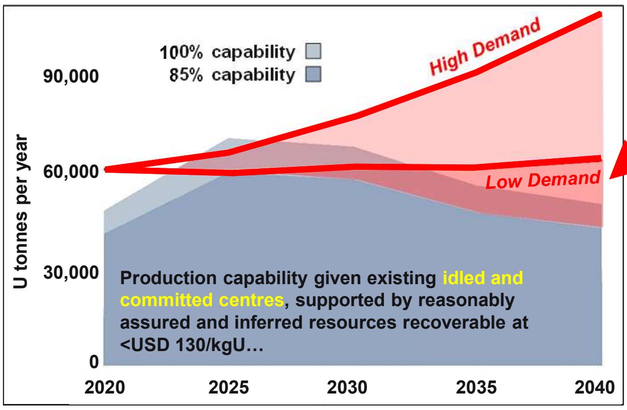
56 NUCLEAR POWER REACTORS UNDER CONSTRUCTION

58 595 MW_e TOTAL NET INSTALLED CAPACITY

19 516 REACTOR-YEARS OF OPERATION

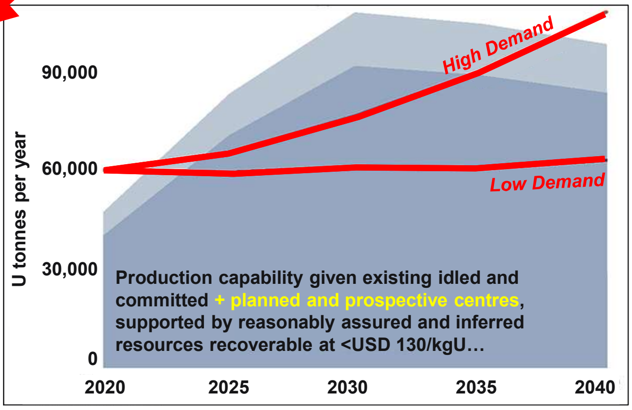
https://pris.iaea.org/pris/

Red Book… Uranium Production and Demand, Projection to 2040 (based on 2019 & 2020 data)



Production capability given existing idled and committed centres, supported by reasonably assured and inferred resources recoverable at <USD 130/kgU…

Gap between high demand and 85% capability production…

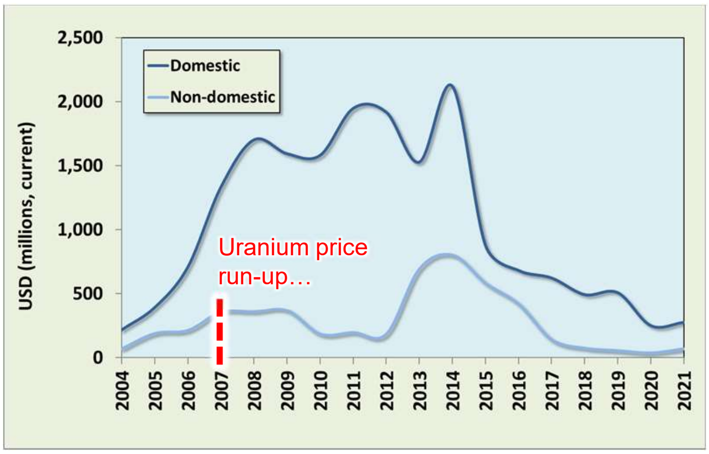


Production capability given existing idled and committed + planned and prospective centres, supported by reasonably assured and inferred resources recoverable at <USD 130/kgU…

- Actual uranium production seldom, if ever, matches full production capability
- It is assumed that secondary supply will fill the gaps when requirements are greater than production

Red Book… Exploration & Mine Development Expenditures (2019 & 2020)

- Decreased to ~USD 250M in 2020 from ~USD 500M in 2018, and ~*USD 2B* in 2014
- Preliminary 2021 expenditures show small increase to ~USD 280M

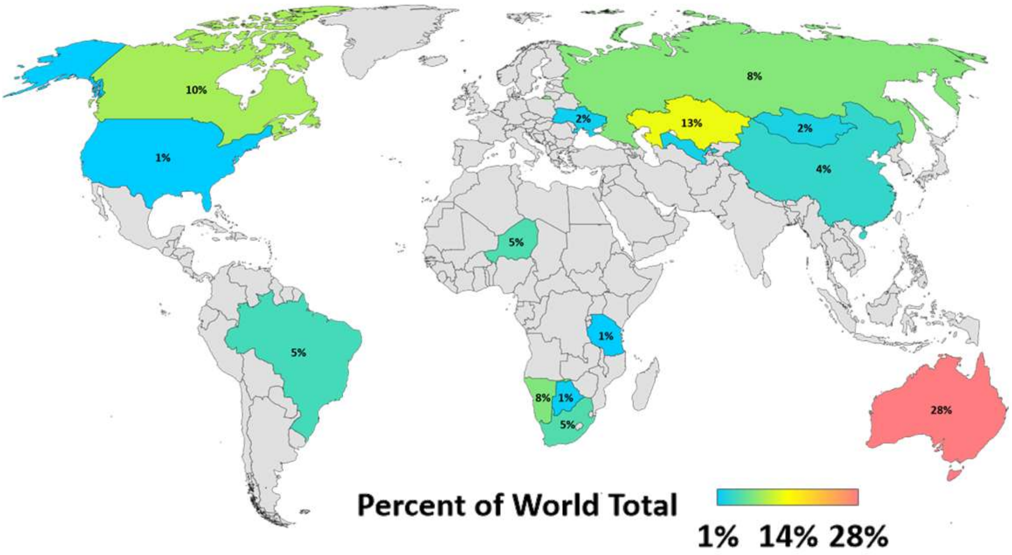


Uranium price run-up…

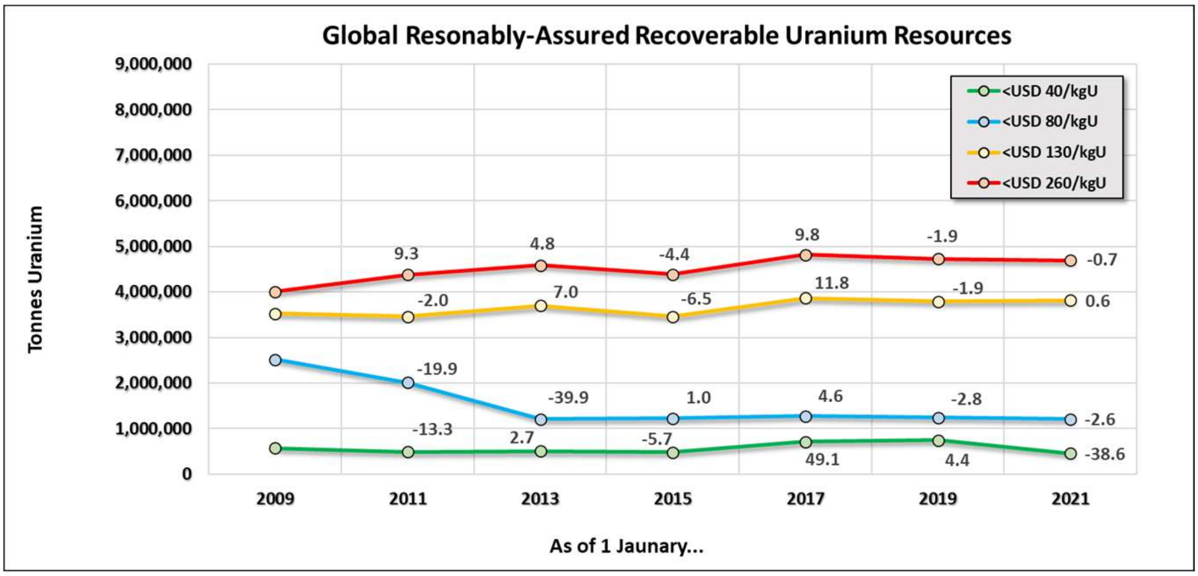
- Total expenditures continue to decrease in response to a depressed uranium market that has lasted since mid-2011

Red Book… Identified Recoverable Resources Distribution at <USD 130/kgU (2019 & 2020)

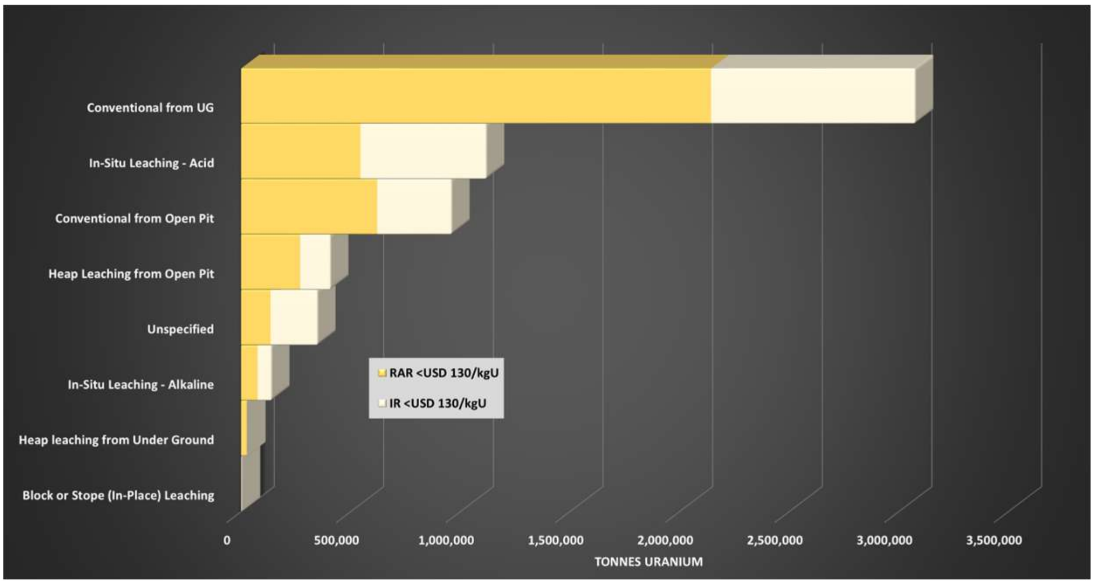
Australia	28%
Kazakhstan	13%
Canada	10%
Russia	8%
Namibia	8%
South Africa	5%
Niger	5%
Brazil	5%
China	4%
Mongolia	2%
Uzbekistan	2%
Ukraine	2%
Botswana	1%
United States	1%
Tanzania	1%



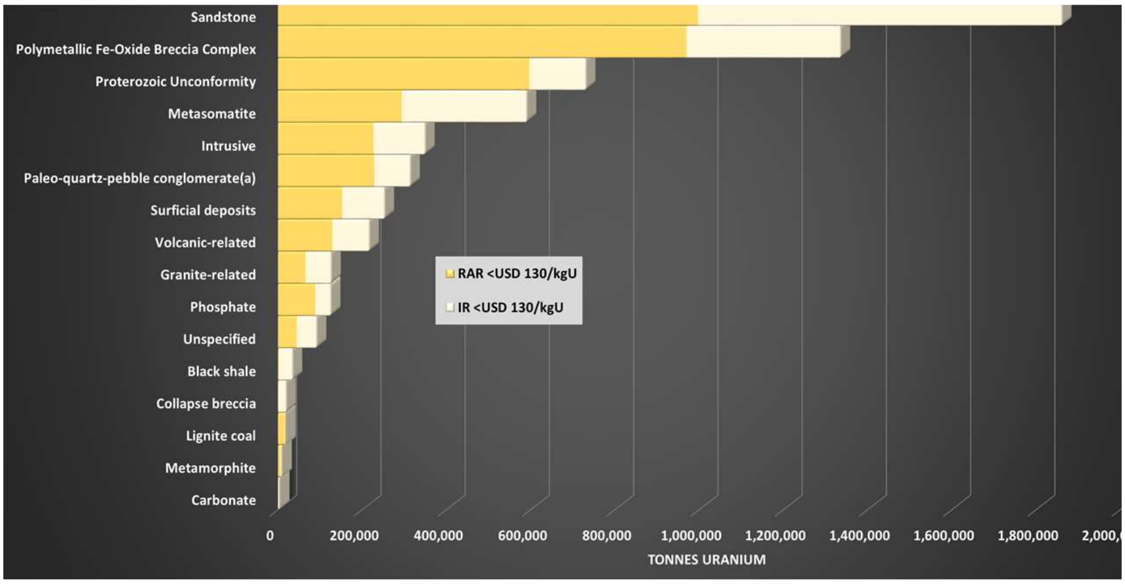
Red Book… Changes in Global Uranium Reasonably Assured Recoverable Resources



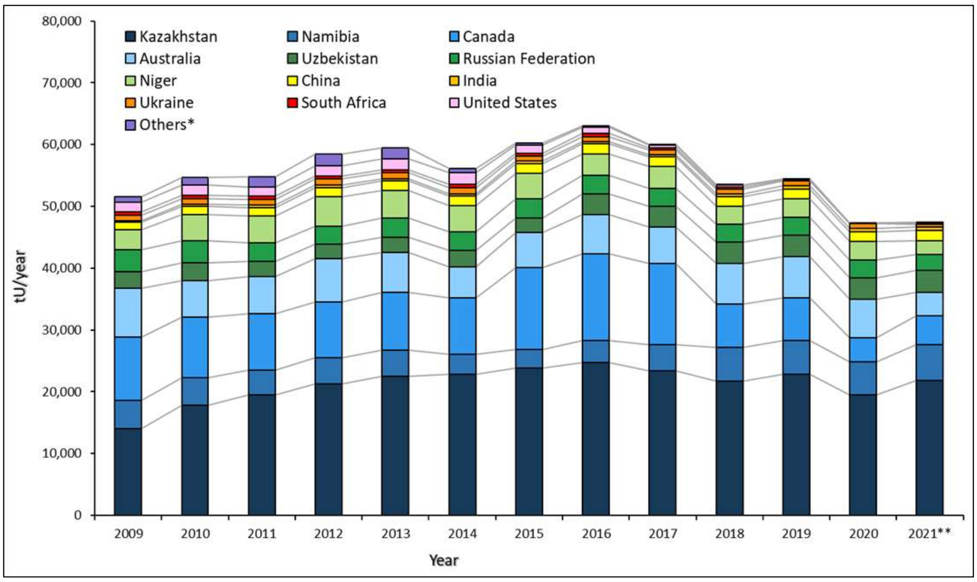
Red Book… Identified Recoverable Resources, by Processing Method, at <USD 130/kgU (2019 & 2020)



Red Book… Identified Recoverable Resources by Deposit Type, at <USD 130/kgU (2019 & 2020)

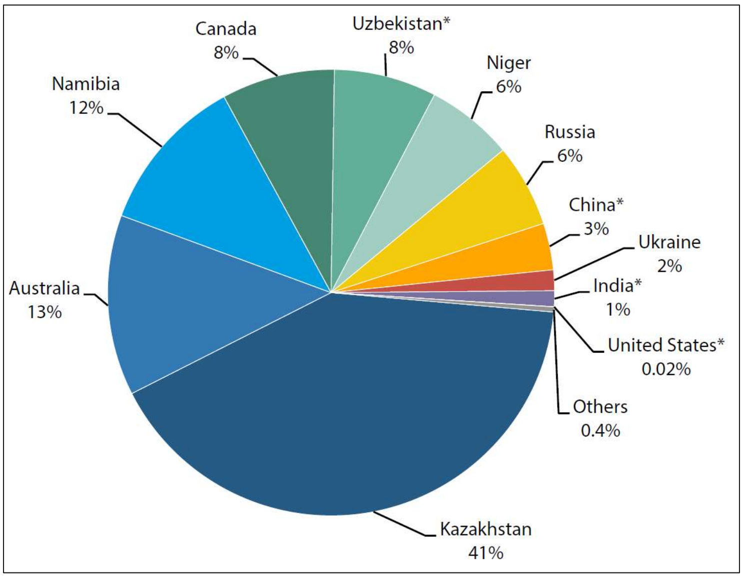


Red Book… World Total Recent Uranium Production 2009-2021 (~0.72M tU)

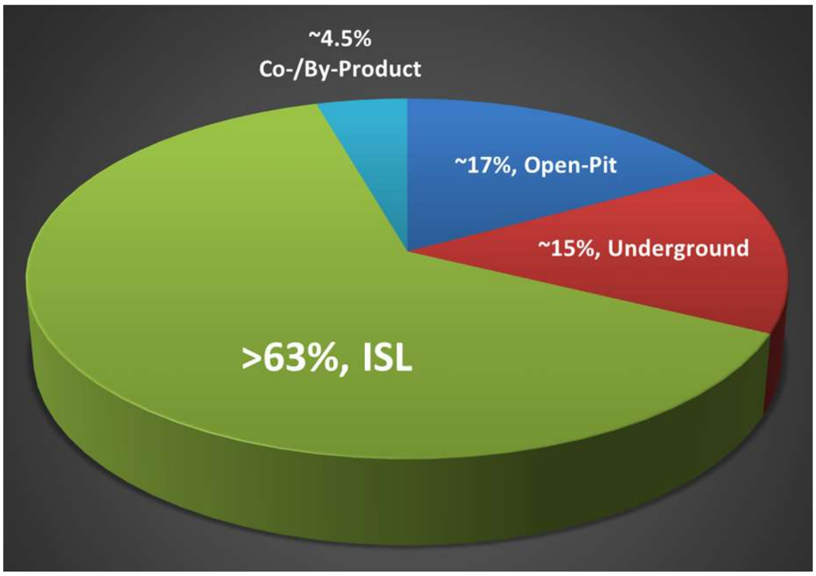


Red Book… World Uranium Production (~47,300 tU)

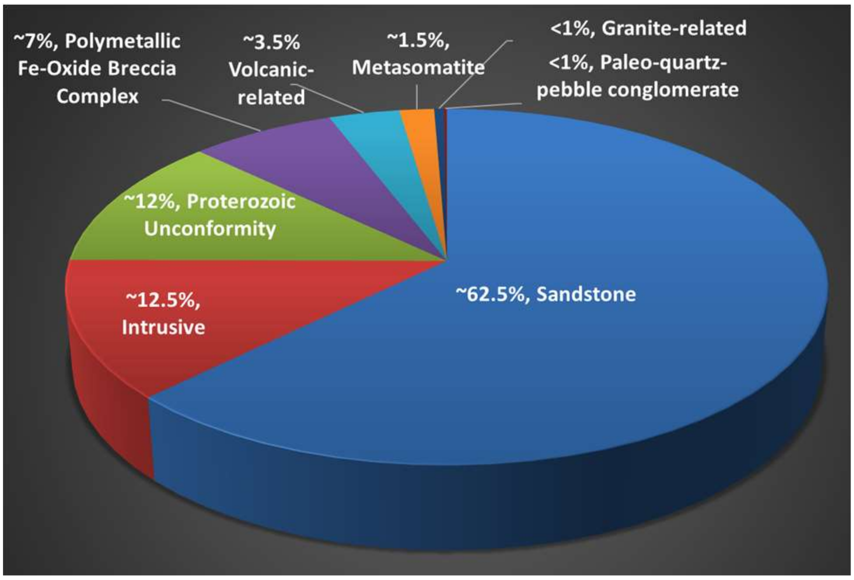
(2019 & 2020)



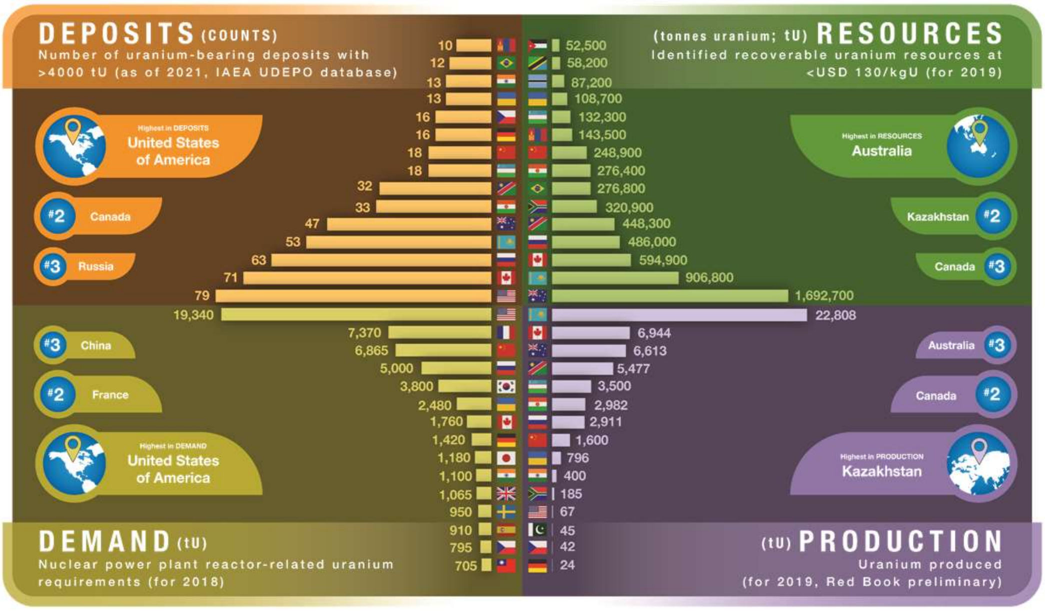
Red Book… World Uranium Production by Methods
(2019 & 2020)



Red Book… World Uranium Production by Deposit Type (2019 & 2020)



Red Book & UDEPO Uranium… Who, What, Where



https://nucleus.iaea.org/sites/connect/UPCpublic/PublishingImages/Infographics/Red_Book_2020_Uranium_Depos-Res-Prod-Demd.png

URANIUM- RARE EARTHS KEYNOTE

THE WHAT'S AND WHYS OF URANIUM ORE PROCESSING INNOVATIONS PAST, PRESENT AND FUTURE

By

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ABSTRACT

The presentation tracks uranium ore processing innovation from the early formative period in the 1950s through to the 2022. It is divided into the following periods:

1950-1970 Early Process Development Period
1970-1980 Innovation To Combat Changing Conditions
1980-2000 Innovation During Prolonged Industry Downturn
2001-2022 Innovation During An Up And Down Period

The major drivers and major process developments in each period are briefly reviewed.

The presentation concludes with the 2023+ Prognosis for Innovation.

Keywords: Uranium ore processing, innovation, major drivers, future prognosis

1950-1970 EARLY PROCESS DEVELOPMENT PERIOD

Major initial process development period 1950-70 mainly in the USA, Canada, South Africa , Australia, Former Soviet Bloc.

Major drivers included: (Excluding the Soviet Bloc):

- Increasing demand due to growth of nuclear power stations.
- Guaranteed government purchase contracts.
- Small operations suitable for entrepreneurial mining companies.
- Free interchange of process technology and operating experience.
- Technical support from government organizations such as Oak Ridge in the USA, Mines Branch in Canada and National Institute for Metallurgy in South Africa, as well as commercial laboratories.
- Innovations by reagent suppliers and equipment manufacturers.

1950-1970 EARLY PROCESS DEVELOPMENT PERIOD

This was a pioneering period in which the basics of uranium ore processing were developed. Major developments included:

- Solid/liquid separation with thickeners and filters.
- The use of chemical flocculants.
- Acid and alkaline leaching.
- Key leaching parameters, PSD, temp., pressure, time, pH, Eh.
- The use of oxidants for tetravalent minerals.
- Separation and purification by IX, SX, as well as precipitation.
- Product recovery by precipitation and roasting/calcining.
- Ore upgrading methods including various combinations of screening, gravity, washing classifiers, cyclones, flotation.

1970-1980 INNOVATION TO COMBAT CHANGING CONDITIONS

Major drivers included: (Excluding Former Soviet Bloc):

- Phasing out of government contracts.
- Reduced demand.
- Oversupply.
- Competition from new projects based on large deposits with higher production, lower opex, benefitting from new innovations.

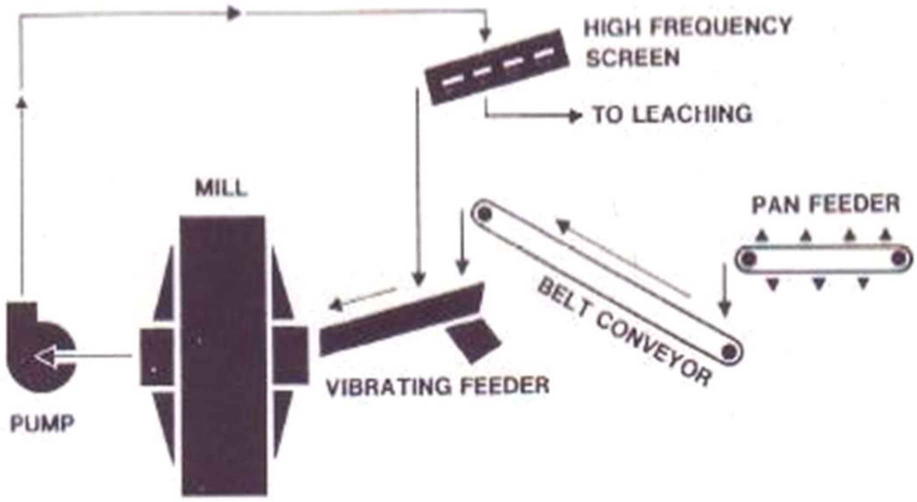
Led to mothballing or closure of many smaller operations.

1970-1980 INNOVATION TO COMBAT CHANGING CONDITIONS

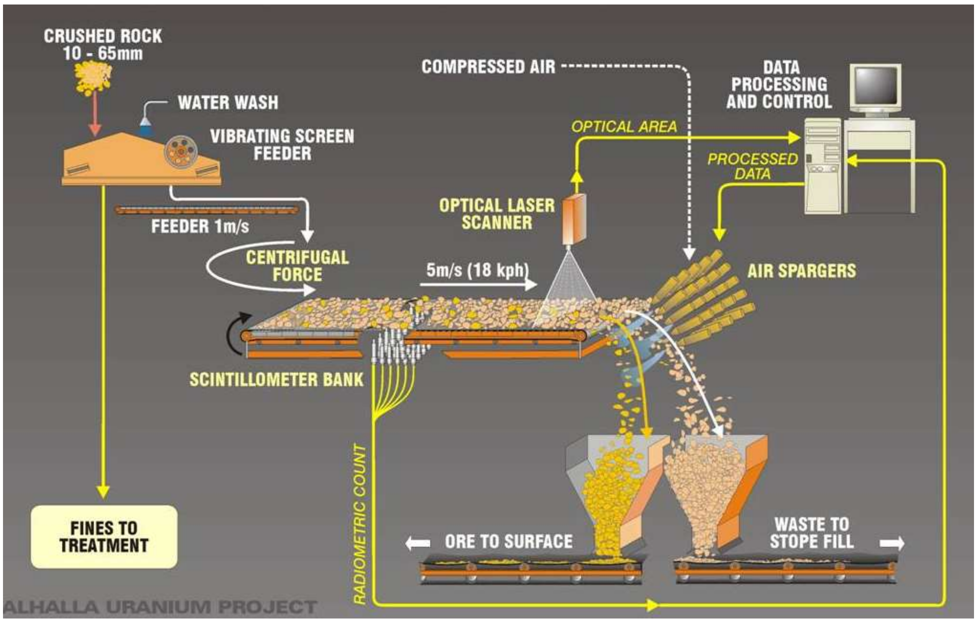
Some significant new innovations introduced in this period included:

- Semi-Autogenous grinding (SAG) - lower capex, inside the building for cold climate operations.
- Radiometric ore sorting.
- High-capacity thickeners - lower capex, low footprint, inside building for cold climates.
- Belt filters – lower footprint and cost than CCD, avoids tailings dam.
- New CIX systems for unclarified solutions – eliminates clarification.
- Krebs SX mixer-settlers – lower capex and reagent inventory, low footprint, located inside building for cold climates.
- Uranium by-product from phosphoric acid and copper leaching- low cost, no mining.

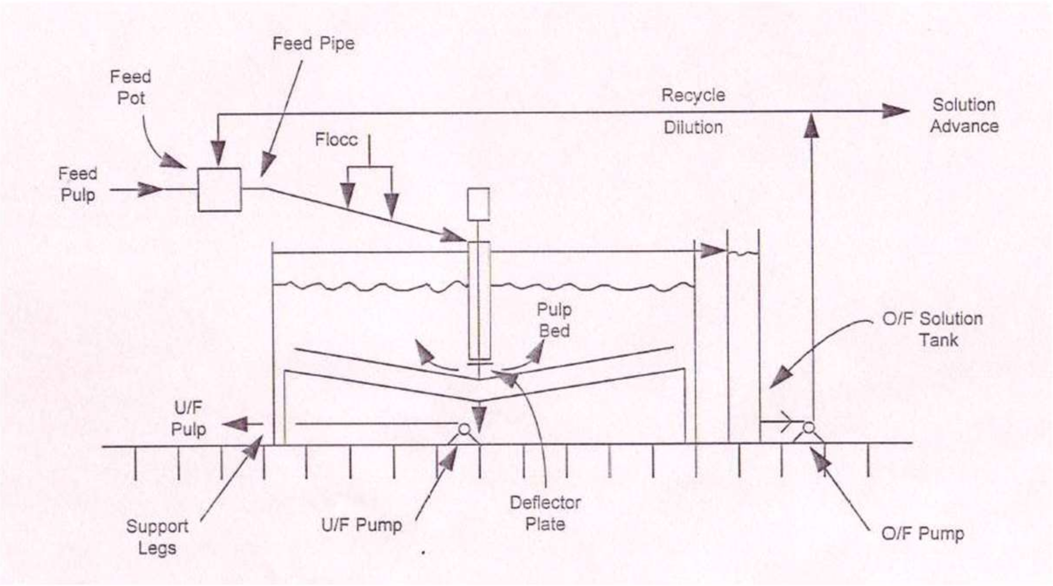
TYPICAL SAG MILL CIRCUIT - SANDSTONE ORE



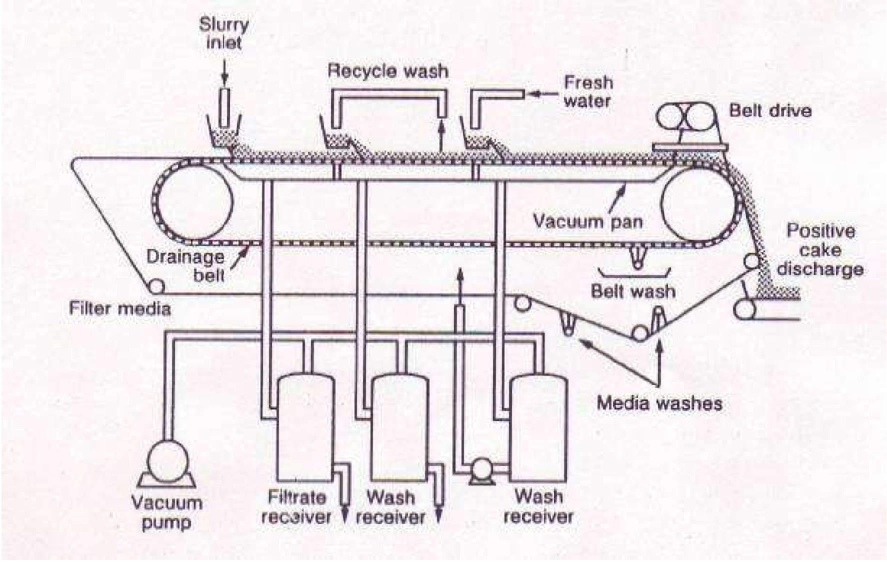
TYPICAL RADIOMETRIC ORE SORTING SYSTEM



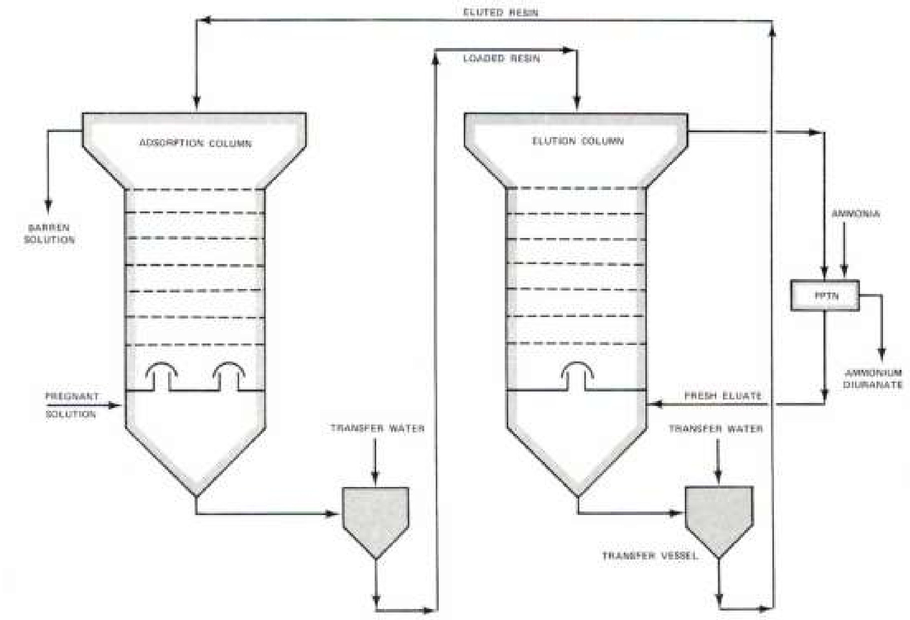
HIGH CAPACITY THICKENER ARRANGEMENT (ENVIRO-CLEAR)



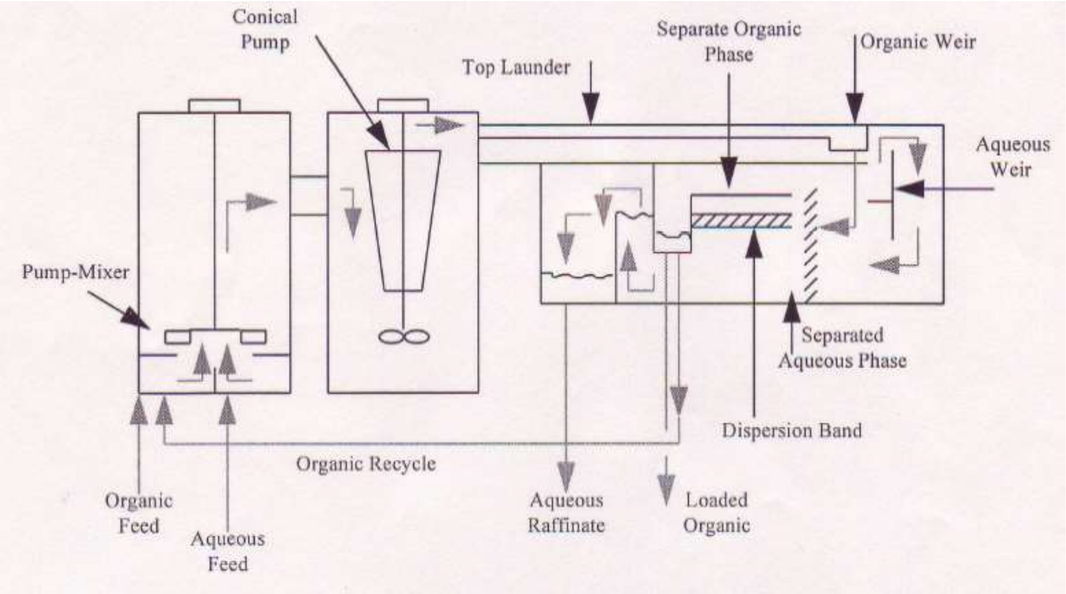
BELT FILTER ARRANGEMENT



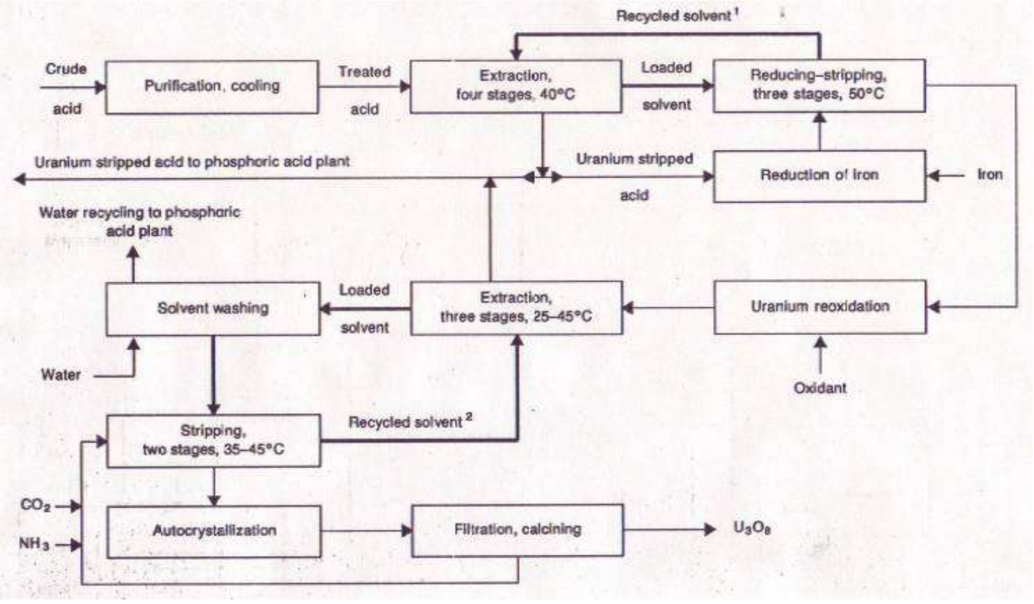
TYPICAL NIMCIX SYSTEM



KREBS MIXER-SETTLER WITH TWO MIX BOXES AND ORGANIC RECYCLE



D2EHPA-TOPO PROCESS FOR RECOVERY OF URANIUM FROM PHOSPHORIC ACID



1980-2000 INNOVATION DURING PROLONGED INDUSTRY DOWNTURN

Drivers included:

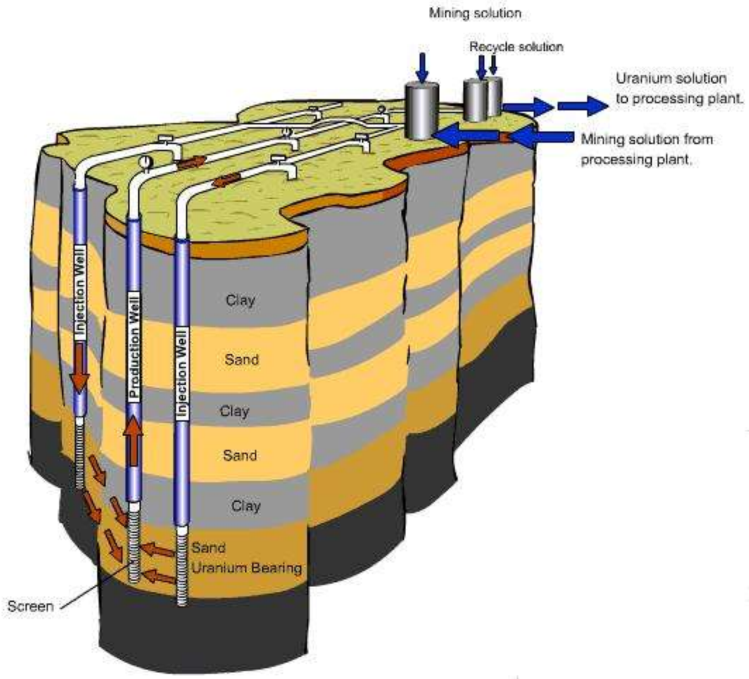
- New operations limited to ISR and very high-grade Canadian ores
- Limited new nuclear power stations.
- Uranium oversupply.
- Low price.
- Chernobyl accident in 1986.
- New operations mainly limited to ISR and very high-grade ore treatment in Canada.

1980-2000 INNOVATION DURING PROLONGED INDUSTRY DOWNTURN

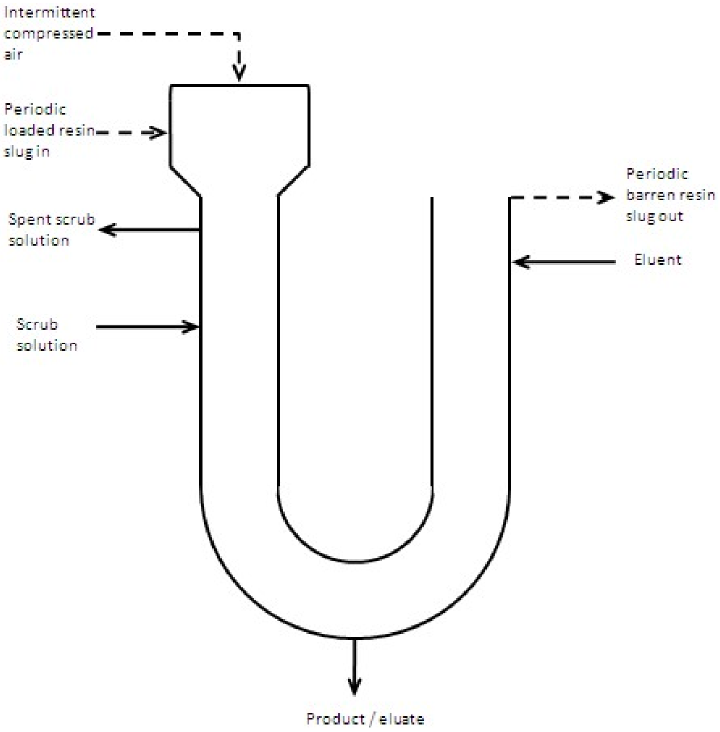
Significant innovations included:

- Development of acidic and alkaline ISR technology – low cost, no conventional mine, minimal surface impact.
- U-Tube IX elution system, especially for ISR operations in Kazakhstan - optimized resin inventory, high concentration eluate and purity product solutions.
- Pulsed Columns for SX – low footprint, lower organic evaporation and fire risk.
- Strong acid SX strip – avoids need for ammonia bleed.
- Peroxide precipitation - more selective than ammonia or magnesia, avoids product calcination and off-gas scrubbing.

TYPICAL ISR SYSTEM

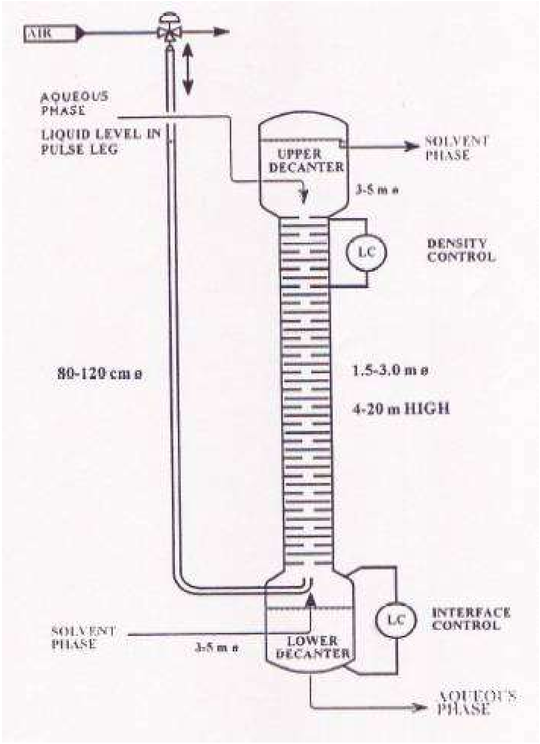


U-TUBE ELUTION CONCEPT



PULSED COLUMN

SCHEMATIC OF TENOVA DESIGN



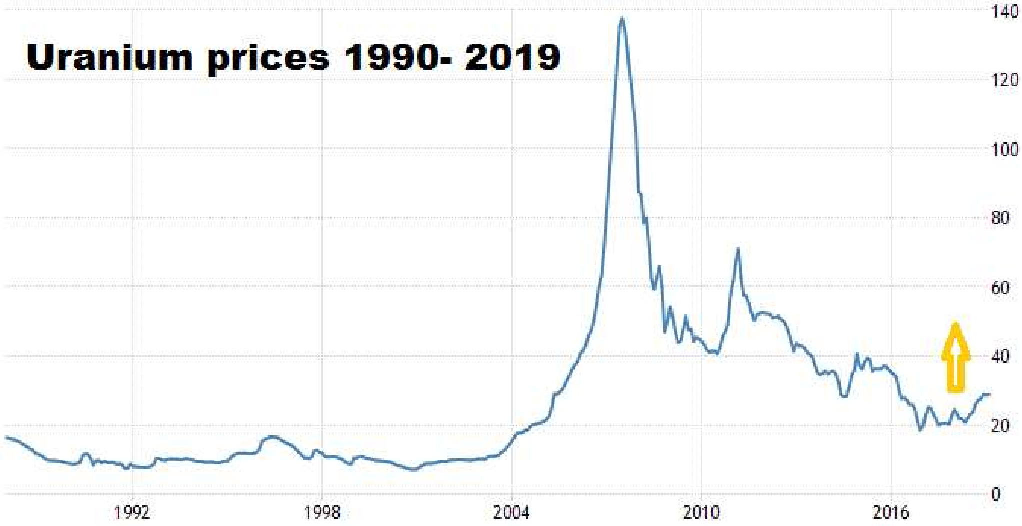
2001-2021 INNOVATION DURING AN UP AND DOWN PERIOD

Major driver:

- A steep price rise from 2004 peaking in 2007 and followed by a steep fall.
- Increased interest in nuclear power generation as a base load power alternative to fossil fuels.
- Concern over depletion of uranium stockpile.

URANIUM PRICE CHART

(Seeking Alpha Website seeking alpha.com)



2001-2021 INNOVATION DURING AN UP AND DOWN PERIOD

Drivers for process development work despite the long turndown included:

- Trend towards lower grade and difficult ores.
- Reliance on saline process water in some locations, such as Australia and Namibia.
- Capital and operating cost pressures.
- Tightening environmental regulations.

2001-2022 INNOVATION DURING AN UP AND DOWN PERIOD

Innovations during the downturn include:

- Ablation and U-pgrade^{TM} ore preconcentration processes.
- Nanofiltration Membranes for upgrading IX eluate and SX strip liquors, and recovering and recycling reagents.
- A potential major breakthrough for alkaline SX.
- IX for high chloride acid leach solutions.
- Application of IX to strong acid strip solution.
- Fluidized bed product precipitation system.
- Permeability enhancement for hard Rock ISR.

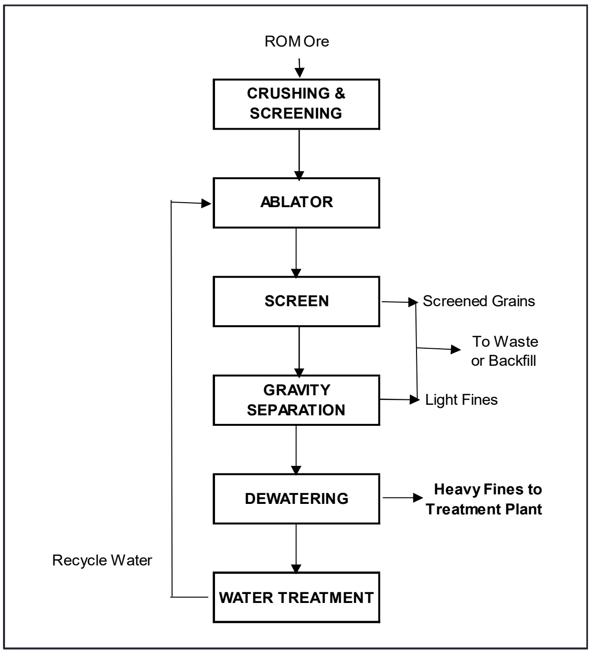
ORE PRECONCENTRATION – ABLATION PROCESS

- Invented by Ablation Technologies, Casper, Wyoming, USA, initially for gold, then patented for uranium in 2012.
- Mineral Ablation, a joint venture with Black Range Minerals, Australia, was formed in 2012 to market the technology. Black Range was then taken over by Western Uranium, Toronto, Canada, in 2015.
- Western Uranium successfully tested a 5 t/h pilot plant on stockpiled ore at their Sunday Mine Complex in Colorado, and constructed a 20 t/h facility with a view to moving into commercial operation.

ABLATION PROCESS

- Mechanical process using kinetic energy and water to force ore grains against each other through opposing nozzles.
- Removes uranium in coatings and interstitial deposits.
- The fines commonly contain a high percentage of the uranium, and can be separated by screening into a high-grade, low-volume, concentrate.
- Concentrate may be further upgraded by removal of light barren fines by gravity processing.
- Extensive testwork shows typically more than 90% of the uranium can be recovered into about 10% of initial mass.

ABLATION PROCESS FLOW DIAGRAM



U-PGRADE^{TM} PROCESS

- The process was developed by Marenica Energy, Australia (patent pending), initially for the Marenica Project in Namibia. Has been subsequently tested for a number of other projects.
- It is a physical beneficiation process for upgrading low-grade surficial uranium deposits typically containing carbonates, clay minerals, and often sulphates.
- It involves the sequential removal of gangue minerals by commonly used unit operations to achieve a comparatively high-grade concentrate without using chemicals.

U-PGRADE^{TM} PROCESS

- The rejection of carbonate minerals produces a leach feed suitable for acid leaching, and generally simpler and cheaper than alkali leaching normally used for carbonate ores.
- The reduction in mass typically lowers opex by 50-70% and capex by 30-50% compared with conventional processing of deposits of this type.
- The low mass also provides the flexibility to process the concentrate on site, or to transport it to a third-party operation which reduces project development costs and can render a small deposit financially viable.

U-PGRADE^{TM} PROCESS

- The initial step typically comprises wet scrubbing and screening to separate into fine and coarse fractions.
- The undersize fraction contains most of the uranium as an intermediate concentrate that may be further processed in a secondary beneficiation stage to produce a high-grade uranium concentrate.
- Possible methods for secondary beneficiation include desliming, gravity separation, flotation, reflux classification and magnetic separation.
- Testwork indicates concentration to less than 3% of the mass and upgrading by more than 30 times without the use of leaching chemicals, producing an inert waste.

NANOFILTRATION

- A commercial nanofiltration system designed by BMS Engineers, Perth, Western Australia was installed at the Kayelekera uranium operation in Malawi in 2013 for recovering and recycling acid from IX eluate prior to precipitation.
- A second commercial plant was installed at Langer Heinrich, Namibia, in 2015 to recover sodium bicarbonate from the IX eluate.
- Nanofiltration has been proposed and/or tested for a number of developing projects including Mulga Rock and Honeymoon in Australia, Letlhakane in Botswana, Ivana in Argentina, Michelin in Canada, and Mkuju River in Tanzania.

KAYELEKERA NANOFILTATION SYSTEM

NANOFILTRATION POTENTIAL

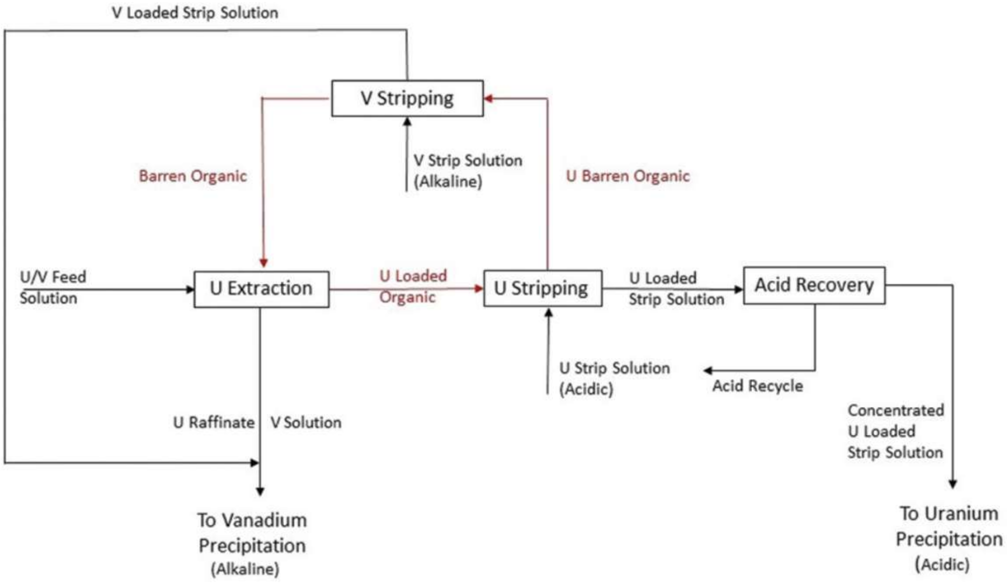
Potential applications in uranium operations include:

- Concentration of SX or IX feed solution to reduce the capex of the leaching facility and recover and recycle acid or carbonate reagents.
- Treatment of waste or bleed streams.
- Treatment of acid rock and mine drainage.

A MAJOR BREAKTHROUGH FOR ALKALINE SX?

- Cyphos 101, a tri-hexyl(tetradecyl)phosphonium salt and Aliquat 336, a quaternary amine, were both tested by CSIRO and the Parker Centre, Perth, Australia, for the recovery and separation of uranium and vanadium from alkaline leach solutions with promising results. (Ref: CSIRO paper, ALTA 2013).
- The CSIRO SX concept is included in the proposed flowsheet being tested for Blue Sky Uranium Corporation's Ivana Uranium-Vanadium Project in Argentina. (Ref: Process design for the Ivana Uranium-Vanadium mill, Chuck Edwards, CIM Journal, 11:4, 231-237, 2020)
- SX from alkaline leach solutions is a key missing link in uranium ore treatment and, if successful, the application at Ivana will be a major industry breakthrough.

PROPOSED IVANA ALKALINE SX FLOWSHEET



V Loaded Strip Solution

V Stripping

Barren Organic

V Strip Solution (Alkaline)

U Barren Organic

U/V Feed Solution

U Extraction

U Loaded Organic

U Stripping

U Loaded Strip Solution

Acid Recovery

U Strip Solution (Acidic)

Acid Recycle

U Raffinate

V Solution

Concentrated U Loaded Strip Solution

To Vanadium Precipitation (Alkaline)

To Uranium Precipitation (Acidic)

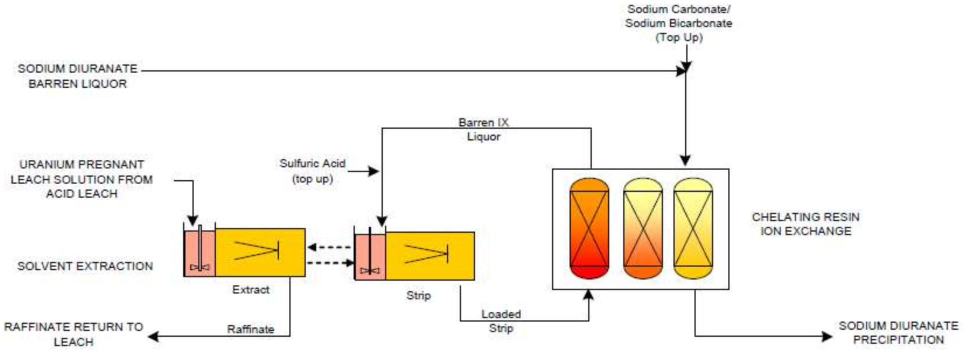
IX FOR HIGH CHLORIDE SOLUTIONS

- Chloride has a negative impact on the recovery of uranium from sulfuric acid leach liquors using ion exchange.
- ANSTO Minerals investigations indicated that WBA resins are more effective than SBA up to 12 g/L Cl and can be eluted in a conventional manner using 1 M NaCl. (Coupled with nanofiltration for eluate reagent recycle, this process can be quite attractive.)
- However, in an extensive testing program for the Boss Resources Honeymoon ISR project, South Australia, a newly released high capacity SBA resin outperformed a WBA resin, which in turn has been shown to outperform conventional SBA resins.
- The laboratory findings have been validated by a continuous pilot plant trial. Future work will focus on optimising the elution process, which is based on the use of NaCl.

APPLICATION OF IX TO STRONG ACID SX STRIP SOLUTION

- Novel application of IX (chelating type) to recover uranium from strong acid SX strip solution to recycle acid to SX strip and reduce acid and lime consumptions in product recovery circuit.
- Sodium diuranate is precipitated from eluate then redissolved in sulphuric acid, and UO_4 product is precipitated with peroxide.
- Developed, tested and patented for the Letlhakane heap leaching project in Botswana, where a strong acid leach is required.
- Could render strong acid leaching of refractory ores feasible. and economic.
- Nanofiltration was considered as an option for Letlhakane 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).

IX PROCESS FOR STRONG ACID SX STRIP SOLUTION



ORANO FLUID BED PRECIPITATION PROCESS

(Ref: Adelaide Control Engineering presentation, ALTA 2013)

- Patented process developed and commercialized by Areva (now Orano)
- 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

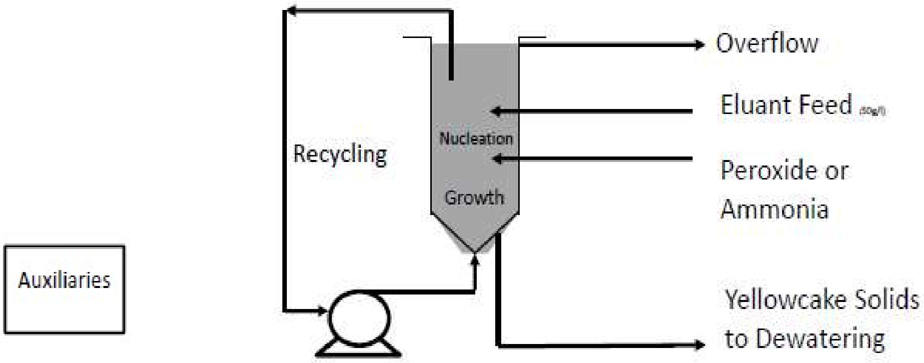
  - Reduced fines, less dust and lower risks to operators

ORANO FLUID BED PRECIPITATION PROCESS (CONT.)

- Improved dewatering reduces calcining costs or allows increased throughput
  - Increasing calcined product bulk density - lower transport cost.
  - Facilitating drying or calcining with horizontal kiln – previously, too much product was lost in off gas and stuck inside tube.
  - Flexibility for peroxide or ammonia precipitation.
  - Modular construction, smaller site footprint.
- Retrofitting a Fluid Bed Crystalliser can significantly debottleneck systems by:
  - Increasing filtering and dewatering equipment capacity.
  - Increasing drying and calcining equipment capacity.
  - Reducing product waste and recycle.
  - Improving utilization.

ORANA FLUID BED PRECIPITATION PRINCIPLE

(Ref: ACE presentation, ALTA 2013)



(AREVA Patent)

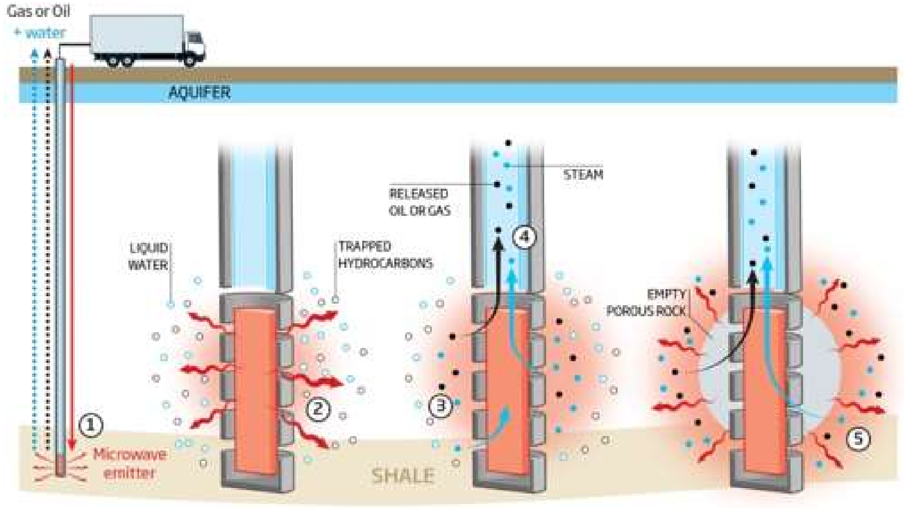
ISR PERMEABILITY ENHANCEMENT

- Uranium ISR is currently limited to permeable ores, typically sandstones
- However, there are extensive R&D programs to enhance the permeability of hard rock ores for recovery of gold, copper, and nickel as well as uranium.
- Enhancement methods being investigates include:
  - Further development of previously used methods including underground basting, drilling and blasting, hydraulic fracturing, and directional hydraulic fracturing.
  - Newer techniques including microwave fracturing, thermal fracturing, acoustic or electrical stimulation, laser fracturing, biomineral alteration, liquid nitrogen fracturing, non-explosive demolition agents, non-explosive demolition agents.

Permeability enhancement is one of the key focuses of the annual ALTA ISR Conference held in partnership with CSIRO who had the vision for an annual event.

MICROWAVE FRACTURING CONCEPT

(Mining3 Presentation ALTA 2019)



2023+ PROGNOSIS FOR INNOVATION

- Uranium market prospects are improving due:
  - to falling inventory
  - increasing interest in nuclear as a clean energy for base load power
  - potential of **small modular reactors** (SMRs).
- According to the IAEA, Small Modular Reactors:
  - offer better upfront capital cost affordability
  - are suitable for cogeneration and non-electric applications
  - offer options for remote regions with less developed infrastructures
  - possibility for synergetic hybrid energy systems that combine nuclear and alternate energy sources, including renewables.

A RISING MARKET SHOULD ENCOURAGE INNOVATION

A rising market should lead to funding becoming available for new innovations. Candidates could include:

- Use of NF membranes for leach solution upgrading.
- Commercialization of SX for alkaline leach solutions.
- Application of IX for strong acid SX strip solutions for processing of refractory ores.
- ISR for hard rock ores after permeability enhancement.

Acknowledgement

First Presented at IAEA “Technical Meeting to Collect and Document Innovations in the Uranium Production Cycle”
Virtual Event 6-10 June 2022

HIGH-PRESSURE SLURRY ABLATION (HPSA) ‑ A NEW LIBERATION TECHNOLOGY

By

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ABSTRACT

Of the total energy consumed by the mining industry, more than 50% is spent on ore comminution. Disa has demonstrated in various testing campaigns that it provides significant energy savings with its High-Pressure Slurry Ablation (HPSA) technology. HPSA is a new particle attrition technology that works on the principle of particle-to-particle collisions between two or more high-pressure slurry jets. Particle disassociation is realized through the intense collisions created by high-pressure pumps moving slurry through a series of nozzles within the collision chamber. Preliminary testing using both lab and pilot-scale HPSA units has demonstrated promise to effectively be applied to a diverse group of materials, specifically soft to medium hard ores. Materials include uranium, vanadium, rare earth elements, potash, iron, molybdenum, copper, gold, phosphate, graphite, and others.

A rare earth element mining company provided samples from its current operation to test the expected benefits of HPSA. After minutes of processing the ore in HPSA, a particle size shift was observed. Furthermore, HPSA was able to concentrate over 95% of the total rare earth elements (TREEs) in the fine fraction (-37 micron). These results from processing in a single HPSA unit show a substantial increase over the current operation's multistage regrind.

HPSA is also uniquely suited to uranium bearing material due to its unique ability to liberate material along its intergranular boundary lines. During particle-to-particle collisions in the HPSA chamber, natural uranium bearing minerals such as carnotite which exhibit quartz association are selectively fractured and liberated from the quartz grains allowing the natural uranium and other constituents of concern to be separated by size, typically performed by screening at 53 micron. HPSA has repeatedly demonstrated that it can concentrate greater than 90% of the uranium in less than 30% of the processed mass.

Keywords: Liberation, comminution, remediation, reclamation, HPSA, REE, Uranium, Vanadium, Critical Minerals

SUSTAINABLE TECHNOLOGY FOR MINERALS PROCESSING AND REMEDIATION APPLICATIONS THAT :

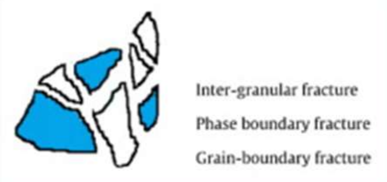
INCREASES RECOVERIES

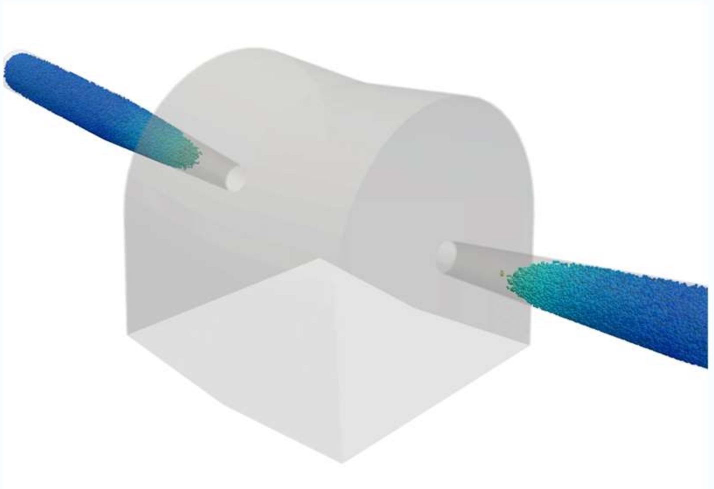
NEUTRALIZES WASTE

CONCENTRATES CRITICAL MINERALS

TECHNOLOGY OVERVIEW

- **High-Pressure Slurry Ablation (HPSA)**
  - Slurry formed with feed material and water
  - Mechanical process creating particle-particle collisions
  - Creates an intergranular fracture using the intrinsic material properties.





TECHNOLOGY OVERVIEW

TECHNOLOGY DEVELOPMENT

TECHNOLOGY PORTFOLIO

Pilot Units (7)

COMPLETE

GEN ALPHA

COMPLETE

GEN BRAVO

IN FABRICATION

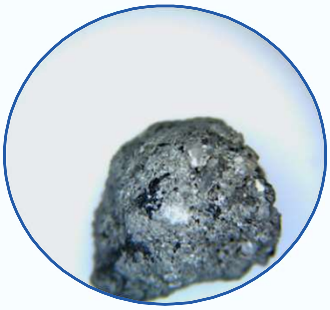
2018 Q3

2019 Q3

2023 Q2

SELECTIVE LIBERATION

Novel system that reduces energy and neutralizes waste that can be applied to multiple verticals



Sand grain is heavily coated with Uranium and Vanadium minerals

Particle-particle collisions allow for efficient Uranium and Vanadium separation

Coating is completely removed yet the sand grain remains intact

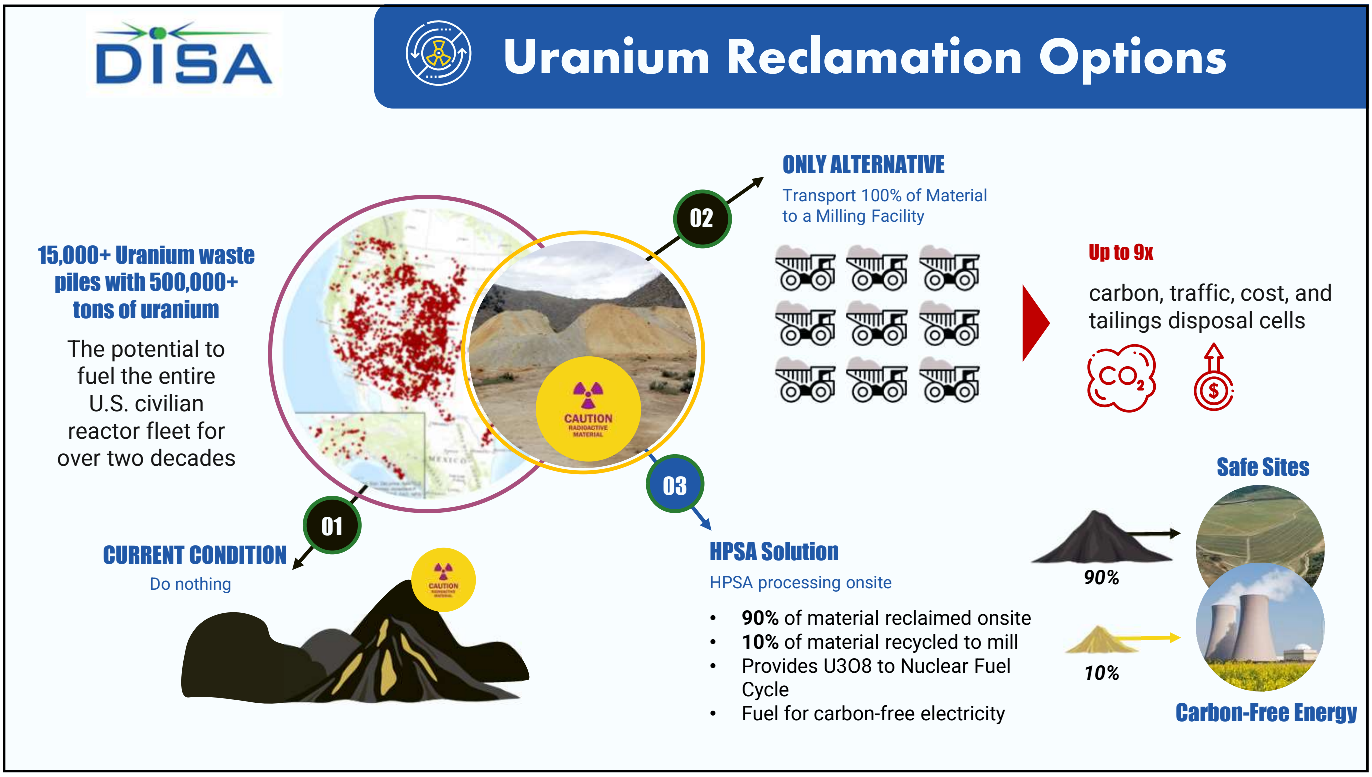
Reduces overall project costs by up to 50%

Reduces energy needs by up to 40%

Neutralizes waste by up to 95%

URANIUM RECLAMATION

- Remediation of waste piles and contaminated materials at abandoned mines and other sites
- Over 15,000 abandoned uranium mines (or waste piles) in the Western United States
- Many of these waste piles are on or near tribal locations
- Approximately 1 in 5 people in the West live within 50 miles from an abandoned uranium mine
- Most of these waste piles:
  - -Created over 4 decades ago
  - -Sit on the surface where uranium has oxidized
  - -Limits use of the land
  - -May cause dose and contamination issues



Uranium Reclamation Options

15,000+ Uranium waste piles with 500,000+ tons of uranium

The potential to fuel the entire U.S. civilian reactor fleet for over two decades

01 CURRENT CONDITION

Do nothing

02 ONLY ALTERNATIVE

Transport 100% of Material to a Milling Facility

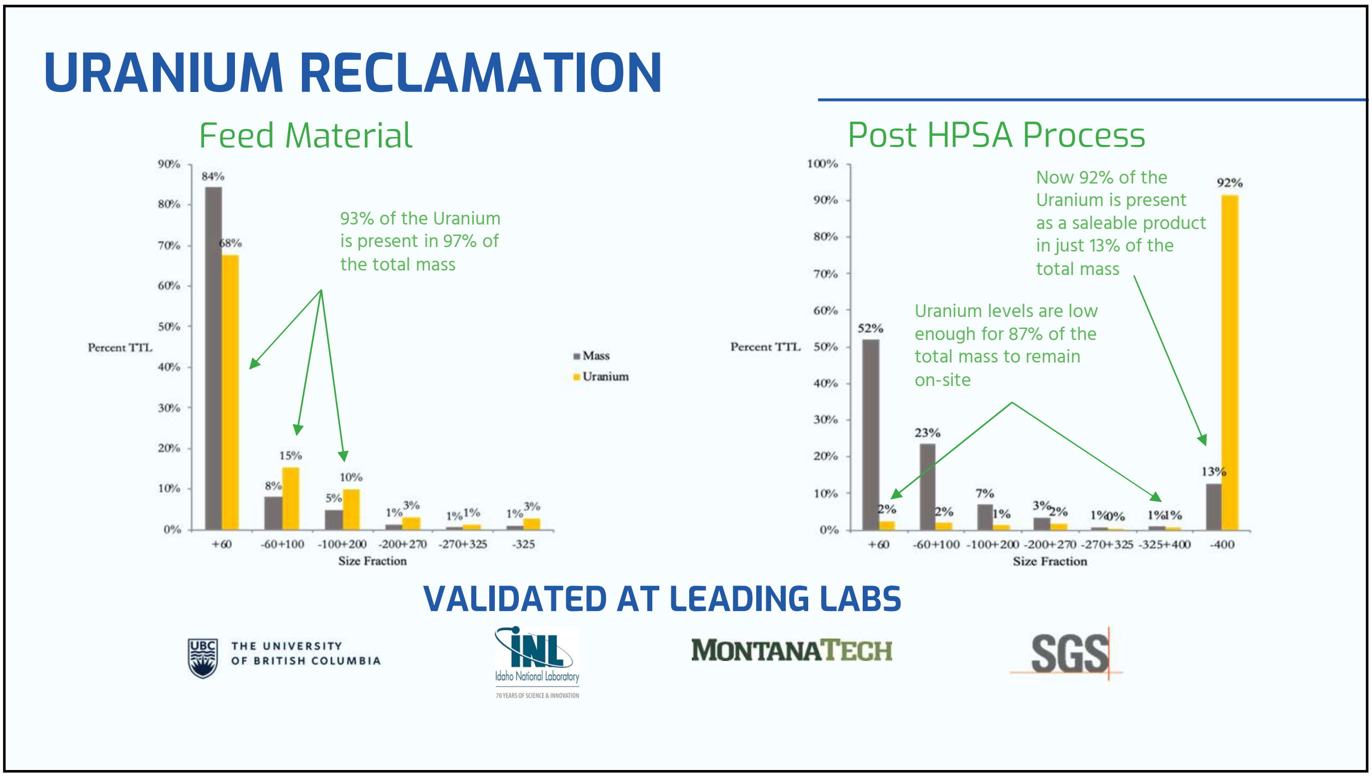
Up to 9x

carbon, traffic, cost, and tailings disposal cells

03 HPSA Solution

HPSA processing onsite

- **90%** of material reclaimed onsite
- **10%** of material recycled to mill
- Provides U3O8 to Nuclear Fuel Cycle
- Fuel for carbon-free electricity



URANIUM RECLAMATION

Feed Material

93% of the Uranium is present in 97% of the total mass

Post HPSA Process

Now 92% of the Uranium is present as a saleable product in just 13% of the total mass

Uranium levels are low enough for 87% of the total mass to remain on-site

VALIDATED AT LEADING LABS

THE UNIVERSITY OF BRITISH COLUMBIA

Idaho National Laboratory

MONTANATECH

SGS

MINE WASTE PHOTOGRAPHS

Site Location – Western Colorado

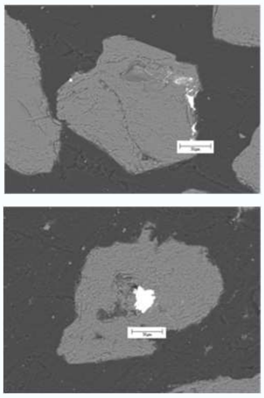
RADIOLOGICAL & MINERALOGICAL COMPONENTS

Parameter	Units	Waste Rock	Clean Coarse Fraction	Total Reduction	Percent Reduction
Lead 210	pCi/g	149	37.1	111.9	**75.10%**
Radium 226	pCi/g	125	70.4	54.6	**43.68%**
Radium 228	pCi/g	1.9	1	0.9	**47.37%**
Thorium 230	pCi/g	153	74.7	78.3	**51.18%**
Thorium 232	pCi/g	ND	ND	NA	NA
Vanadium	mg/kg	1,362	409	953	**70%**
Uranium	mg/kg	912	129	782	**86%**

HPSA Reduces the Overall Radiological Signature

MLA LEACHABILITY RESULTS

MLA demonstrates that the clean coarse fraction is stable



Mineral	Color
Albite	🟩
Apatite	🟪
Calcite	🟦
Carnotite	🟥
Chlorite	🟩
Dolomite	🟦
Illite	⬛
Oligoclase	🟦
Orthoclase	🟪
Quartz	🟨
Zircon	🟪

+100-mesh: 51.3% of
total mass, 130 ppm U,
0.00% Leachable

SYNTHETIC PRECIPITATION

Parameter	Units	Waste Rock	Clean Coarse Fraction	% Difference
Arsenic	mg/L	0.664	0.148	**78%**
Lead	mg/L	0.014	0.006	**57%**
Selenium	mg/L	0.020	0.006	**70%**
Uranium	mg/L	0.10	0.06	**40%**
Vanadium	mg/L	0.57	0.14	**75%**
Lead 210	pCi/L	9.9	6.2	**37%**
Radium 226	pCi/L	20.0	9.8	**51%**
Radium 228	pCi/L	ND	ND	NA
Thorium 230	pCi/L	7.4	4.0	**46%**
Thorium 232	pCi/L	ND	ND	NA

POST-REMEDIATION CLEAN COARSE FRACTION DOSE

Individual Type	Hours/ Day	Months	Total Days	Total Hours
Public	8	6	180	1440

Case	Type	Dose Rate (mrem/hr)	Annual Dose (mrem/yr)	Dose Limit (mrem/yr)	% of limit
Maximum[a]	Public	0.006	**8.8**	25[b]	35.2%
	[a] Maximum dose occurred at the closest modeled distance, 0.1 m, from the surface of the source volume. [B] Unrestricted release limit				

Maximum Public Exposure to Clean Fraction is Well Below Regulatory Limits

NAVAJO NATION STUDY

Supported by US EPA and Navajo Nation EPA

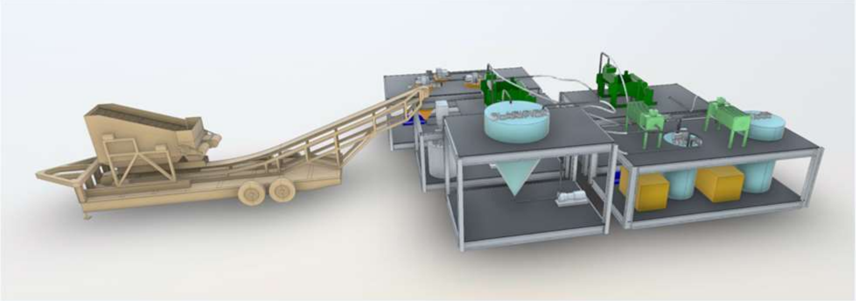
PUBLIC POLICY & BENEFIT

Waste Remediation -

- Return mine sites to useable recreational areas
- Reduce radiological signatures to ALARA
- Disposal of concentrated materials addresses long-standing environmental justice concerns

HURDLES TO REMEDIATION

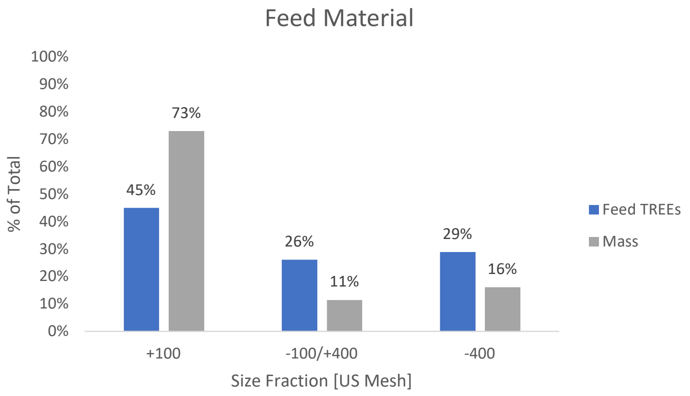
- Regulators understanding how to license innovative technology
- Operating technology at scale (Gen Bravo)
- Funding to cleanup sites

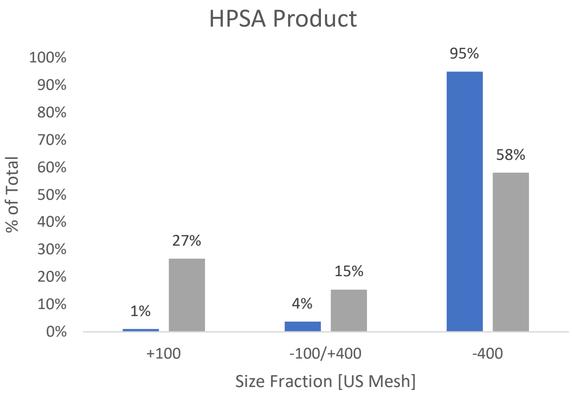


TRADITIONAL MINERAL PROCESSING CIRCUITS

RARE EARTH ELEMENTS

- HPSA processing improved concentration of the TREEs from 29.0% in the Feed to 95%





PHOSPHATE

ROD MILL

Rod Mill Discharge							
Sample Data Used	P2O5 wt%	P2O5 recovery	CaO wt%	SiO2 wt%	Al2O3 wt%	Fe2O3 wt%	MgO wt%
Average	25.1%	84.5%	45.2%	11.8%	2.4%	0.9%	0.7%

HPSA Unit

HPSA Product							
Sample Data Used	P2O5 wt%	P2O5 recovery	CaO wt%	SiO2 wt%	Al2O3 wt%	Fe2O3 wt%	MgO wt%
SC01 T15	29.8%	87.4%	48.8%	6.9%	1.4%	0.5%	0.3%

- HPSA increased both grade and recovery of the P2O5 while reducing other gangue material

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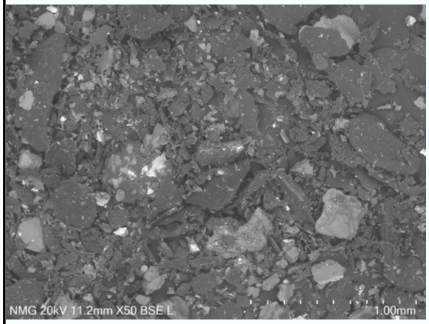
GRAPHITE



Current Process

Rougher Flotation

Grade – 55%

Recovery – 96%

P_{80} = 350 µm

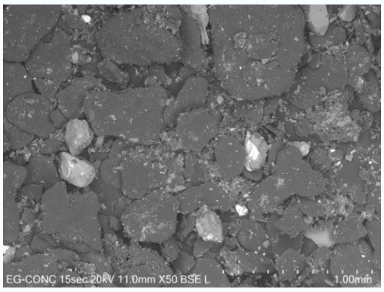
HPSA Test 1

Rougher Flotation

Grade – 74%

Recovery – 94%

P_{80} = 372 µm



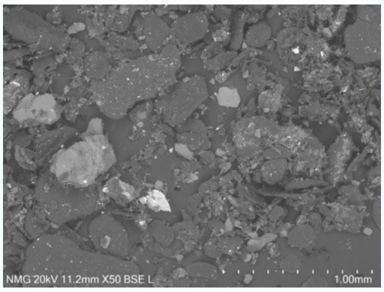
HPSA Test 2

Rougher Flotation

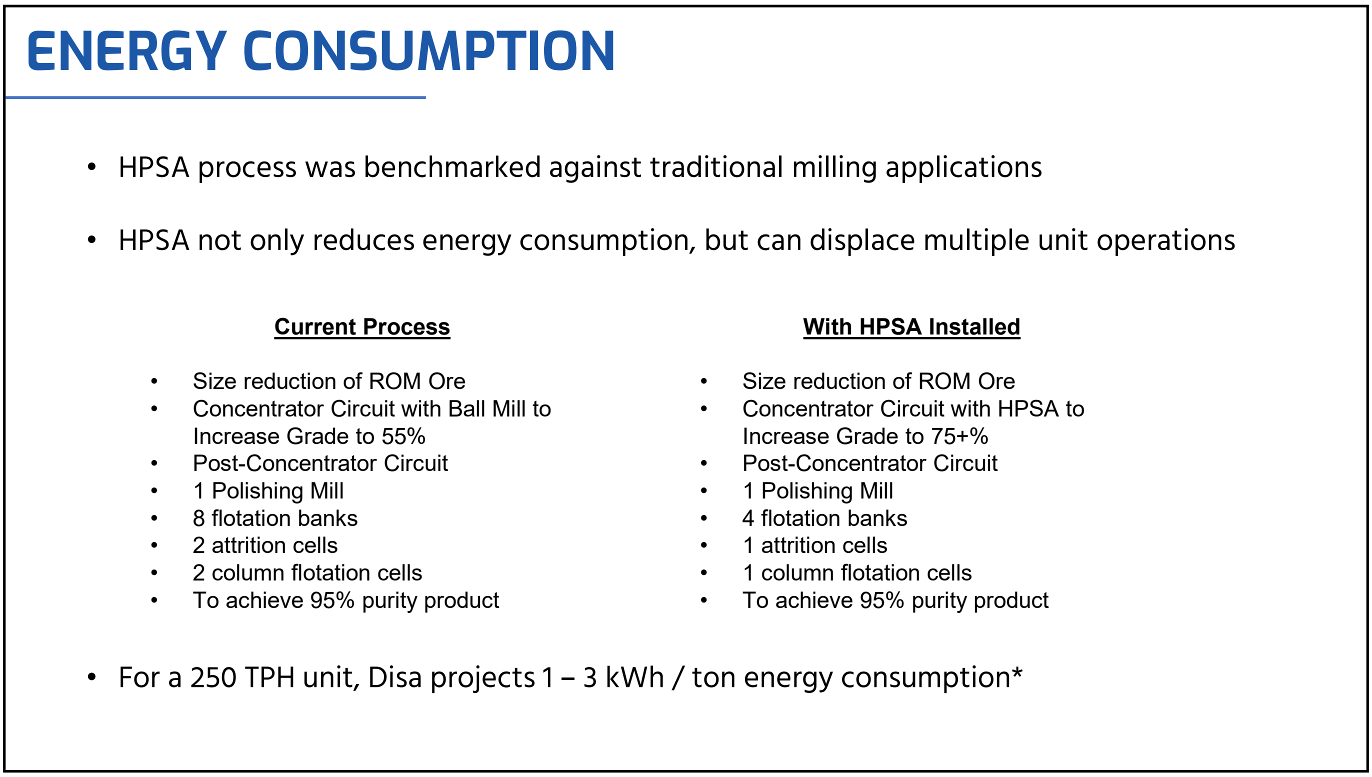
Grade – 80%

Recovery – 96%

P_{80} = 352 µm



- **Post process flotation concentrate showed increased grade**
- **Replaces current ball mill prior to rougher flotation step and associated OPEX**



ENERGY CONSUMPTION

- HPSA process was benchmarked against traditional milling applications
- HPSA not only reduces energy consumption, but can displace multiple unit operations

Current Process	**With HPSA Installed**
• Size reduction of ROM Ore	• Size reduction of ROM Ore
• Concentrator Circuit with Ball Mill to Increase Grade to 55%	• Concentrator Circuit with HPSA to Increase Grade to 75+%
• Post-Concentrator Circuit	• Post-Concentrator Circuit
• 1 Polishing Mill	• 1 Polishing Mill
• 8 flotation banks	• 4 flotation banks
• 2 attrition cells	• 1 attrition cells
• 2 column flotation cells	• 1 column flotation cells
• To achieve 95% purity product	• To achieve 95% purity product

- For a 250 TPH unit, Disa projects 1 – 3 kWh / ton energy consumption*

IAEA SUPPORT TO MEMBER STATES FOR EXPLORATION AND DISCOVERY OF UNDISCOVERED URANIUM RESOURCES

By

Mark Mihalasky

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ABSTRACT

The IAEA provides support to 175 Member States through several nuclear fuel cycle programmatic areas. To help ensure sustainability of uranium fuel supply for the current and future fleet of nuclear power plants, the IAEA directly engages 52 Member States that have, or wish to initiate, activities related to the uranium production cycle. Much of this direct support involves the front-end of the uranium production cycle, including the development and refinement of national uranium exploration program strategies and management, identification of promising areas for prospecting, and estimation of possible resources.

To enhance support to Member States' efforts to develop new, or refine existing national uranium exploration programmes, the IAEA provides a number of publications, databases, and technical training workshops and meetings/conferences relating to uranium deposit geology and metallogeny, deposit type classification and mineral systems models, statistical data on global deposit distribution and resources, as well as reviews and case studies of quantitative and qualitative geospatial evaluations of undiscovered uranium resources.

This presentation will provide an overview of some methodologies and case study applications for the evaluation of undiscovered uranium deposits and resources that IAEA has supported through a variety of publications, databases, and technical training workshops.

Keywords: Uranium, Exploration, Prospecting, Undiscovered Deposits, Quantitative Mineral Resource Assessment, Mineral Prospectivity Mapping, Supply, Sustainability, Nuclear Fuel, Nuclear Power

Talking Points

- IAEA Uranium Production Cycle & UPC Team
- Application of UPC Team Outputs
- Assessment of Undiscovered Mineral Resources
- Examples / Case Studies

IAEA Nuclear Fuel Cycle & Materials Section (NFCMS), Uranium Production Cycle (UPC) Team…

- Mission…
  - Collect & share knowledge of uranium resources and support the development of a sustainable uranium production cycle in Member States

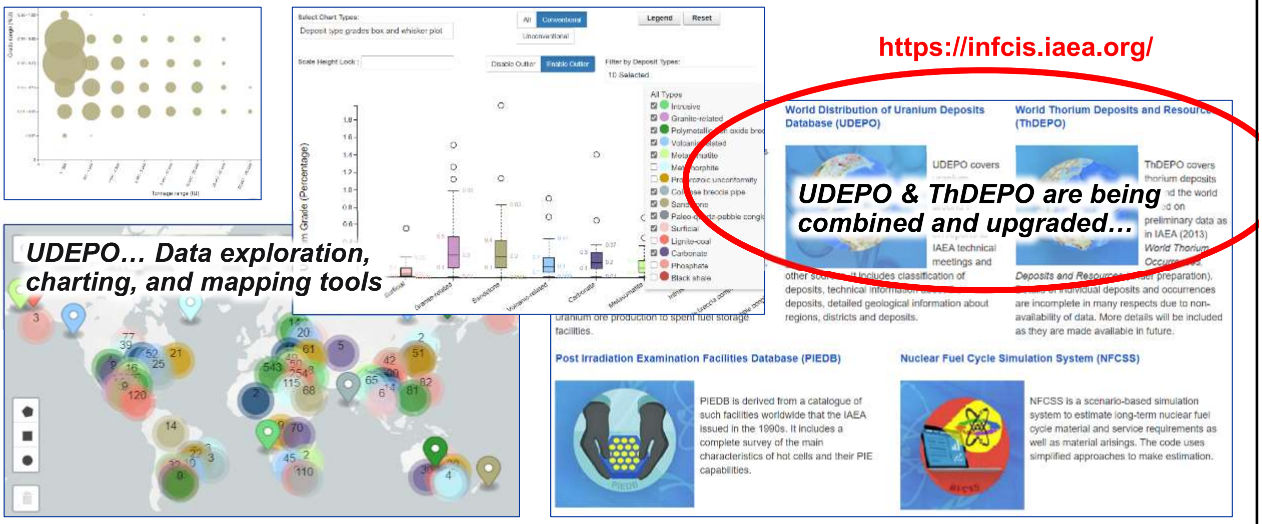
https://nucleus.iaea.org/sites/connect/UPCpublic/Pages/default.aspx

IAEA NFCMS UPC Team Outputs (Resources-Related)

- Authoritative, objective, and reliable information
- Databases…
  - UDEPO, ThDEPO, INFCIS, etc.
- Publications & technical meetings…
  - Red Book, technical documents and nuclear energy series, proceedings
- Inputs for assessing / modelling future raw material supply…
  - Resource & statistical data
  - Geology & metallogeny
  - Deposit types, models, and distribution
  - Assessment methodologies

Carnotite Mineralization, Trekkoptje Mine, Namibia

Databases & Data Explorers… Integrated Nuclear Fuel Cycle Information Systems, UDEPO & ThDEPO



https://infcis.iaea.org/

UDEPO… Data exploration, charting, and mapping tools

UDEPO & ThDEPO are being combined and upgraded…

World Distribution of Uranium Deposits Database (UDEPO)

UDEPO covers … IAEA technical meetings and other sources. It includes classification of deposits, technical information … deposits, detailed geological information about regions, districts and deposits.

World Thorium Deposits and Resources (ThDEPO)

ThDEPO covers thorium deposits … the world … preliminary data as in IAEA (2013) *World Thorium Occurrences, Deposits and Resources* (under preparation). Details of individual deposits and occurrences are incomplete in many respects due to non-availability of data. More details will be included as they are made available in future.

… uranium ore production to spent fuel storage facilities.

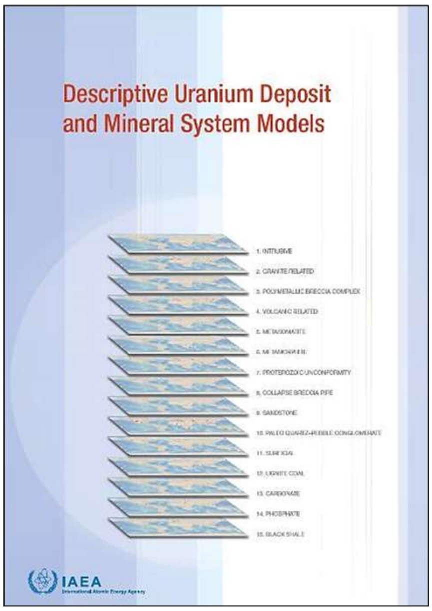
Post Irradiation Examination Facilities Database (PIEDB)

PIEDB is derived from a catalogue of such facilities worldwide that the IAEA issued in the 1990s. It includes a complete survey of the main characteristics of hot cells and their PIE capabilities.

Nuclear Fuel Cycle Simulation System (NFCSS)

NFCSS is a scenario-based simulation system to estimate long-term nuclear fuel cycle material and service requirements as well as material arisings. The code uses simplified approaches to make estimation.

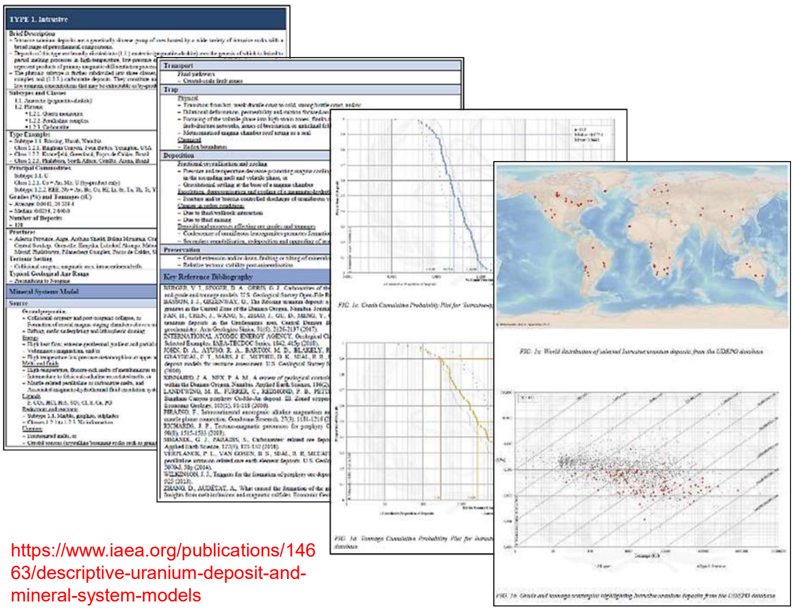
Publications… Uranium Deposit Types and Models



Descriptive Uranium Deposit and Mineral System Models

1. INTRUSIVE
2. GRANITE RELATED
3. POLYMETALLIC BRECCIA COMPLEX
4. VOLCANIC RELATED
5. METASOMATITE
6. METAMORPHITE
7. PROTEROZOIC UNCONFORMITY
8. COLLAPSE BRECCIA PIPE
9. SANDSTONE
10. PALEO QUARTZ-PEBBLE CONGLOMERATE
11. SURFICIAL
12. LIGNITE COAL
13. CARBONATE
14. PHOSPHATE
15. BLACK SHALE

IAEA
International Atomic Energy Agency

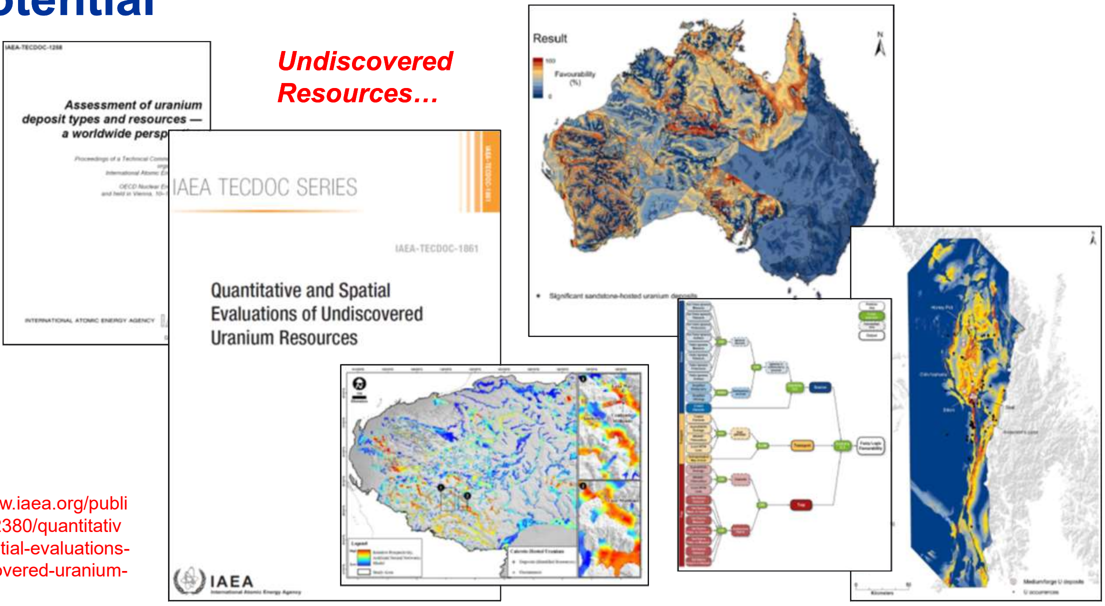


TYPE 1. Intrusive

https://www.iaea.org/publications/14663/descriptive-uranium-deposit-and-mineral-system-models

Publications… Resource Assessment & Mineral Potential

Undiscovered Resources…



IAEA-TECDOC-1258

Assessment of uranium deposit types and resources — a worldwide persp

INTERNATIONAL ATOMIC ENERGY AGENCY

IAEA TECDOC SERIES

IAEA-TECDOC-1861

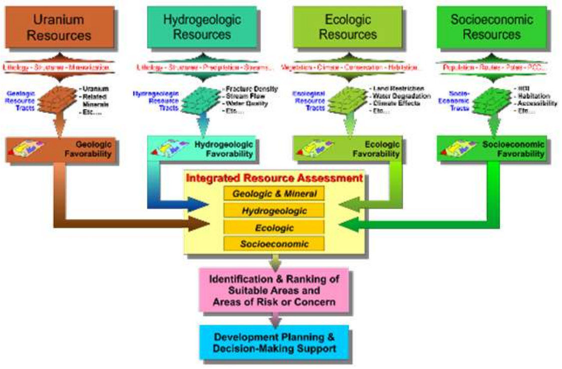
Quantitative and Spatial Evaluations of Undiscovered Uranium Resources

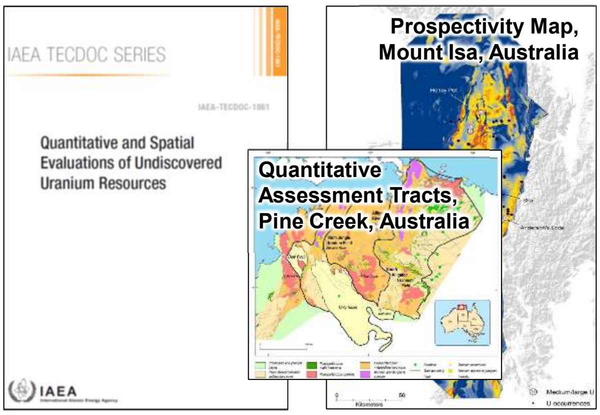
IAEA
International Atomic Energy Agency

https://www.iaea.org/publications/12380/quantitative-and-spatial-evaluations-of-undiscovered-uranium-resources

Methodologies… Assessing / Modelling Future Raw Material Supply

- UPC Team outputs support Member States to utilize rigorous statistical approaches for evaluation of undiscovered uranium resources and multi-resource integrated assessment applications…




IAEA TECDOC SERIES

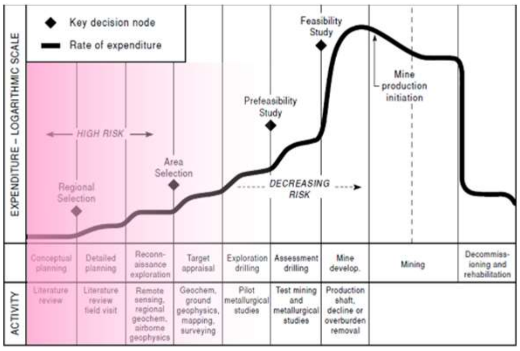
IAEA-TECDOC-1861

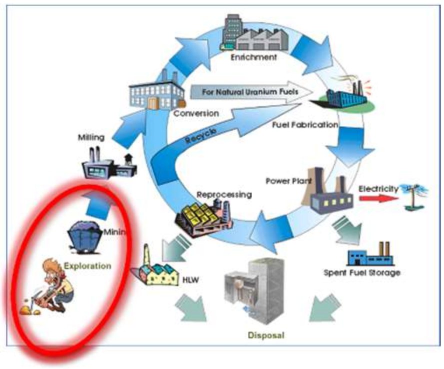
Quantitative and Spatial Evaluations of Undiscovered Uranium Resources

IAEA

Assessment of Undiscovered Mineral Resources

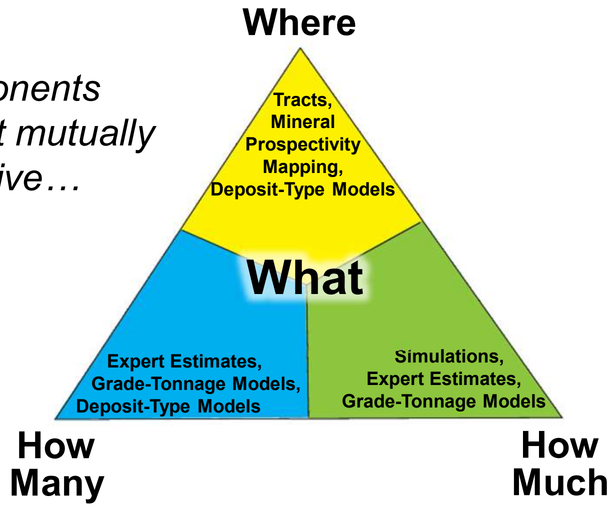
- Concepts and methods/techniques utilized in early exploration are “predictive”…
  - Optimizes later, boots-on-the-ground, exploration activities
  - Can determine where uranium mineralization is possible and unlikely





Assessment of Undiscovered Mineral Resources… What, Where, How Many, How Much?

Components are not mutually exclusive…



- Qualitative will provide information on what, where, and how many
- Quantitative will additionally provide information on how much

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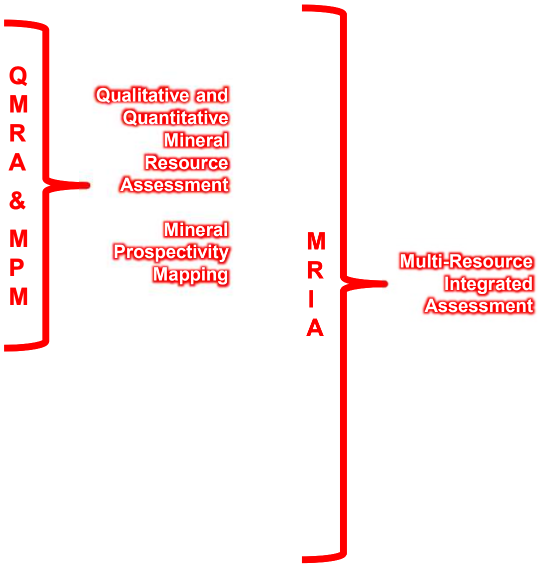
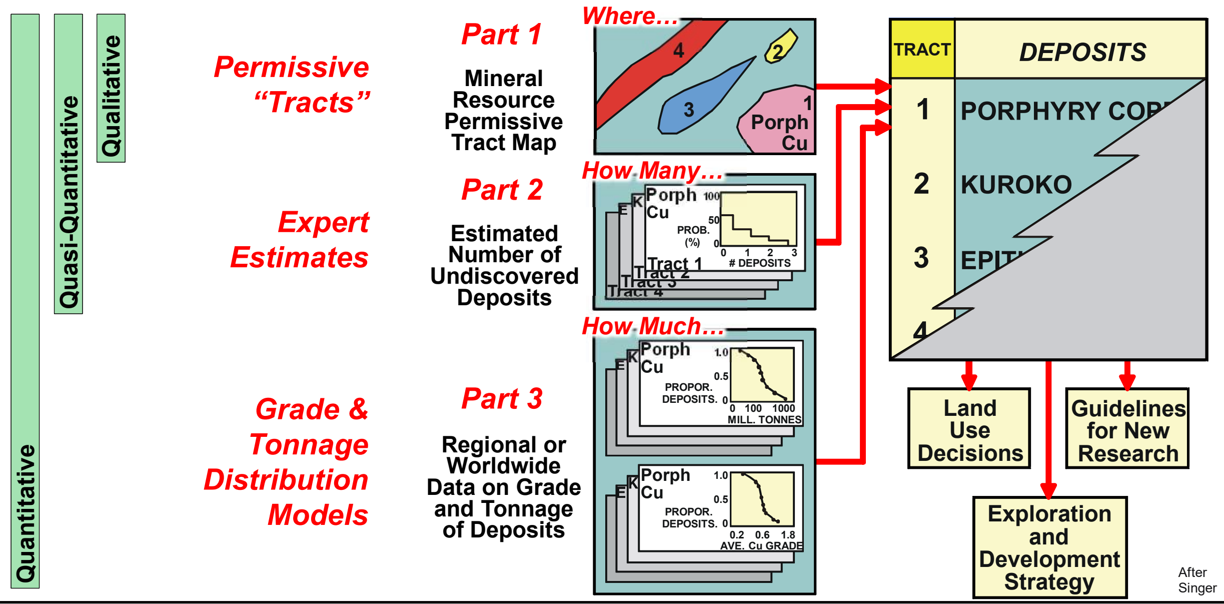
Assessment of Undiscovered Mineral Resources… What Data Do I Use?

- Typical data inputs…
  - Exploration history
  - Statistical (grade, tonnage, etc.)
  - Geologic
  - Deposit-scale
  - Regional-scale metallogenic
  - Infrastructure / accessibility
  - Environmental / ecologic
  - Hydrogeologic / water
  - Socioeconomic



Quantitative Mineral Resource Assessment (3-Part)



Quantitative

Quasi-Quantitative

Qualitative

Permissive “Tracts”

Part 1

Mineral Resource Permissive Tract Map

Expert Estimates

Part 2

Estimated Number of Undiscovered Deposits

Grade & Tonnage Distribution Models

Part 3

Regional or Worldwide Data on Grade and Tonnage of Deposits

Where…

How Many…

How Much…

TRACT	*DEPOSITS*
1	PORPHYRY COP
2	KUROKO
3	EPIT
4	

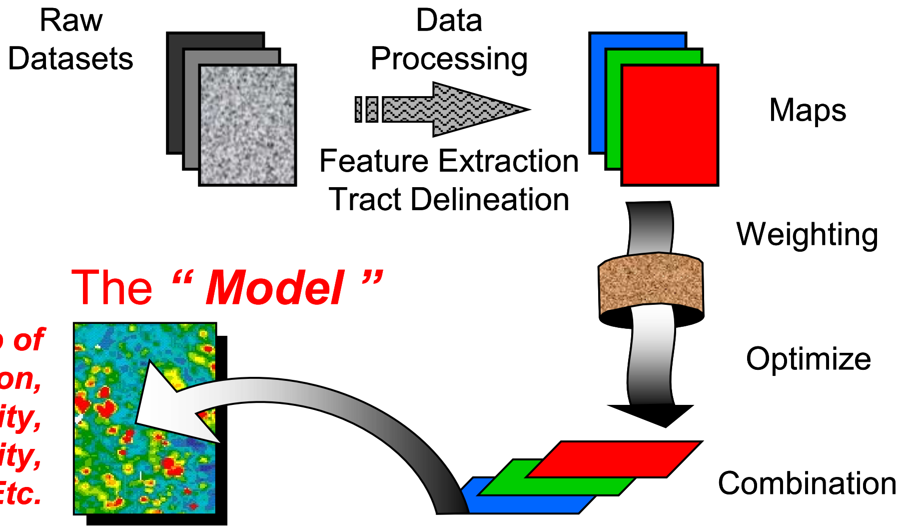
Land Use Decisions

Guidelines for New Research

Exploration and Development Strategy

After Singer

Mineral Potential Modelling / Prospectivity Mapping



Raw Datasets

Data Processing

Feature Extraction
Tract Delineation

Maps

Weighting

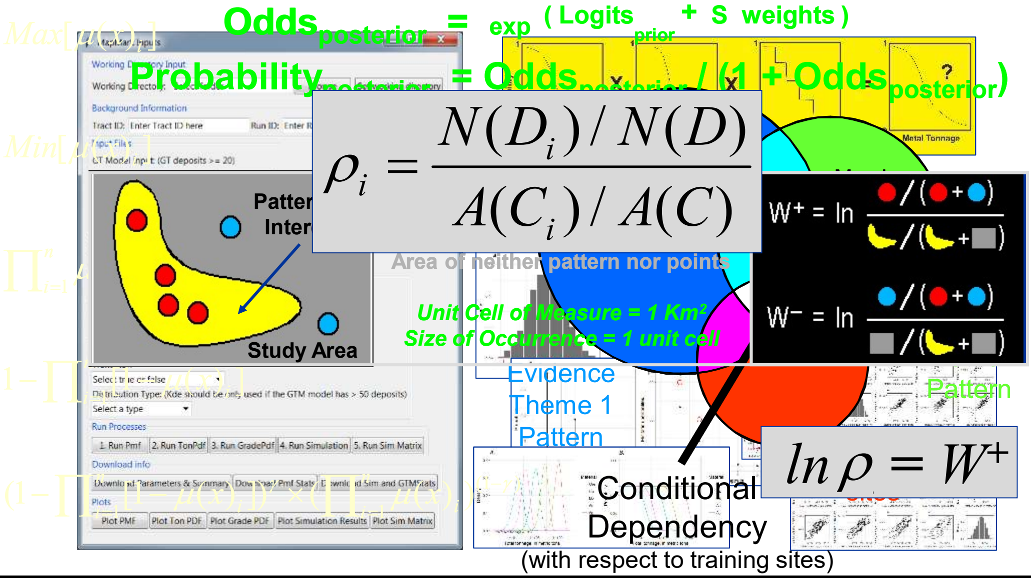
Optimize

Combination

The “ *Model* ”

Map of Correlation, Suitability, Favorability, Probability, Etc.

Assessment of Undiscovered Uranium (and other) Mineral Resources… Statistical Methodologies



$$\rho_i = \frac{N(D_i)/N(D)}{A(C_i)/A(C)}$$

$$W^{+} = \ln \frac{●/(●+●)}{▨/(▨+■)}$$

$$W^{-} = \ln \frac{●/(●+●)}{■/(▨+■)}$$

$$\ln \rho = W^{+}$$

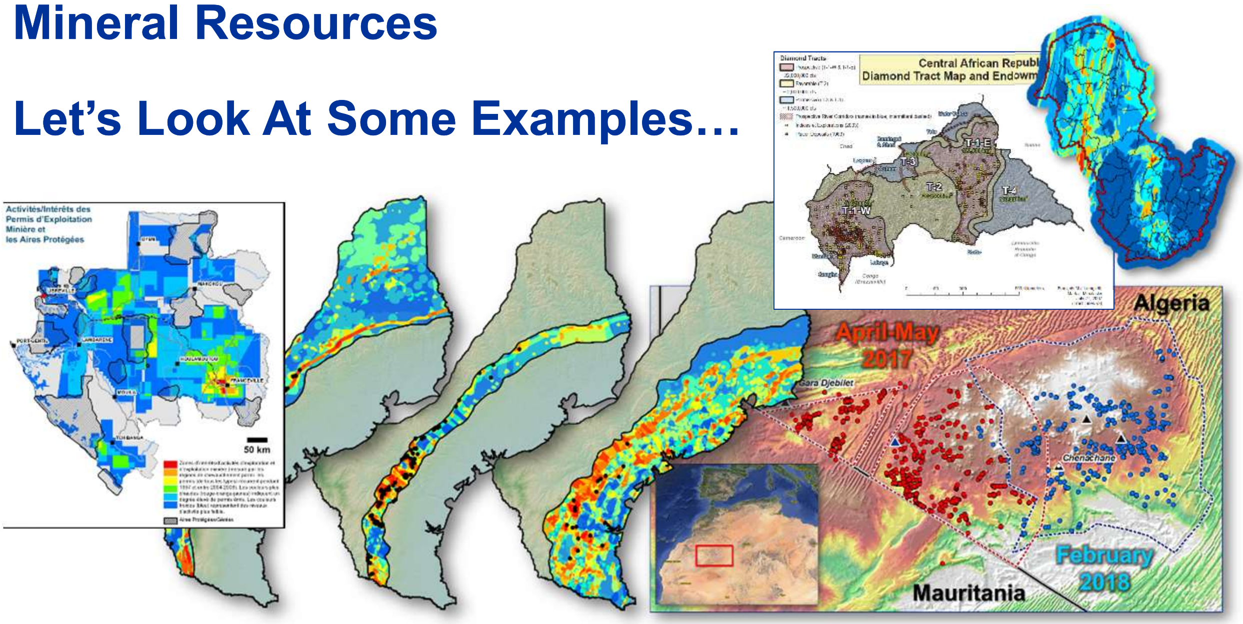
Unit Cell of Measure = 1 Km²

Size of Occurrence = 1 unit cell

Conditional Dependency
(with respect to training sites)

Assessment of Undiscovered Uranium (and other) Mineral Resources

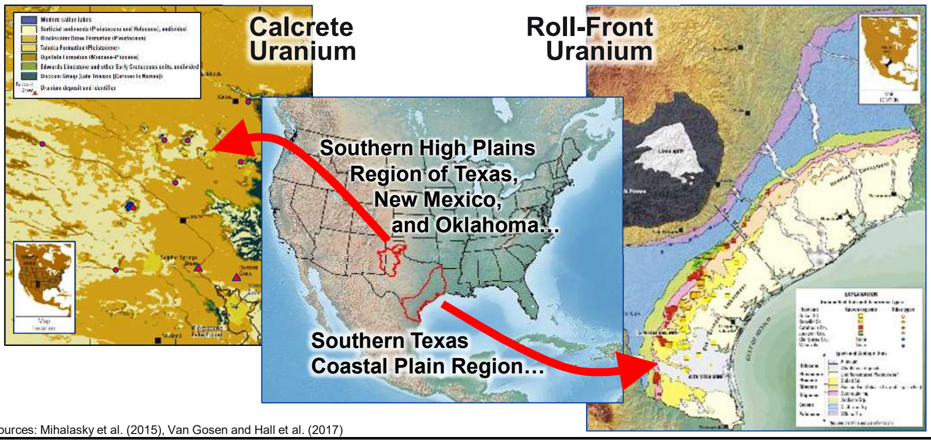
Let's Look At Some Examples…



Quantitative & Mineral Prospectivity Assessment for Undiscovered Uranium Resources, Texas, USA

- Mid-Pleistocene units
- Mineralization occurs in calcareous fine-grained sediments deposited in saline lakes

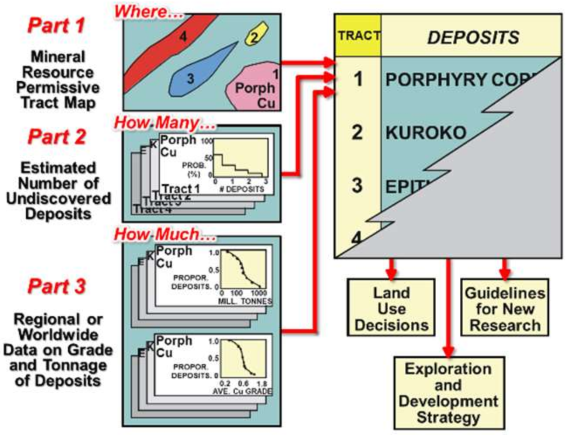
- Tertiary coastal plain units
- Mineralization occurs in semi- and consolidated mixed fluvial-beach and younger fluvial facies



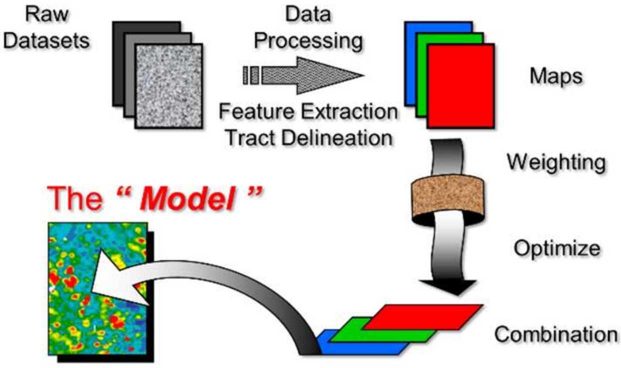
Sources: Mihalasky et al. (2015), Van Gosen and Hall et al. (2017)

Combined Quantitative and Mineral Prospectivity Mapping Resource Assessment

3-Part Quantitative Method…

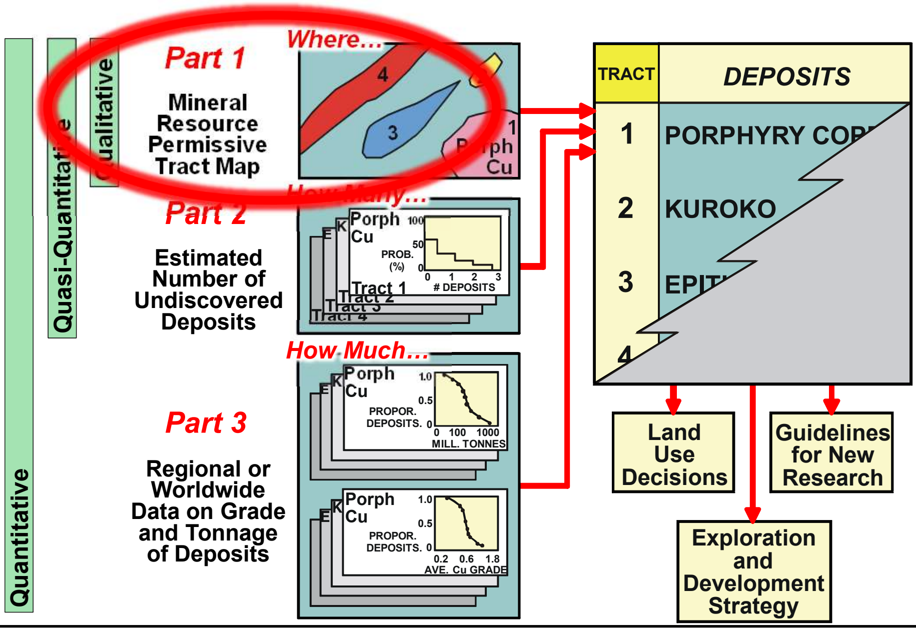


Mineral Prospectivity Mapping…



…also known as mineral potential modeling

Where… Delineate Permissive Areas



Part 1

Mineral Resource Permissive Tract Map

Part 2

Estimated Number of Undiscovered Deposits

Part 3

Regional or Worldwide Data on Grade and Tonnage of Deposits

TRACT	DEPOSITS
1	PORPHYRY COP
2	KUROKO
3	EPIT
4	

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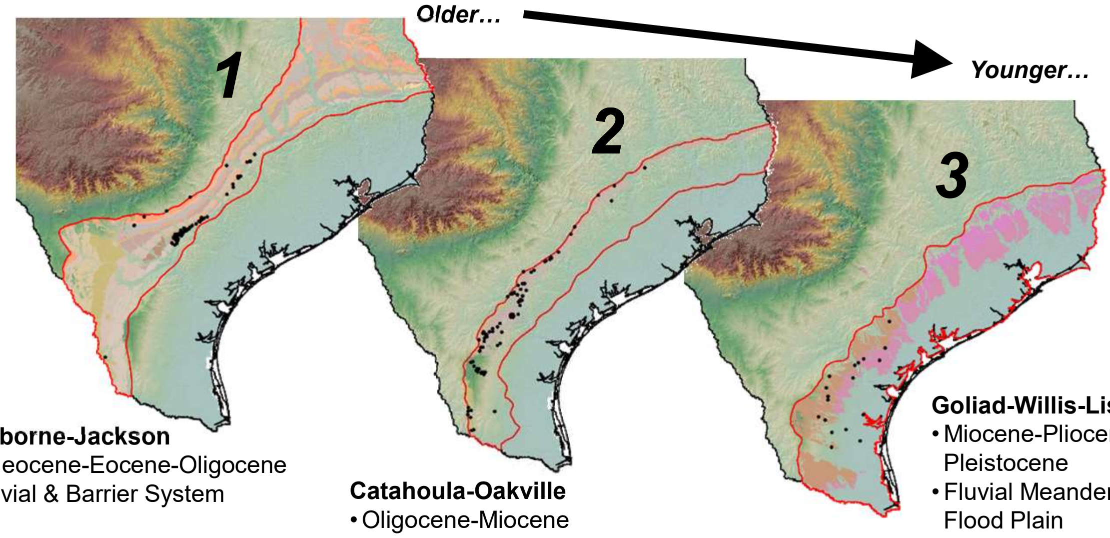
After Singer

Where… 3 Areas Permissive for Sandstone Roll-Front Uranium Mineralization (Permissive Tracts)



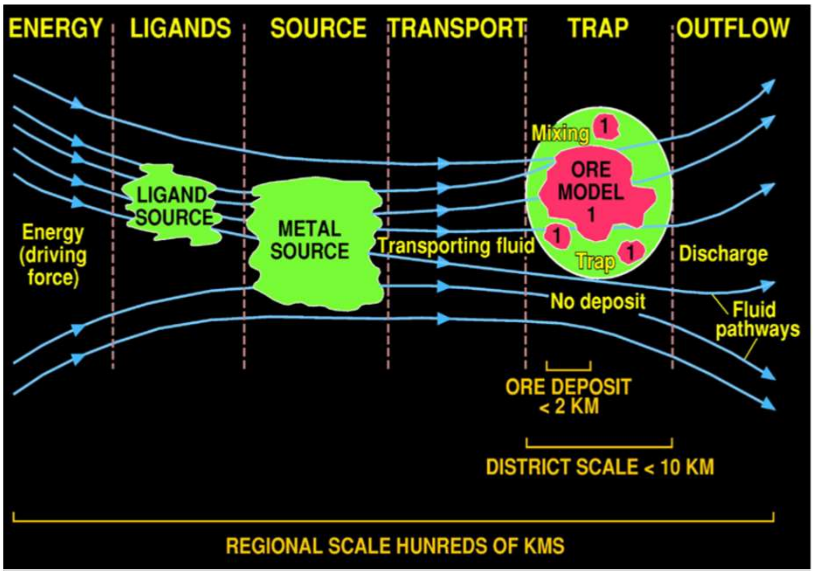
Claiborne-Jackson
- Paleocene-Eocene-Oligocene
- Fluvial & Barrier System

Catahoula-Oakville
- Oligocene-Miocene
- Fluvial Channel, Flood Plain, Deltaic

Goliad-Willis-Lissie
- Miocene-Pliocene-Pleistocene
- Fluvial Meanderbelts, Flood Plain

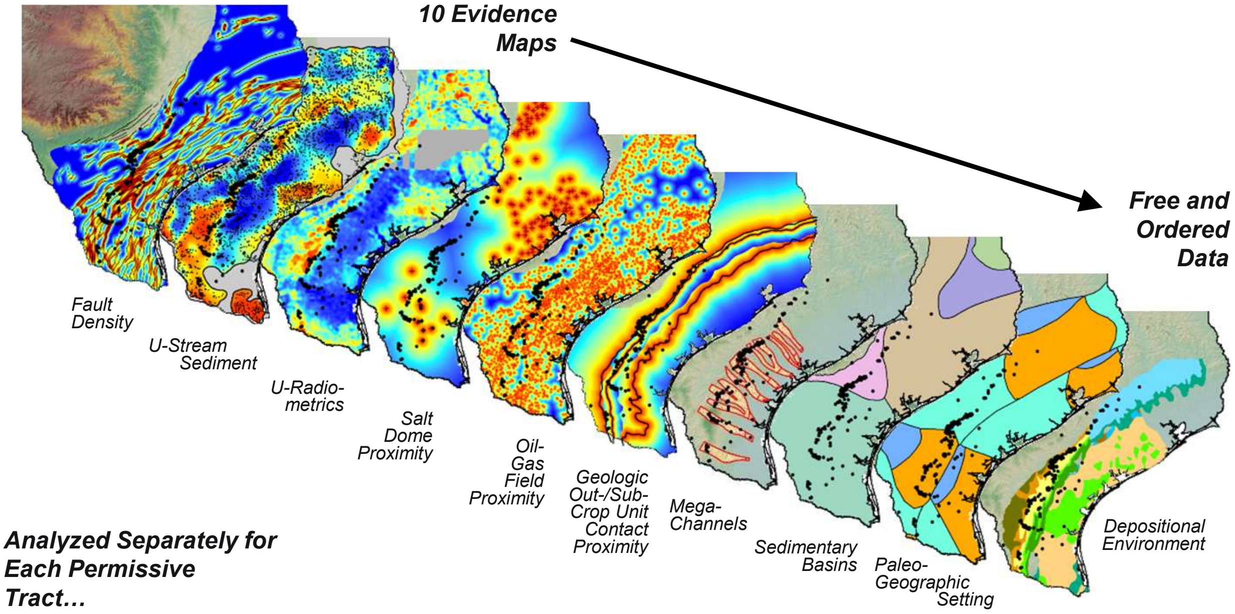
Where… Favourable & Prospective Areas

- “Mineral systems” approach to identify what mappable criteria can be used to delineate the favourable and prospective areas within the permissive tracts



After Wyborn et al. (1994), Knox-Robinson and Wyborn (1997)

Where… Deposit-Indicator Evidence Maps



10 Evidence Maps

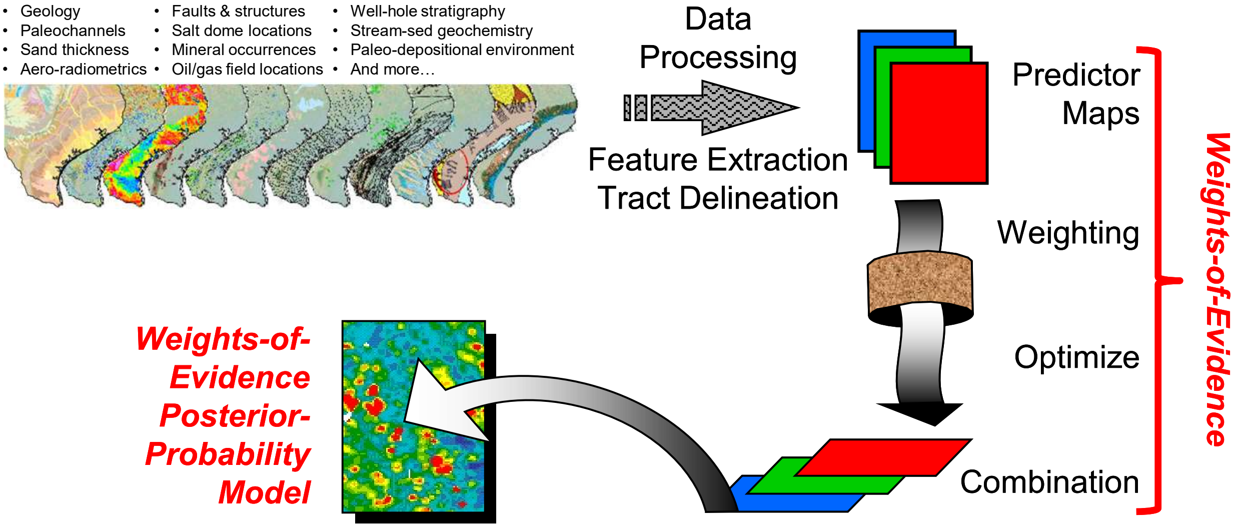
Free and Ordered Data

Analyzed Separately for Each Permissive Tract…

Where… Combine Deposit-Indicator Evidence Maps

Evidence Maps

- Geology
- Paleochannels
- Sand thickness
- Aero-radiometrics
- Faults & structures
- Salt dome locations
- Mineral occurrences
- Oil/gas field locations
- Well-hole stratigraphy
- Stream-sed geochemistry
- Paleo-depositional environment
- And more…



Data Processing

Feature Extraction
Tract Delineation

Predictor Maps

Weighting

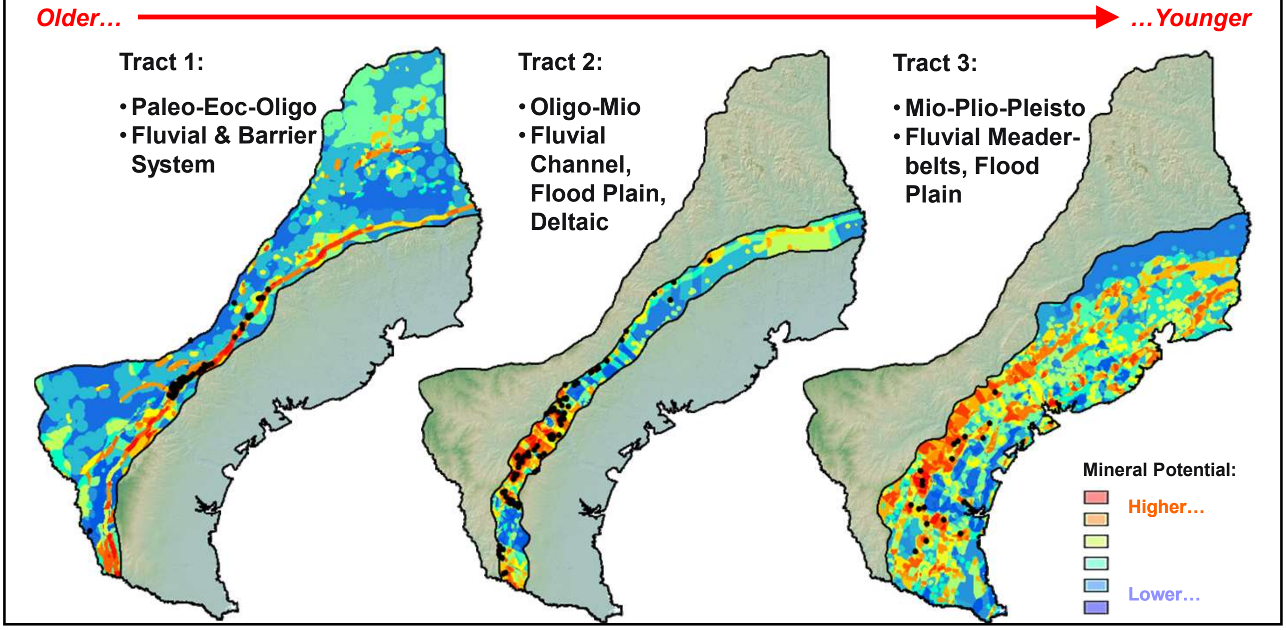
Optimize

Combination

Weights-of-Evidence

Weights-of-Evidence Posterior-Probability Model

Where… Mineral Prospectivity Maps



Tract 1:

- **Paleo-Eoc-Oligo**
- **Fluvial & Barrier System**

Tract 2:

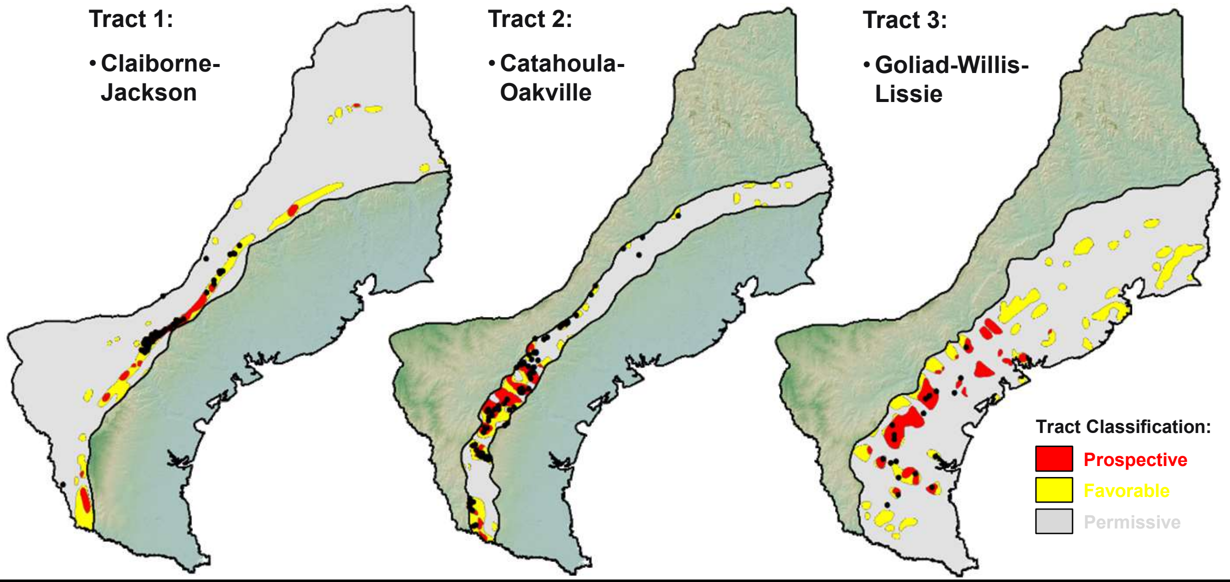
- **Oligo-Mio**
- **Fluvial Channel, Flood Plain, Deltaic**

Tract 3:

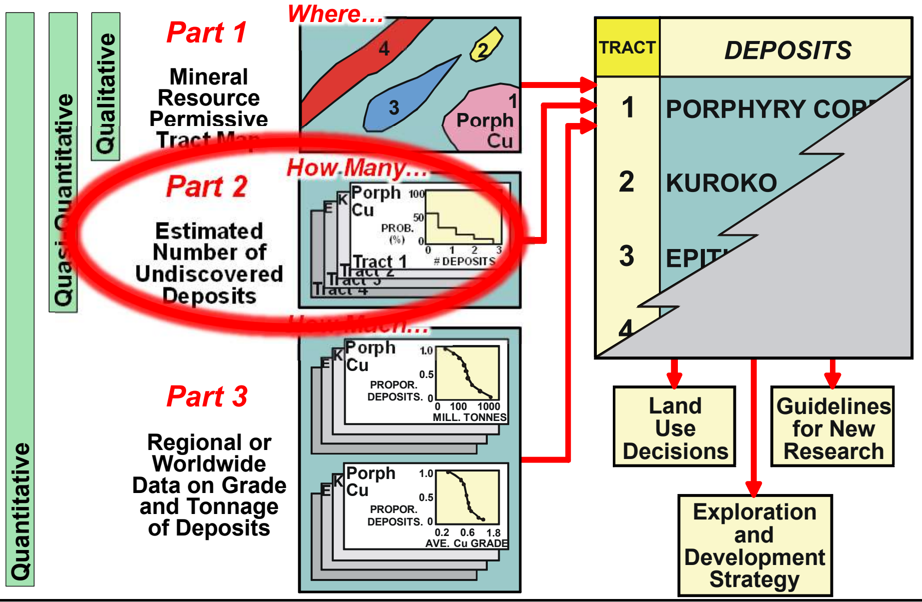
- **Mio-Plio-Pleisto**
- **Fluvial Meander-belts, Flood Plain**

Where… Permissive, Favourable, Prospecitive Areas

Older… → *…Younger*



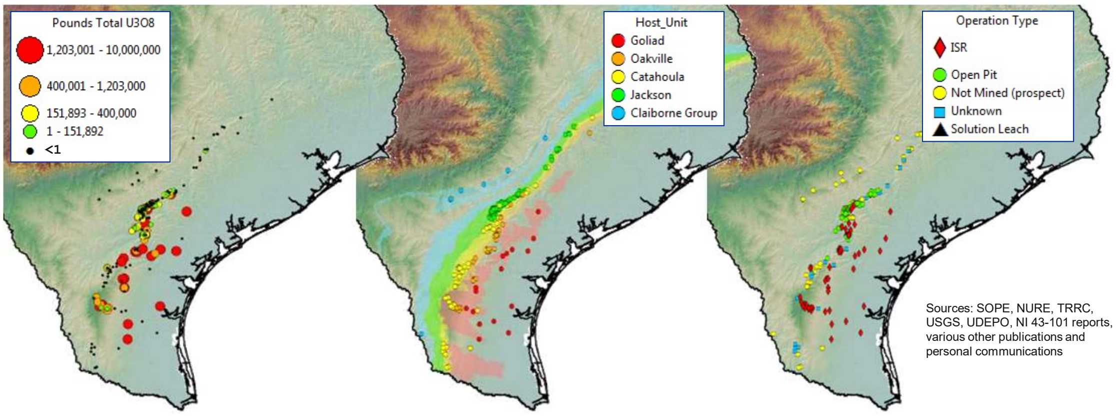
How Many… Estimating What? Define a Deposit?



After Singer

How Many… Estimating What? Define a Deposit?

254 "Occurrences" of Known Roll-Front Uranium Mineralization



Sources: SOPE, NURE, TRRC, USGS, UDEPO, NI 43-101 reports, various other publications and personal communications

- 169 Deposits – sites with recorded production or in-place resources
- 74 Prospects – sites with some level of exploration
- 6 Showings – sites of interest that have been investigated
- 5 Anomalies – sites with indications of mineralizing processes

How Many… Expert-Estimated Number of Undiscovered Roll-Front Uranium Deposits

- Experts estimate for 3 levels of "confidence" or "certainty"…

An analogy:

90%... I'll invest *my money*

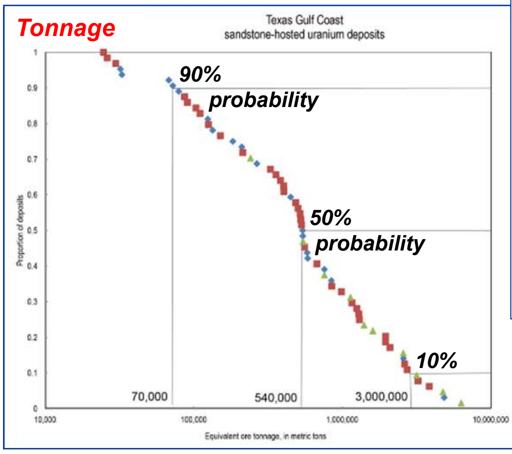
50%... I'll invest *your money*

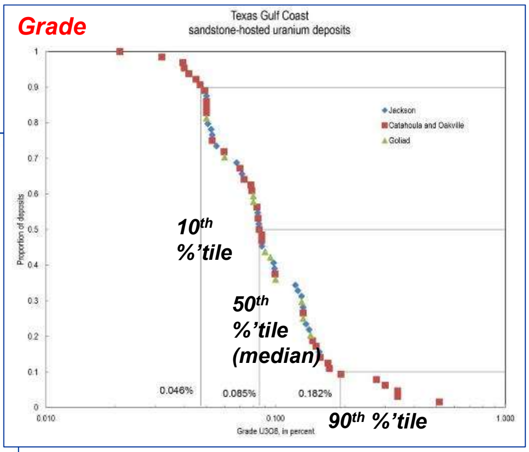
10%... I'll invest *a stranger's money*

How Much… Regional Data on Uranium Deposit Grade & Tonnage

Grade & Tonnage Models…

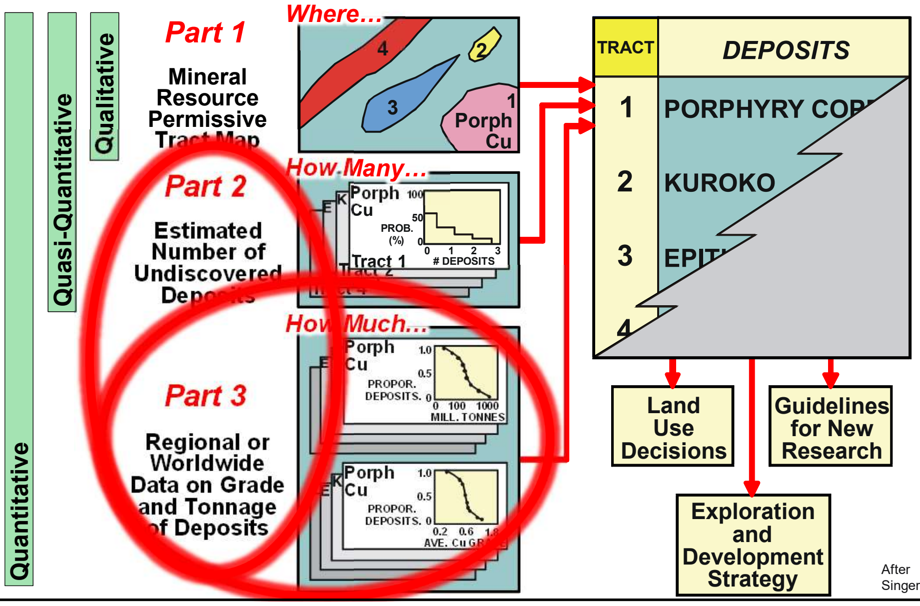
540,000 metric tons (median)





0.085% grade U_3O_8 (median)

How Much… Combine With How Many



Quantitative

Quasi-Quantitative

Qualitative

Part 1

Mineral Resource Permissive Tract Map

Part 2

Estimated Number of Undiscovered Deposits

Part 3

Regional or Worldwide Data on Grade and Tonnage of Deposits

Where…

How Many…

How Much…

TRACT	*DEPOSITS*
1	PORPHYRY COP
2	KUROKO
3	EPIT
4	

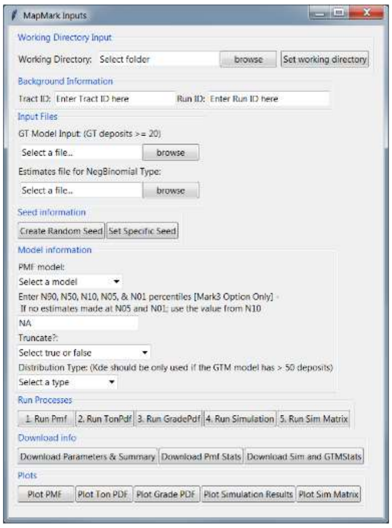
Land Use Decisions

Guidelines for New Research

Exploration and Development Strategy

After Singer

How Much… Combine The Number Undiscovered Deposit Estimates and Grade & Tonnage Data



Working Directory: Select folder

Tract ID: Enter Tract ID here Run ID: Enter Run ID here

GT Model Input: (GT deposits >= 20)

Select a file..

Estimates file for NegBinomial Type:

Select a file..

PMF model:

Select a model

Enter N90, N50, N10, N05, & N01 percentiles [Mark3 Option Only]
If no estimates made at N05 and N01: use the value from N10

NA

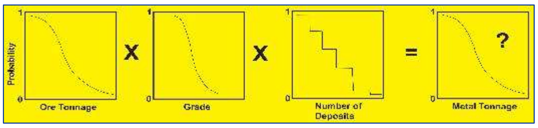
Truncate?:

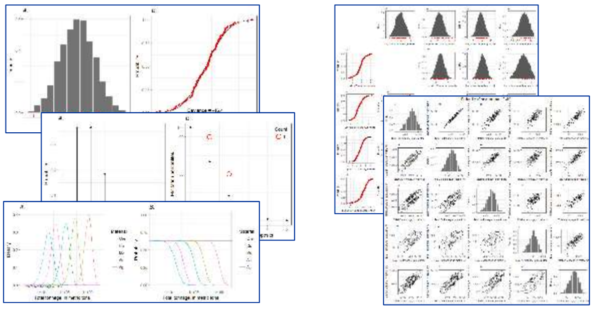
Select true or false

Distribution Type: (Kde should be only used if the GTM model has > 50 deposits)

Select a type

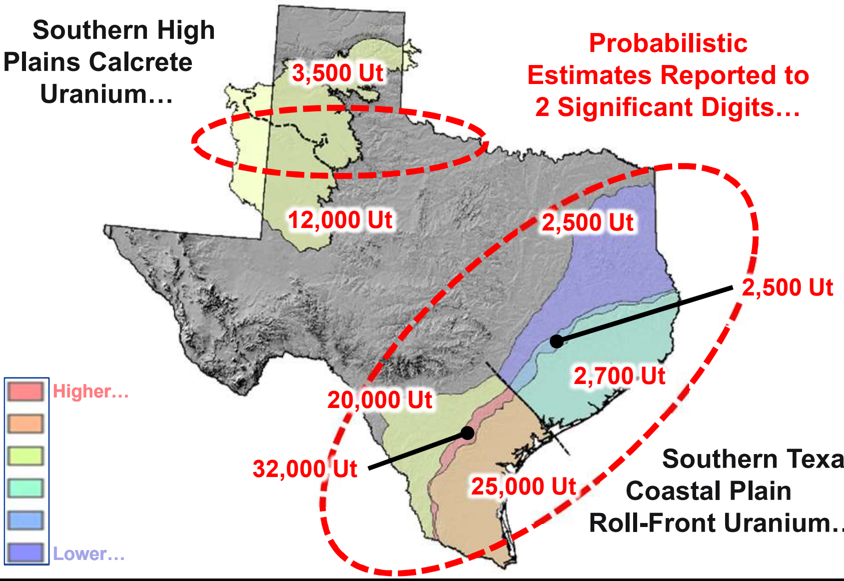
Monte Carlo approach to combine probabilistic estimates of undiscovered mineral deposits with empirical models of grade and tonnage…





Sources: Ellefsen (2017); Jason Shapiro

How Much… Mean Amount of Undiscovered Calcrete and Roll-Front Uranium Resources



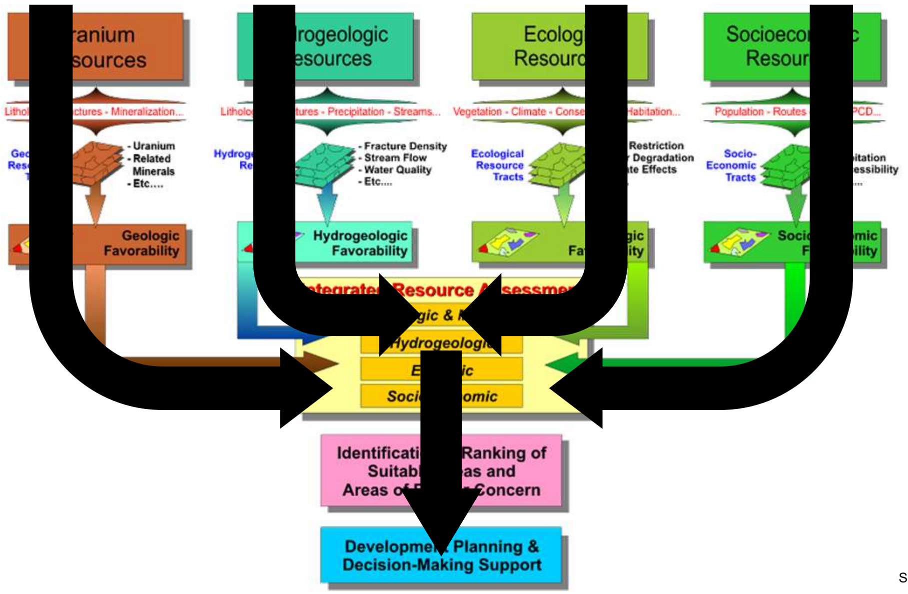
Southern High Plains Calcrete Uranium…

Probabilistic Estimates Reported to 2 Significant Digits…

Southern Texas Coastal Plain Roll-Front Uranium…

Multi-Resource Integrated Assessment (MRIA)

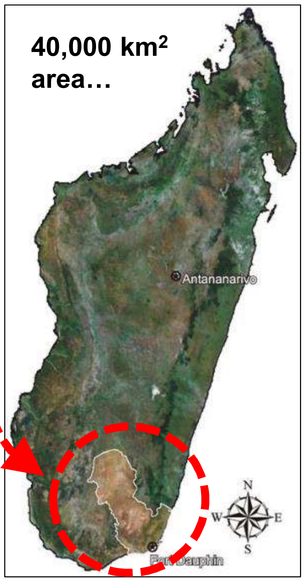
A Framework for Data Integration, Analysis, and Management of Disciplines…



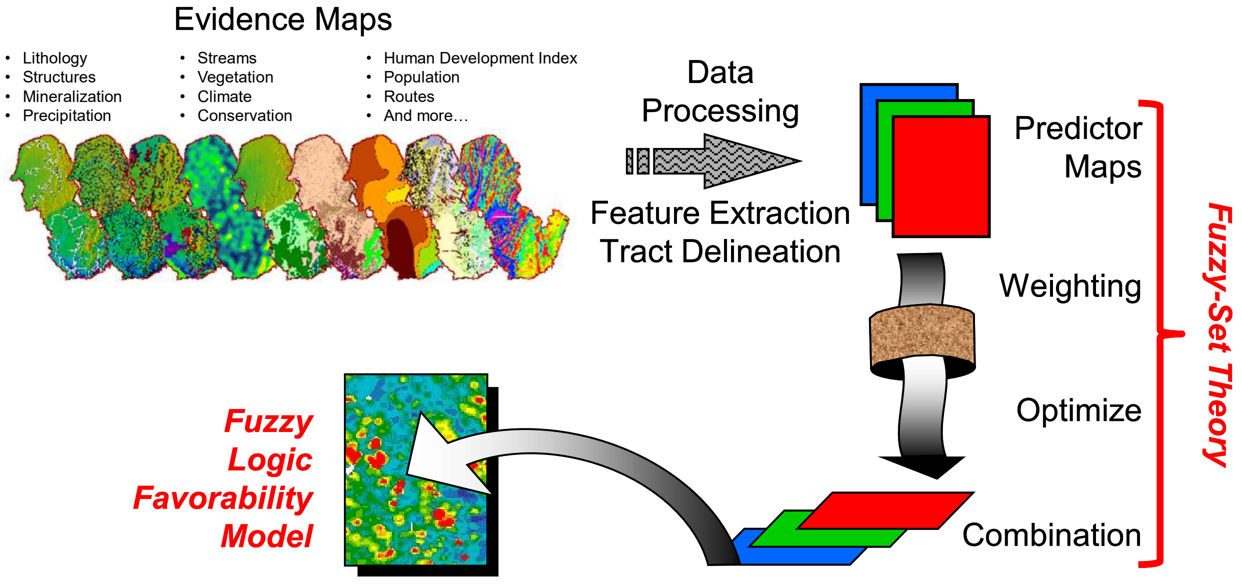
Source: Mihalasky et al. (2006)

Multi-Resource Integrated Assessment (MRIA): Anosy, Southeastern Madagascar

- Sustainable economic development driven by mineral resources…
  - Mineral & natural resource potential (including uranium resources)
  - Areas of elevated mineral potential
  - Highlight suitable priority areas based upon mineral, water, environmental, and socioeconomic resource considerations
  - Promising growth poles & corridors



MRIA: Anosy, Geospatial Modelling Approach



Evidence Maps

- Lithology
- Structures
- Mineralization
- Precipitation
- Streams
- Vegetation
- Climate
- Conservation
- Human Development Index
- Population
- Routes
- And more…

Data Processing

Feature Extraction
Tract Delineation

Predictor Maps

Weighting

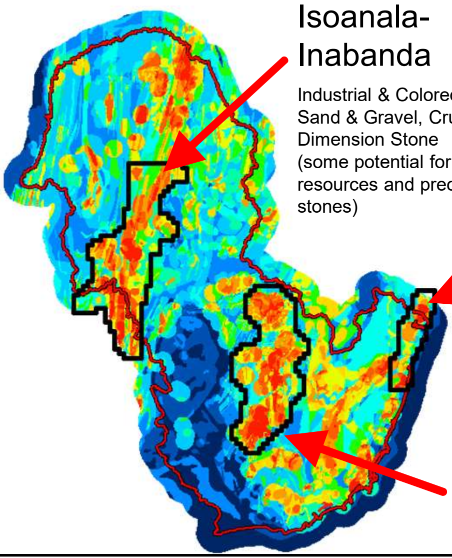
Optimize

Combination

Fuzzy-Set Theory

Fuzzy Logic Favorability Model

MRIA: Anosy – Fuzzy Logic Favourability Map for All Mineral Commodities Combined: 3 Priority Areas



Isoanala-Inabanda

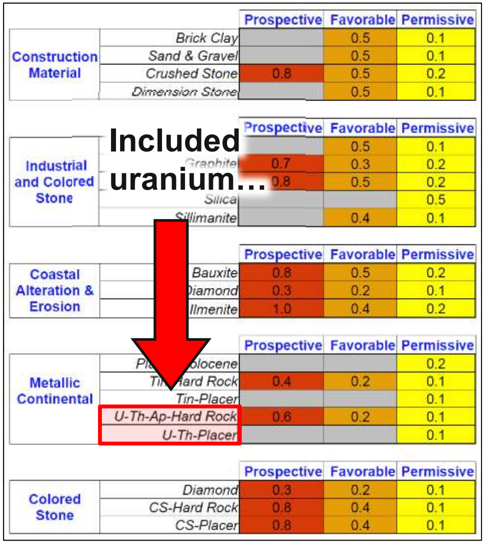
Industrial & Colored Stone, Sand & Gravel, Crushed & Dimension Stone (some potential for metallic resources and precious stones)

Mananetina

Bauxite, Ilmenite, Diamond (some potential for building material)

Tranomaro-Maromby

Industrial & Colored Stone, Crushed & Dimension Stone, Sand & Gravel (some potential for metallic resources and precious stones)

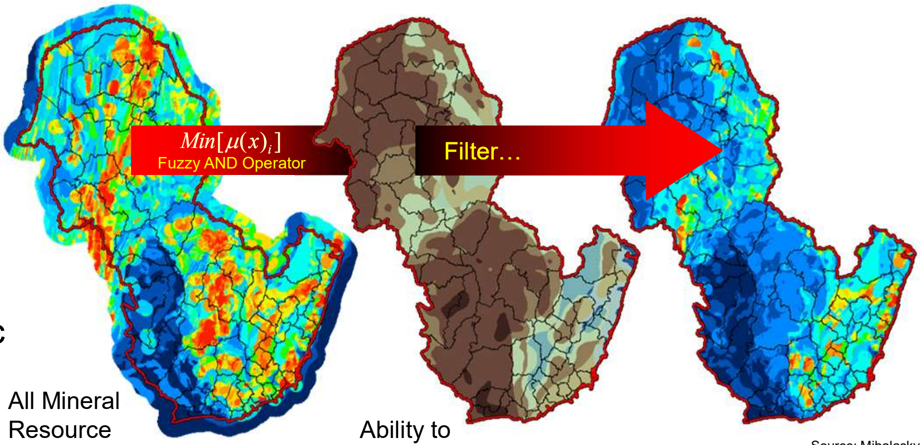


Included uranium…

		Prospective	Favorable	Permissive
Construction Material	*Brick Clay*		0.5	0.1
	Sand & Gravel		0.5	0.1
	Crushed Stone	0.8	0.5	0.2
	Dimension Stone		0.5	0.1
		Prospective	**Favorable**	**Permissive**
Industrial and Colored Stone			0.5	0.1
	Graphite	0.7	0.3	0.2
		0.8	0.5	0.2
	Silica			0.5
	Sillimanite		0.4	0.1
		Prospective	**Favorable**	**Permissive**
Coastal Alteration & Erosion	*Bauxite*	0.8	0.5	0.2
	Diamond	0.3	0.2	0.1
	Ilmenite	1.0	0.4	0.2
		Prospective	**Favorable**	**Permissive**
Metallic Continental	*Pl[illegible]olocene*			0.2
	Ti[illegible]ard Rock	0.4	0.2	0.1
	Tin-Placer			0.1
	U-Th-Ap-Hard Rock	0.6	0.2	0.1
	U-Th-Placer			0.1
		Prospective	**Favorable**	**Permissive**
Colored Stone	*Diamond*	0.3	0.2	0.1
	CS-Hard Rock	0.8	0.4	0.1
	CS-Placer	0.8	0.4	0.1

MRIA: Anosy – Integrate Mineral Favourability Map with Socioeconomic “Resource” Favourability Maps

- Example…
  - Mineral resource favourability map “filtered” through maps hydrogeologic, ecologic, and socioeconomic resources



Mineral Favorability

Regrowth Favorability

Filtered Mineral Resource Favorability

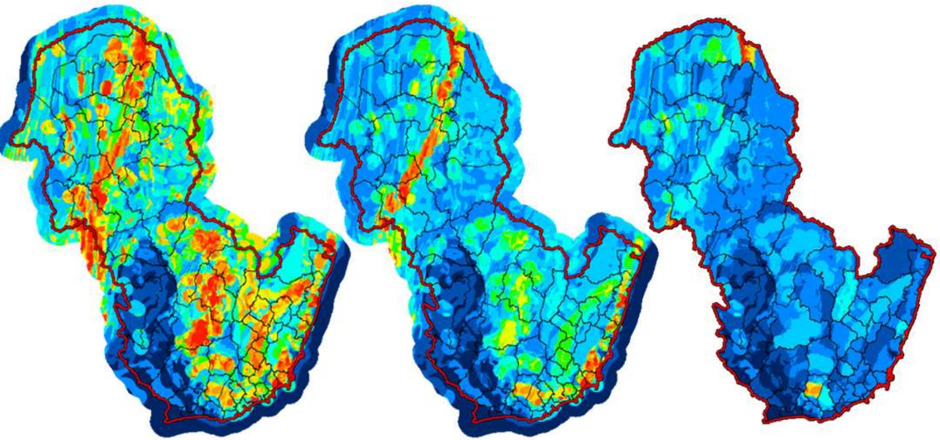
All Mineral Resource Groups

Ability to Rebound

Source: Mihalasky et al. (2006)

MRIA: Anosy – Build Scenarios and Ask Questions for Development and Planning Decision Support

- Example…
  - Where are areas of high mineral favourability that are near roads ***and*** in communes with low Human Development Index?



Mineral Favorability

1st Filter: Proximity to Roads

2nd Filter: Human Development Index

Source: Mihalasky et al. (2006)

SANTA QUITÉRIA PROJECT, CEARÁ, BRAZIL: BUILDING THE FUTURE

By

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ABSTRACT

Industrias Nucleares do Brasil (INB), the company responsible for the nuclear fuel cycle in Brazil, and Galvani, a Brazilian national fertilizer company that produces phosphates, have been working together since 2009, and plan to develop the Santa Quitéria Project (also known as the Itataia uranium/phosphate mine project), which includes the construction and operation of an industrial mining complex in the state of Ceará, Brazil.

The primary objective of the Santa Quitéria Project is to mine and process an ore composed of phosphate and uranium, known as colophanite, a massive cryptocrystalline variety of apatite. A phosphoric acid purification unit will be built for the removal of radioactive elements and production of uranium concentrate through the transformation of phosphate ore into phosphoric acid, then recovering uranium as a by-product using solvent extraction.

It is estimated that Santa Quitéria will annually produce about 1.05 million tonnes of phosphate-based fertilizers to supply agriculture, 220,000 tonnes of bicalcium phosphate (used for animal feed), and 2,300 tonnes of uranium concentrate. The uranium concentrate will be processed abroad and converted into uranium hexafluoride (UF_6) and enriched, then returned to Brazil and used in the production of fuel for the nuclear power plants Angra 1, Angra 2 and, in the future, Angra 3.

Galvani and INB refined the phosphate ore processing technology, having already developed a dry-processing mineral beneficiation technique, which does not require a mine tailings dam, and consequently consumes less water while improving metallurgical recovery.

Currently, the Santa Quitéria Project has two licensing procedures underway: (1) an environmental impact study and report, reviewed by the Brazilian Institute of Environment and Renewable Natural Resources (IBAMA), and (2) a review by the National Commission for Nuclear Energy (CNEN), Brazil's nuclear regulatory body responsible for licensing nuclear power plants and nuclear facilities. As an important part of the environmental licencing process, public hearings were held in the cities of Santa Quitéria, Itatira, and Canindé (Ceará Estate) in June of 2022. In addition, INB and Galvani have been very transparent, openly discussing the project with local and regional stakeholders over the last few months, including leaders from several surrounding communities.

SUMMARY

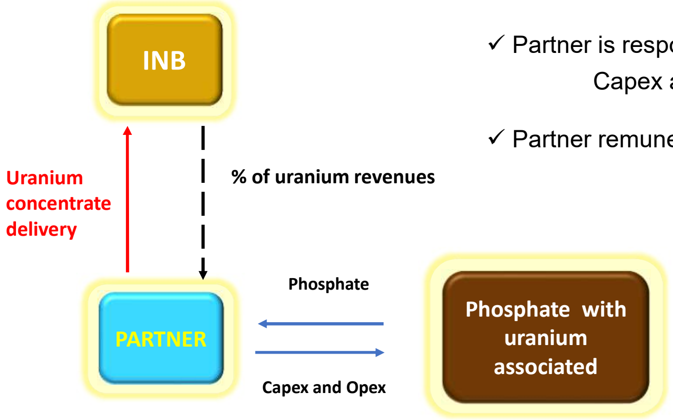
- SANTA QUITÉRIA CONSORTIUM
- INB ACTIVITIES
- SANTA QUITÉRIA PROJECT - SQP
- LICENSING PROCESS
- URANIUM CONCENTRATE PRODUCTION
- FINAL CONSIDERATIONS

SANTA QUITÉRIA CONSORTIUM

SANTA QUITÉRIA PROJECT
CONSORTIUM BETWEEN

- **INB – Indústrias Nucleares do Brasil -**
- **Galvani Phosphates**

SANTA QUITÉRIA CONSORTIUM: Business Framework



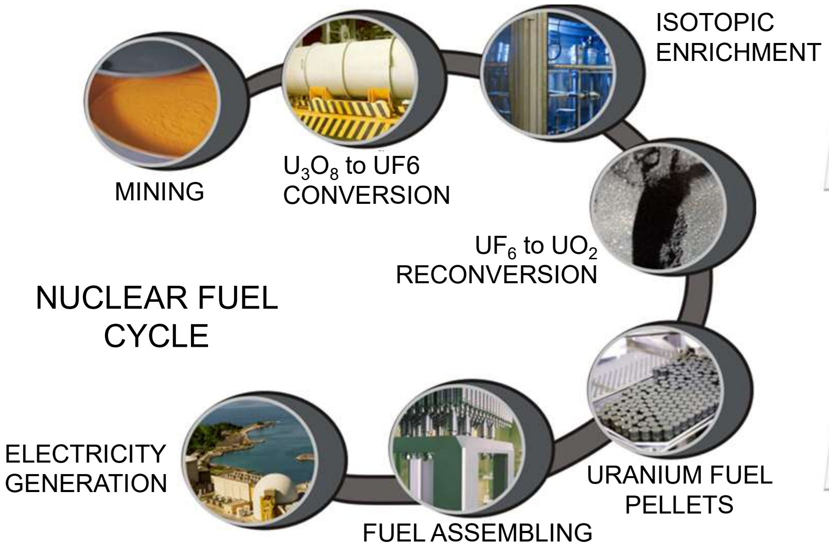
BUSINESS MODEL FOR URANIUM AS A COPRODUCT

✓ Partner is responsible for:

Capex and Opex for mining and beneficiation activities.

✓ Partner remuneration: Phosphate products.

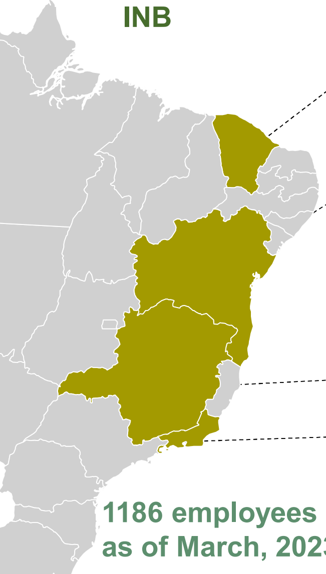
INB ACTIVITIES: Nuclear Fuel Cycle



CAETITÉ SITE – BA STATE

RESENDE SITE – RJ STATE

INB ACTIVITIES: Sites and Projects



INB

Santa Quitéria Project *– CE state*

URA (Uranium Concentration Unit) – Caetité – BA state

- *Underground Mine*
- *Beneficiation Plant Expansion*

UDC (Caldas Decommissioning Unit) – MG state

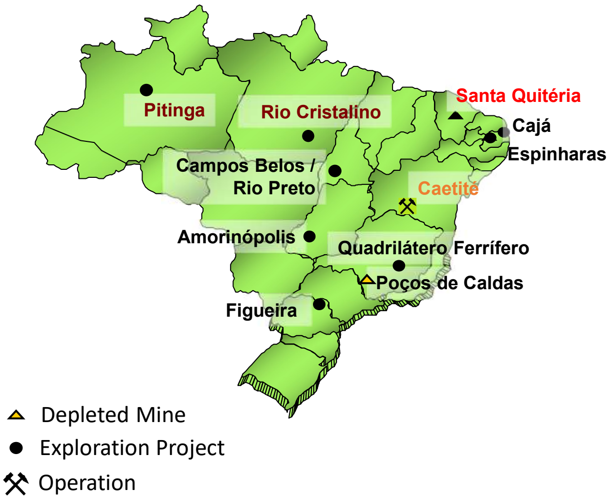
FCN (Nuclear Fuel Plant) – Resende – RJ state

- *Conversion Plant U_3O_8 to UF6*

1186 employees as of March, 2023

- *INB is a state company in charge of Constitutional Monopoly execution.*
- *INB is a subsidiary of the ENBPar and operates in the ore production chain and in the nuclear fuel cycle. ENBPar is linked to the Ministry of Mines and Energy (MME).*

BRAZIL URANIUM MINERAL RESOURCES



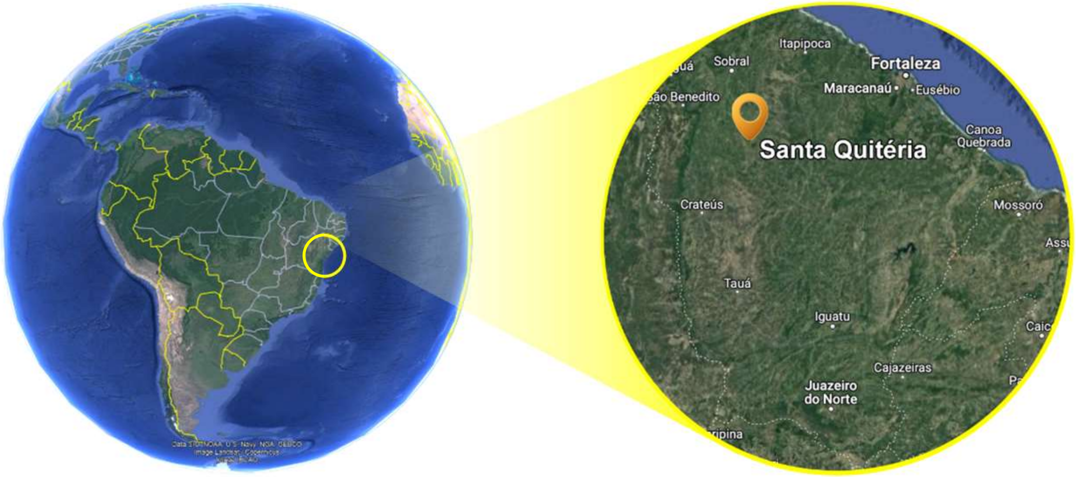
(Ref.: INB internal reports)

Resources and Potential of Mineralization

Deposit	Tonnes of U_3O_8 (Uranium Concentrate)		
	Measured & Indicated	Infered	Total
Caetité	51,520	35,569	87,089
Santa Quitéria	75,010	4,614	79,624
Others	39,500	26,600	66,100
TOTAL	166,030	66,783	232,813

Potential of Mineralization: Pitinga/AM 150,000 t U_3O_8
Rio Cristalino/PA 150,000 t U_3O_8

SANTA QUITÉRIA PROJECT: Location



Brazil - Ceará

Ceará - Santa Quitéria

SANTA QUITÉRIA PROJECT: Deposit and Resources

Deposit Name: Itataia Deposit

Location: Santa Quitéria/CE

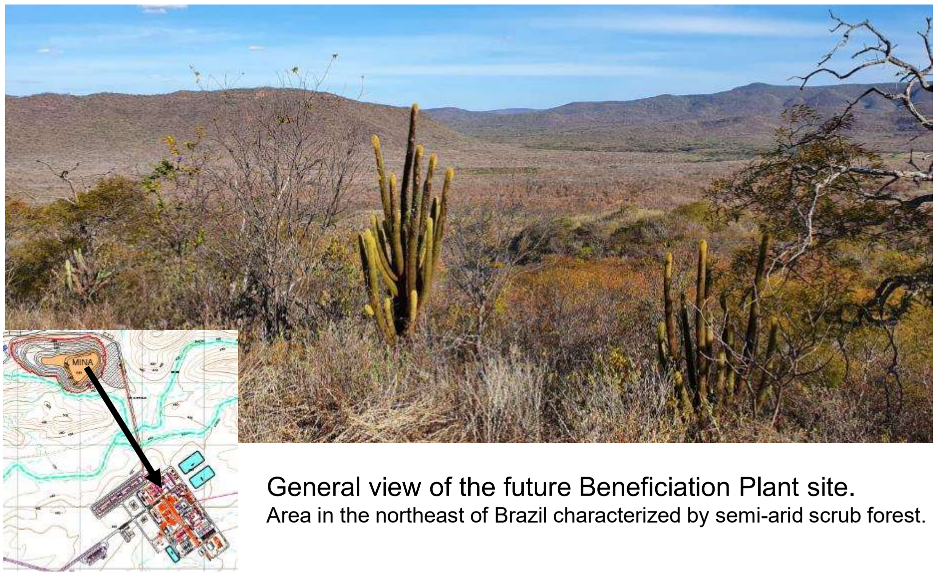
Ore: Colophanite (Uranium associated with Phosphate)

Resources:

Uranium: 79,624 t U_3O_8 Phosphate: 111 Million t P_2O_5


Future waste pile site overview

SANTA QUITÉRIA PROJECT: General View



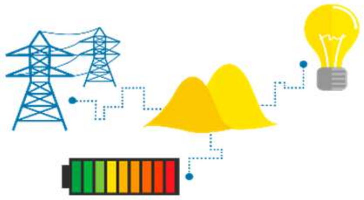
General view of the future Beneficiation Plant site.
Area in the northeast of Brazil characterized by semi-arid scrub forest.

SANTA QUITÉRIA PROJECT

- The **phosphate ore** will be extracted and processed to obtain the phosphoric acid, used in the fertilizers production and animal feed.
- Uranium will be extracted from phosphoric acid and used to generate **electricity.**

URANIUM = MORE ELECTRICITY

- 10.700 MW Capacity
- Energy for 16 million Brazilians



PHOSPHATE = MORE FOOD

FERTILIZERS:

N, NE and Midwest regions: states of Pará, Maranhão, Piauí, Ceará, Bahia, Tocantins and Mato Grosso.

ANIMAL NUTRITION:

Northeast, North and Midwest

SANTA QUITÉRIA PROJECT: Products

Phosphate Fertilizers

- *Production of **1.050,000 t/year of high content** P_2O_5 for agriculture.*

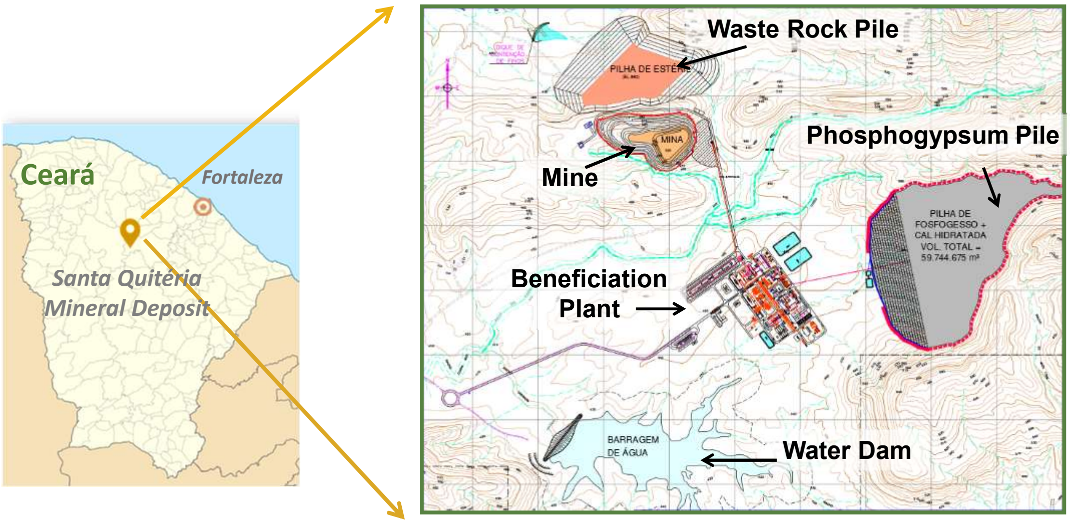
Dicalcium Phosphate

- Production of **220,000 t/year** of inorganic source to supply phosphorus and calcium for animal nutrition.

Uranium Concentrate

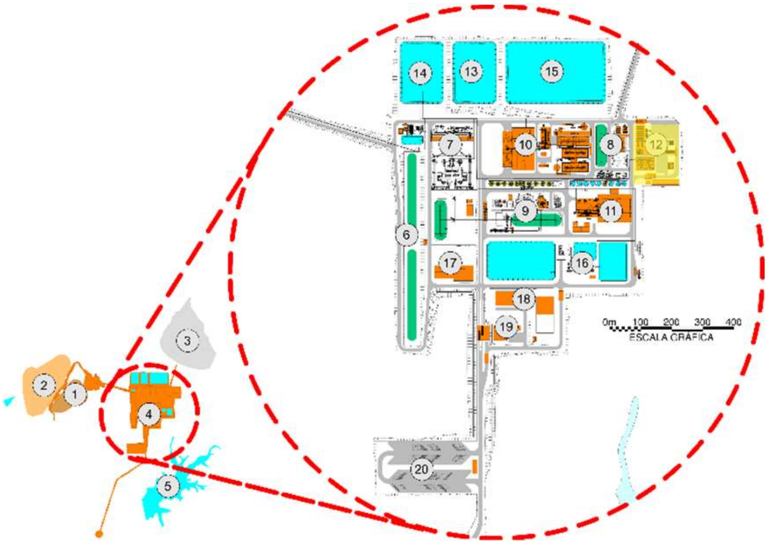
- Production of **2,300 t/year** of U_3O_8, as a **uranium concentrate** (*yellowcake*), extracted from phosphoric acid.

SANTA QUITÉRIA PROJECT: General Layout



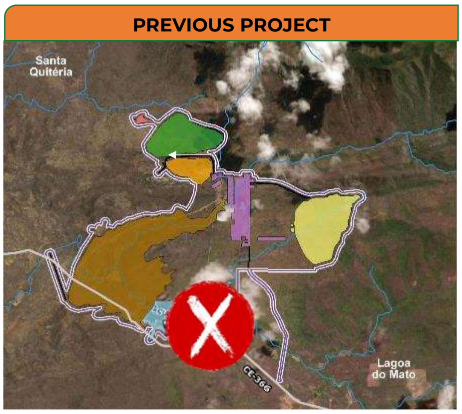
SANTA QUITÉRIA PROJECT: Beneficiation Plant Layout

1. Mine;
2. Tailings Pile;
3. Phosphogypsum and Lime Pile;
4. Industrial Area;
5. Quixaba dam;
6. Homogenization and Milling;
7. Calcination and Concentration;
8. Phosphoric Acid Plant;
9. Sulfuric Acid Plant;
10. Fertilizer Plant;
11. Dicalcium Phosphate Plant;
12. **Uranium Concentrate Plant;**
13. Raw water;
14. Treated water;
15. Percolated water;
16. Wastewater treatment;
17. Stockroom;
18. Forest Garden and Community Center.

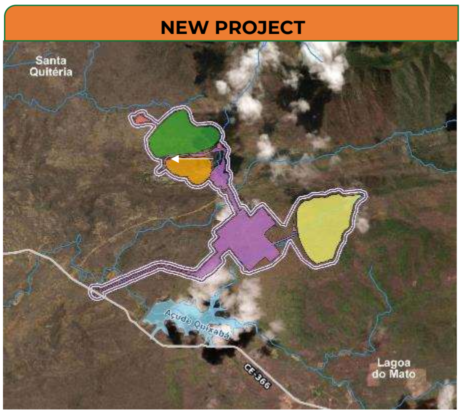


SANTA QUITÉRIA PROJECT: Beneficiation Plant Layout

PREVIOUS PROJECT



NEW PROJECT



Adoption dry process
Increase production
Reduction of occupied area
Without Tailing dam
Water consumption reduced

NEW PROJECT IMPROVEMENTS

-	PREVIOUS PROJECT	NEW PROJECT
Global recovery (P_2O_5)	**60%**	**84%**
Global recovery (Uranium)	**48%**	**82%**
Water consumption	**1036 m³/h**	**855 m³/h**
Efluents	**Treatment and release**	**Closed-loop treatment and reuse**
Area occupied by the project	**917 ha**	**380 ha**
Vegetation suppression area	**790 ha**	**360 ha**

SOCIAL AND ECONOMIC BENEFITS

JOBS

CONSTRUCTION PHASE

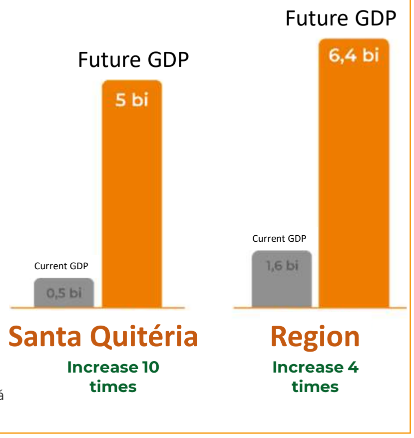
2.800	5.600
Direct employees	Indirect employees

OPERATIONAL PHASE

538	2.300
Direct employees	Indirect employees

ANNUAL ECONOMIC GAINS (OPERATIONAL PHASE)

	Santa Quitéria	Region
Salarial mass R$	60,8 mi	110,0 mi
Total collection R$	14,5 mi	37,9 mi



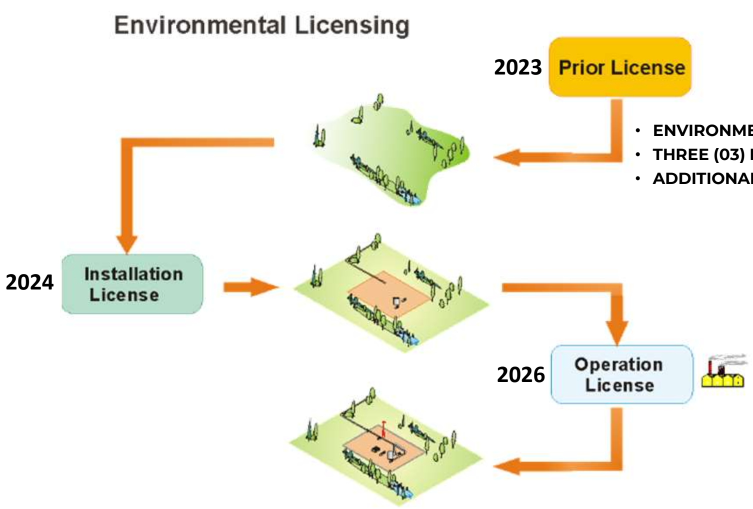
Source: FIEC - Federação das Indústrias do Estado do Ceará

SANTA QUITÉRIA PROJECT: Process

Vamos conhecer as principais etapas de produção do Projeto Santa Quitéria.

LICENSING PROCESS: Environmental

Brazilian Institute of Environment and
Renewable Natural Resources - IBAMA



Environmental Licensing

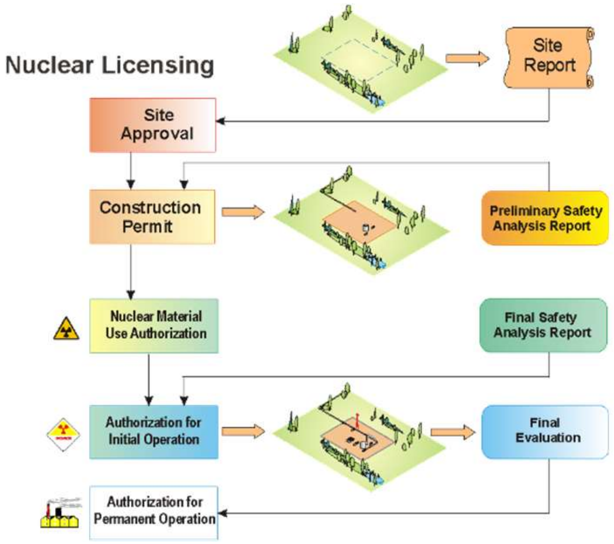
2023 Prior License

- **ENVIRONMENTAL STUDIES (EIA/RIMA)** ✓
- **THREE (03) PUBLIC HEARINGS** ✓
- **ADDITIONAL INFORMATIONS**

2024 Installation License

2026 Operation License

LICENSING PROCESS: Nuclear



National Nuclear Energy Commission - CNEN

- **PRELIMINARY REPORTS FOR MINING-INDUSTRIAL FACILITY**
- **LOCAL AND SAFETY ANALYSIS REPORT FOR NUCLEAR MINING-INDUSTRIAL FACILITY**

LICENSING PROCESS: Stakeholders Engagement

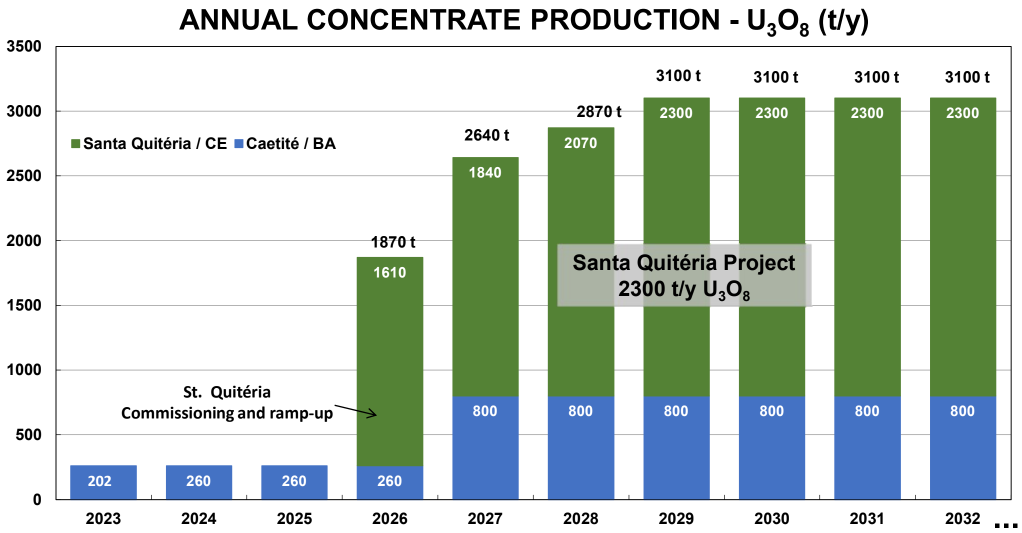
2020 to 2021
- Visits to public authorities and communities to address technical issues of the Physical Project
- Continuous information flow and offices to dialogue with stakeholders

2022
- Prior Meetings and Public Hearings
- *Roadshow "Vamos construir um Futuro Juntos"*

"Let's Build a Future Together"

2023
- Visits to public authorities and communities

URANIUM CONCENTRATE PRODUCTION: Scenario With SQP


ANNUAL CONCENTRATE PRODUCTION - U_3O_8 (t/y)

FINAL CONSIDERATIONS

- ✓ Phosphate and uranium are **strategic minerals for key sectors of the national economy.**
- ✓ **The** SQP contributes to the **National Fertilizer Plan** and the **National Energy Plan PNE 2050.**
- ✓ **High positive impact on the Brazilian trade balance**, with the elimination of uranium concentrate imports and reduction of external dependence on fertilizers.
- ✓ **Sustainability:** Zero CO_2 emission nuclear energy.
- ✓ **Energy:** Uranium concentrate enough to supply 3.1 nuclear power plant complexes such as Angra.
- ✓ **Licensing**: Long and challenging processes, with great **social** involvement.

SUSTAINABLE PRODUCTION OF SCANDIUM PRODUCTS IN EUROPE

By

Edward M. Peters, Robin Scharfenberg, Thore Perlitz, [2]Efthymios Balomenos, [3]Pierre Feydi, [4]Kerstin Forsberg, [5]Beate Orberger, Carsten Dittrich

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[2]Mytilineos SA - Metallurgy Business Unit, Alumina and Aluminium plant, Greece
[3]ORANO Mining, France
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ABSTRACT

Scandium is a metal with increasing demand due to its application in production of high strength, light-weight aluminium scandium alloys for the aerospace industry as well as its use in solid oxide fuel cells (SOFCs) and solid oxide electrolyser cells (SOECs). Currently, China accounts for 66% of the world annual production of scandium and the remainder being produced by Russia and Kazakhstan. Research has been on-going to develop a sustainable process for the recovery of scandium from Europe's mining and metallurgical waste streams, particularly the bauxite residue from the alumina industry and acid waste from the titania production industry. The ongoing SCALEUP and SCAVANGER projects, funded by the European Institute of Innovation and Technology (E.I.T. raw materials) are follow-ups to the SCALE project, which was funded by the European Union Horizon 2020 programme.

The SCALE project demonstrated on bench scale the use of hydrometallurgical techniques such as acidic leaching, ion exchange, solvent extraction and crystallization to produce an ammonium scandium hexafluoride product, which can be further calcined into ScF_3 and Sc_2O_3 products of purity > 99%. The ScF_3 can also be used to produce aluminium scandium master alloy containing 2% scandium. This was accomplished at Technology Readiness Level (TRL) 6 using typical waste resources from Europe's alumina and titania industries.

The SCALEUP project will further demonstrate and optimize the flowsheet developed under the SCALE project to recover scandium from bauxite residue while the SCAVANGER project will demonstrate and optimize the flowsheet for recovery of scandium from titanium dioxide acid waste in light of commercialization. This will pave way for commercial implementation to become the first full-scale production of scandium products of high purity to meet Europe's scandium demand for the aerospace, machinery as well as the SOFCs and SOECs industries. This will reduce the dependence of Europe on Chinese scandium products since China has been dominating the market for scandium and other rare earth metal products. Scandium production from bauxite residues and titanium dioxide pigment production residues is expected to start in Europe in the foreseeable future.

Keywords: scandium, hydrometallurgy, leaching, solvent extraction, crystallization, ScF_3, Sc_2O_3, aluminium scandium alloy

Contents

1. Background
2. Scandium primary and secondary resources
3. European scandium secondary resources
4. Overview of SCALE project
5. Overview of SCALEUP project
6. Overview of SCAVANGER project
7. Future Outlook

Background

Abundance

- Sc concentration in the earth’s crust: 22 ppm
- Rare or not?
- Scarcity of scandium-containing ores[1-2]

Metal	Concentration (ppm)
Co	18
Pb	16
Tn	2.5
Li	18
Ag	0.07
Au	0.004

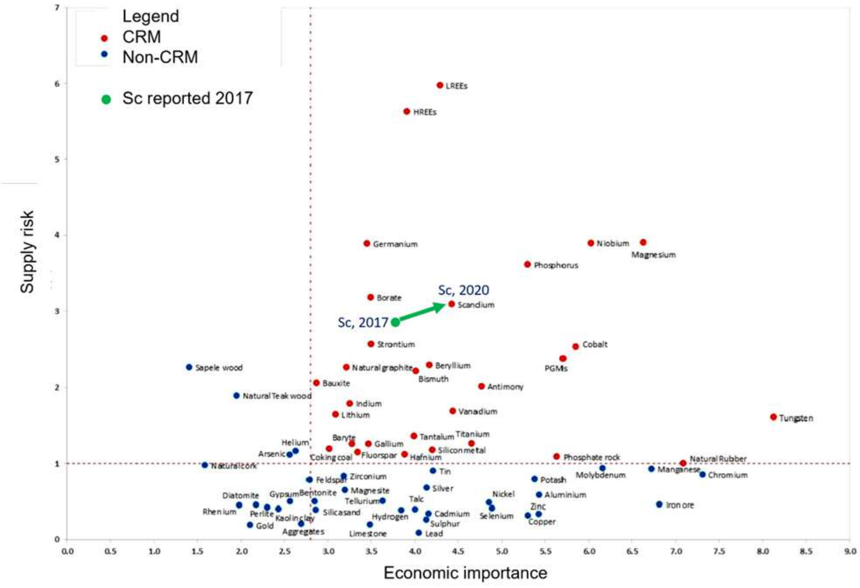
Background

Applications[3,4]

- Al-Sc alloys < 2 wt. % Sc (Aviation industry)
- Solid Oxide Fuel Cells (SOFCs) & Solid Oxide Electrolyzer Cells (SOECs)
- 5G thin films (Al-Sc-N)
- Ceramics
- Lighting
- Lasers
- Electronics
- 3D printing

Background

Supply vs. Demand[4]



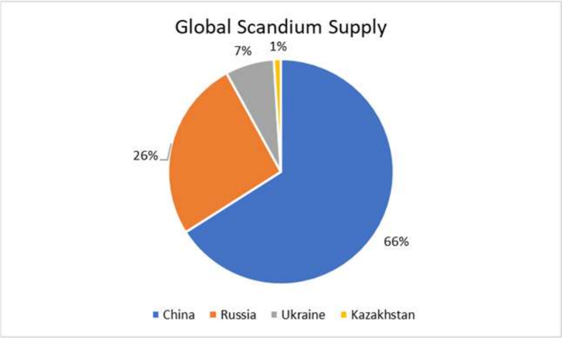
- Scandium was first listed as a CRM in EU in 2014
- Supply risk and economic importance of Sc increased from 2017 and 2020

Background

Trade

- Current prices:[3]

Product	\$US per gram (2022)
ScF_3 99.9% pure	250
Sc_2O_3 99.99% pure	2.1
Sc Ingot	150



[4]

- Current global Sc supply: 15 – 25 t/yr
- EU currently relies on 100% imports

Scandium Primary and Secondary Resources

Primary

- Thortveitite & Kolbeckite ores ($(Sc,Y)_2Si_2O_7$: < 45% Sc_2O_3; Madagascar and Norway[1,5,6]
- Wolframite ores (0.1% Sc) [1]
- Fe-Nb REE deposit (Bayan Obo, China: 0.006 – 0.016% as Sc_2O_3)[1]
- Elk Creek Carbonitite Nb ore, Nebraska (65.7 ppm Sc) [3,5,7]
- Ni-Co laterite ores (0.005 – 0.06% Sc): Nyngan, NSW, Australia[5,8], SCONI project, Queensland[6]

Secondary

- Bauxite Residue (red mud)
- TiO_2 acidic waste
- Waste from U, apatite, Tungsten, tin, Ni-Co laterite processing
- Coal ash

European Scandium Secondary Resources

Bauxite Residue[9,10,11,12]

- Composition 30 – 230 g Sc/t dry basis
- 1 – 1.5 t red mud/t of bauxite ore
- Annual production: 150M t/y
- Europe: 7M t/yr (dry basis) [13]
- Accumulation: 4 billion tons
- Sc: 95% of economic value of REEs

Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	TiO_2 (%)	CaO (%)	Na_2O (%)	Sc (ppm)
41	16	9.6	8.8	8.6	4.5	30 - 230

Origin	Sc, ppm
Greece	121
Australia	54
Canada	31
Russia	73 – 228
China	158

European Scandium Secondary Resources

TiO_2 Acidic Waste

- Composition 5 – 20 g Sc/t dry basis
- EU produces about 1.5M tons of TiO_2 annually
- Sulfate process: 6 – 8 t of acidic waste / t of TiO_2 produced [14]
- Chloride process: Iron chloride waste acid
- Treated with lime/limestone and the residues are landfilled [15]
- SCALE project

[16]

Sc, g/L	Ti, g/L	Fe, g/L	V, g/L	Mn, g/L	Al, g/L	Ca, g/L	Mg, g/L	H_2SO_4, g/L
0.02	3.53	30	0.2	2.4	1.33	0.24	0.29	227

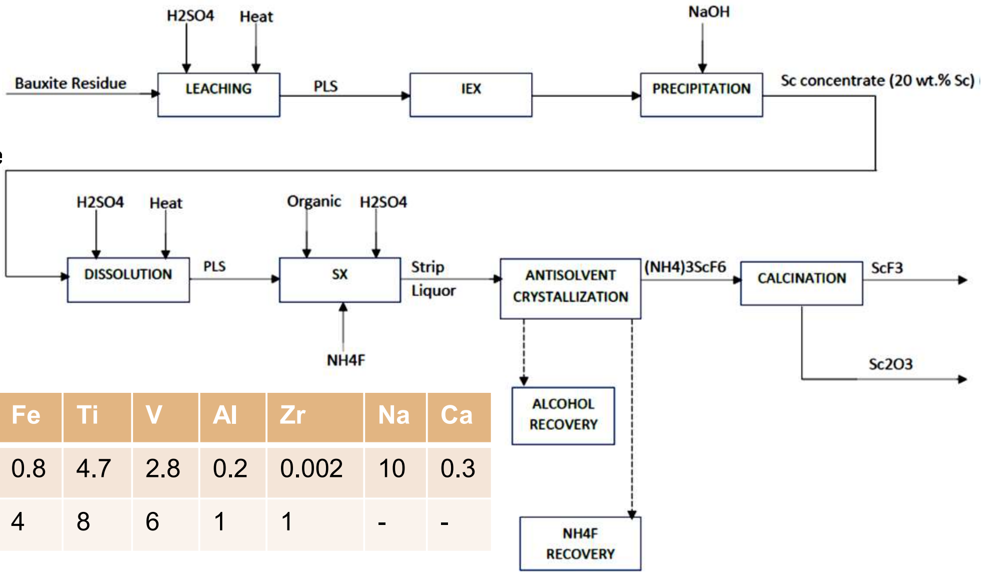
Scale project (Sc-Al Europe: 2017 – 2020)

- Funded by Horizon2020 Research and Innovation Programme
- SCALE developed innovative technologies to economically and sustainably extract Sc from secondary resources
- Validated at appropriate laboratory and industrial environments
- TRL 6
- Developed a flowsheet (Leaching, ion exchange, solvent extraction, crystallization, calcination)

Scale project (Sc-Al Europe: 2017 – 2020)

Flowsheet based on bench-scale testwork

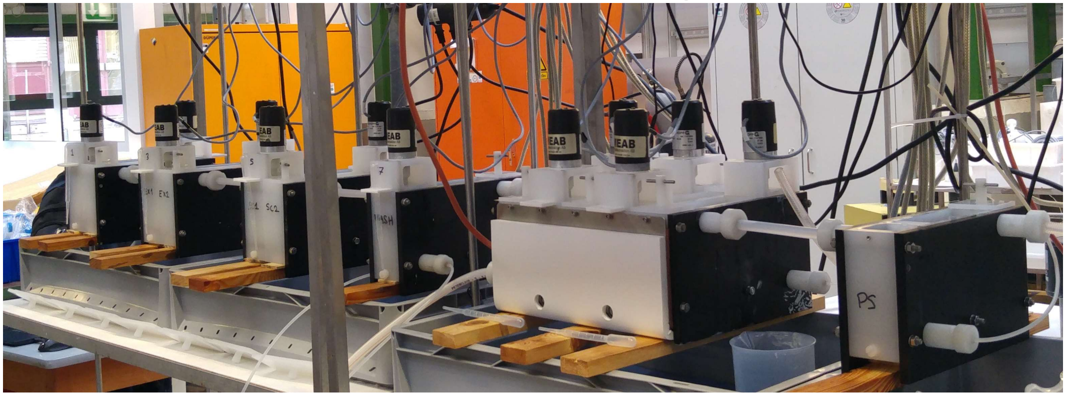
- Strip Liquor: 2.5 g/L Sc
- $(NH_4)_3ScF_6$: >99% pure
- ScF_3: >99% pure



	Sc	Fe	Ti	V	Al	Zr	Na	Ca
Sc concentrate, %	20	0.8	4.7	2.8	0.2	0.002	10	0.3
Strip Liquor, mg/L	2500	4	8	6	1	1	-	-

Scale project (Sc-Al Europe: 2017 – 2020)

Solvent extraction pilot campaign



- Mixer-settler units MSU 0.5 designed by MEAB Metallextraktion AB, Sweden
- Pilot consisted of 12 stages + post settler
- Strip liquors containing ca. 2.5 g/L Sc were obtained

Scaleup project (2022 – 2024)

- Funded by European Institute of Innovation and Technology (EIT) Raw Materials
- Follow-up to the SCALE project
- Demonstrates a commercialization-ready flowsheet for producing Sc-products from Bauxite Residue
- To be validated at TRL 7 – 8
- Engineering scale-up study
- Leads to commercialization and production of Sc-products in Europe (Sc_2O_3, ScF_3, Al-Sc alloy)
- Website (https://scaleup.tesmet.gr/)

Scavanger project (2021 – 2024)

- Funded by European Institute of Innovation and Technology (EIT) Raw Materials
- Follow-up to the SCALE project
- Demonstrates a commercialization-ready flowsheet for producing Sc-products from liquid residues from chloride-based TiO_2 plants
- To be validated at TRL 7 – 8
- Vanadium and niobium by-products
- Engineering scale-up study
- Leads to commercialization and production of Sc-products in Europe (Sc_2O_3, ScF_3, Al-Sc alloy)
- Website (https://www.scavanger.eu/)

Future Outlook

- SCALEUP and SCAVANGER projects are expected to lead to commercialization of Sc extraction technologies from secondary resources in Europe
- Expected to produce 22 t/yr Sc_2O_3, which represents 2/3 of the expected EU consumption in 2028

Co-funded by the European Union

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EHEHP DATABASE TO PREDICT RARE EARTH SOLVENT EXTRACTION

By

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ABSTRACT

We combined a semi-empirical extractant database, a rigorous electrolyte thermodynamic model, and a process simulator to predict solvent extraction of rare earth elements from an HNO_3 solution to a hydrocarbon phase. We then predicted the extractant regeneration and metals separation using a caustic solution.

We created the extractant database using publicly available data for HEHEHP and its reactivity with fifteen rare earth elements. The data included extractant solubility in water, metal extraction isotherms, distribution ratios, dimerization constants, acidity constants and heats of saponification. We created several species for each extractant including the base acid, the ionized acid, and the dimerized acid. We also created several metal-extractant complexes for each of the rare earth elements. In total, over 100 individual species were created for the fifteen rare earth metals with the extractant.

We combined the database with an electrolyte thermodynamic model to compute the liquid-liquid partitioning of the following systems: H_2O-extractant, H_2O-extractant-diluent, and H_2O-HNO_3-$RE(NO_3)_3$ -extractant-diluent. We can match with reasonable accuracy the extractant solubility in water, the heats of saponification, and the partitioning isotherms for all fifteen rare earth elements. We also predicted with limited accuracy, the effects of pH, diluent:extractant ratio, total ion concentration, and temperature on metal partitioning. We present the partitioning isotherms for each element in the individual extractant/diluent mixtures and when both extractants are in a 50:50 mixture.

We then used the speciation model with a process simulator to calculate the mass, chemistry, and energy balance across a series of solvent extraction units. We simulated the process without and with mass transfer limiting parameters. We obtained a reasonable match between predicted and reported extraction efficiencies when we include mass-transfer parameters.

Lastly, we identified areas where we can improve existing chemical properties and partitioning mechanisms and where additional experimental data is needed to make a model more robust.

Keywords: Rare Earth, Solvent Extraction, process simulation

INTRODUCTION

Solvent extraction is an industry-accepted method for separating rare earth elements from pregnant liquor. A commonly-used extractant is HEHEHP, which is identified in the literature by its product identification P-507 or PC88A (HEHEHP) or by its trade name. like Ionquest 801 (Italmach Chemicals AWS©). There are research papers available that report the performance of this chemical for extracting dissolved rare earth metals from nitric and hydrochloric acid solutions. Our goal was to process the extraction data from these papers and create a speciation-based predictive model with the fifteen rare earth elements in HNO_3. The outcome is the ability to model solvent extraction using engineering software to design and optimize solvent extraction operations.

This paper reports on the quantitative study performed in this area. Literature data and plots were used to back calculate the following:

- The extraction isotherms as extractant concentration varies,
- The extraction efficiency as pH varies,
- The coordination chemistry of rare earths with the extractant and NO_3^{-1} and as pH and concentration change,
- The solubility and partitioning of extractants with water and hydrocarbon, and
- The enthalpies for each of the reactions.

Our study focuses on the chemistry of extraction and not the engineering. In this way, the predictions can be used across multiple engineering platforms. Although there are many papers written on extractants, we had limited success finding thermodynamic data (G, H, S, Cp, V). We therefore estimated these values by curve fitting available plots reported or other disparate data points. Consequently, the current predictions are estimations that can be improved once additional scientific data becomes available.

LITERATURE DATA

We searched for literature data containing information on some or all of the following components: HEHEHP, rare earth elements, HNO_3, and hydrocarbon (decane, kerosene, toluene, etc.). We found information on chemical speciation, distribution ratios, separation factors, pKa's plus other equilibrium constants, and partitioning isotherms. Zhang for example studied yttrium extraction using HEHEHP and Cyanex 272 from chloride solutions. They reported HEHEHP separation factors, [i][1]$\bar{\beta}_{(z+1/_{z}\}} = 3.04$ and 1.60 with extraction equilibrium equation as follows,

$$Y^{+3} + 2(H_2A_2)_{(o)} + Cl^- = YCl(HA_2)_{2\,(o)} + 2H^+ \quad (1)$$

A is the HEHEHP molecule and *H_2A_2* is its dimerized form in the immiscible phase. The author also provided plots which were used to curve fit the thermodynamic partitioning coefficients. Qi provides several important plots and a table containing equilibrium constants, distribution ratios, separation factors of adjacent rare earth elements and changes in G, H, and S following extraction. Although these data cannot be used directly (they are measurements) they can be used to confirm the properties created for each of the reacting and product species entered in the database. Qi also identified the following reaction as the main solvation extraction reaction. [ii]

$$Y^{+3} + n(HA)_{2\,(o)} + 3NO_3^- = Y(NO_3)_3 * 2nHA_{(o)} + 2H^+ \quad (1)$$

The coefficient *n* is the solvation number of HA for the reaction. Many of the plots and data provided in the Qi text are presented in journal articles by this author and others. So, this book is a good compilation for the data we needed to complete the effort.

Zhao et al provided useful plots on La and Ce extraction with HEHEHP as a function of extractant concentration and pH. These plots are used in the current work. Mohammadi et al., studied ND, Dy, and Y separation from HCl solutions using HEHEHP and D2EHP. They reported equilibrium constants, chemical reactions, distribution ratios, separation factors, and isotherm plots. This was a key reference paper for developing our predictions.[iii][iv]

APPROACH

We used OLI software (OLI Systems, Inc)[2] to complete this work. We created a custom database containing three sets of species. The first set is for HEHEHP speciation with water and NaOH. This includes acid ionization, dimerization, and partitioning to the immiscible phase.

$$HEHEHP^0 = EHEHP^{-1}$$
$$2HEHEHP^0 = (H_{0.5}EHEHP)_2^{-1} + H^+$$
$$2HEHEHP^0 = (HEHEHP)_2^0$$
$$HEHEHP_{(a)}^0 \leftrightarrow HEHEHP_{(o)}^0$$
$$(HEHEHP)_{2,(a)}^0 = (HEHEHP)_{2(o)}^0$$
$$NaEHEHP_{(o)}^0 + H_{(a)}^{+1} = HEHEHP_{(o)}^0 + Na_{(a)}^{+1}$$

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[1] Rhodia Technical bulletin.

[2] OLI Software tools used include OLI StreamAnalyzer, OLI Databook, and OLI Flowsheet+Optimizer.

The second set included reaction products formed between the REY[3] and HNO3[4]

$$RE^{+3} + NO_3{}^{-1} = RENO_3{}^{+2}$$

The final set of species were the reactions products between REY and the extractants.

$$RE^{+3} + 4HA^0 = RE(A)^{-1}_{(a)} + 4\mathrm{H}^+$$
$$RE^{+3} + 3A^{-1} = RE(A)^0_{3\,(o)}$$
$$RE^{+3} + 6HA^0 = RE[(H_{0.5}A)_2]^0_{3,(o)}$$
$$RE^{+3} + 3NO_3{}^{-1} + 2HA^0 = RE(NO_3)_3(HA)^0_{2\,(o)}$$
$$RE^{+3} + NO_3{}^{-1} + 4HA^0 = RE(NO_3)[(H_{0.5}A)_2]^0_{(o)}$$

There is limited x-y (tabular) data provided in the literature. There are however several plots containing isotherms, distribution ratios, and separation factors. We then fit our predictions to this and other data.

CURVE FITTING RESULTS

HEHEHP + HNO3

Figure 1 is a comparison plot for the fifteen rare earth elements. The thick black lines and circles are results reported by Qi (2018). The thin, colored lines are the current predictions. The conditions are 0.03 m RE and 1 m HEHEHP. Starting HNO_3 concentrations range from 0.9 to 1.5 m and NaOH is added to adjust pH. To go to lower pH's (higher lg[H+] values), HNO_3 is added beyond the starting amounts.

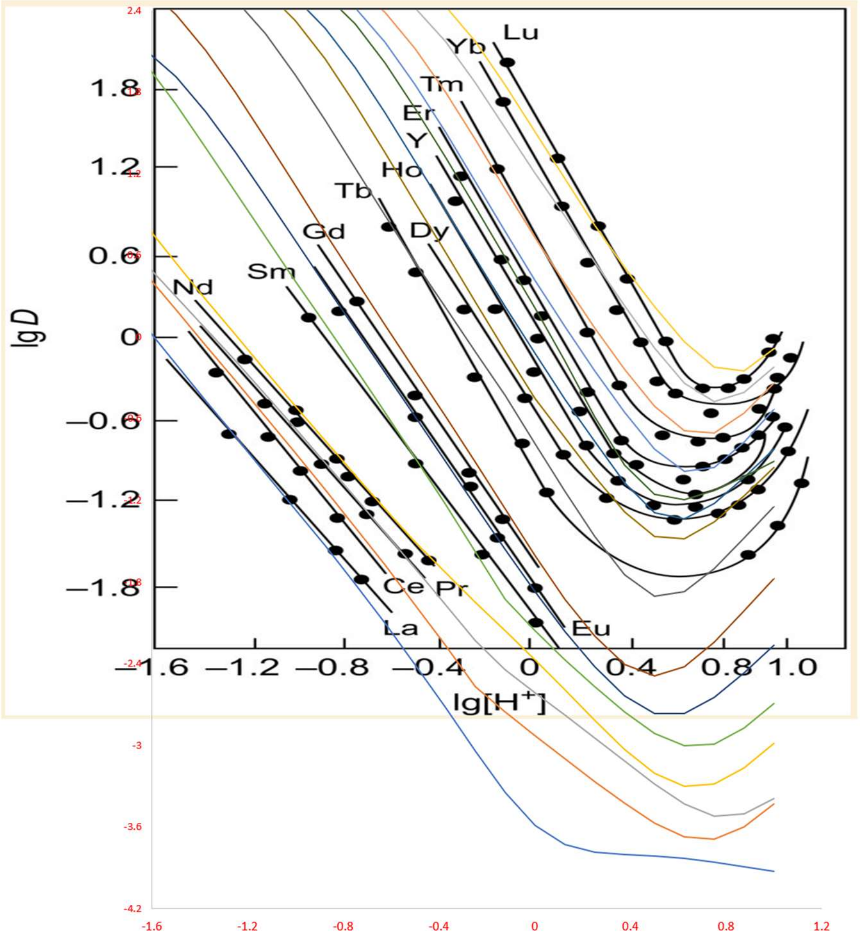

Figure 1 - Comparison between predictions and measured distribution ratios. Plot extracted from Dezhi Qi. 2018.

The predictions show good fit with the slope of each element and the impact of HNO_3 (pH) on the partitioning matches where the curve increases. The effects of $NO_3{}^{-1}$ on Ho partitioning are shown in Figure Figure 2. At high pH, the dominant complex is $Ho[H(EHEHP)_2]_3$. At high HNO_3 concentrations, lower pH, the two NO_3-containing complexes become important and cause the distribution ratio to increase.

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[3] REY=rare earth elements and yttrium

[4] Pm is not included.

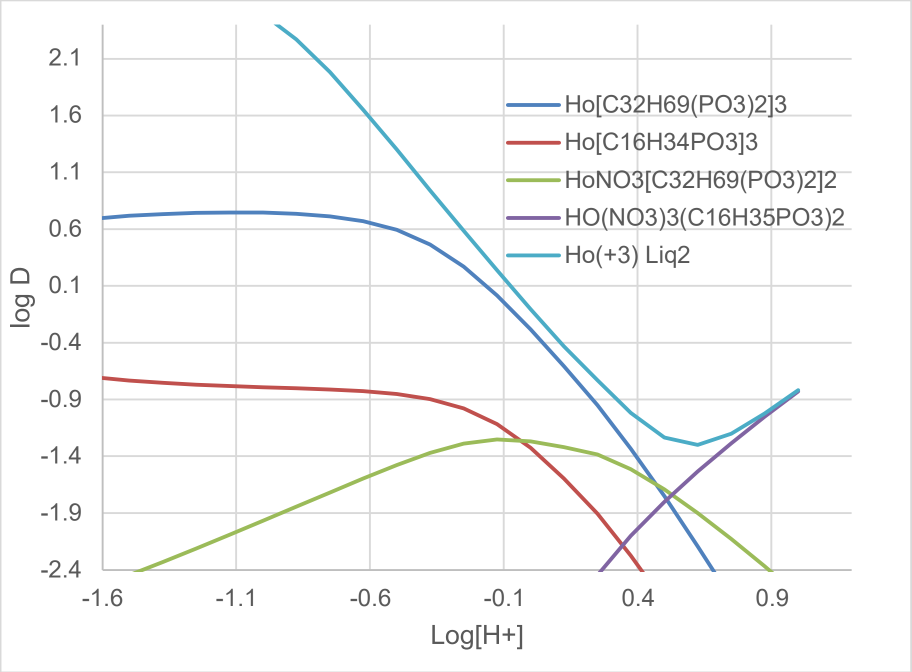


Figure 2 - Contribution of four Re-NO3-HEHEHP complexes to the overall Ho distribution ratio

By comparison, Nd speciation (Figure 3) required that dominant complex be $Nd(NO_3)(HA_2)_2$ in order to match the isotherm plot in Figure 1 but to still show similar curvature as the other elements. This included the slope of the isotherm. Similar speciation was used to match the curves for La, Ce, and Pr. We still are unsure what contribution the $Re[HEHEHP]_3$ complex has. This complex is reported in the literature, but it does not seem to be needed. Also, since the HEHEHP dimerizes in the non-aqueous phase, this complex is not important to modelling RE partitioning.

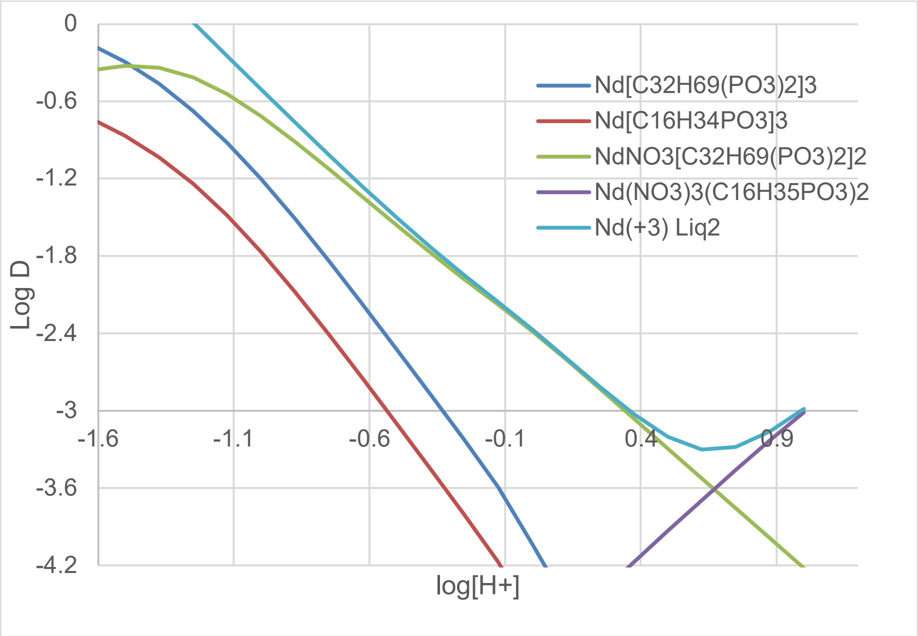


Figure 3 - Contribution of four RE-NO3-HEHEHP complexes to the overall Nd distribution ratio

Figure 4 is a comparison plot between the predicted Log D values and those reported by Qi (2018). We could not find the precise composition for this published plot and therefore used 0.005 m RE, 0.15 M HEHEHP, 0.132 m HNO_3 (pH=1) and 1L n-C13. There is good qualitative fit for most, but not for the four LREE and for Y. We think that this can be improved by modifying the $RE(NO_3)(H[EHHP]_2)_2$ and $RE(NO_3)_3(H[EHHP]_2)$ stability constants but would need more precise data to support this.

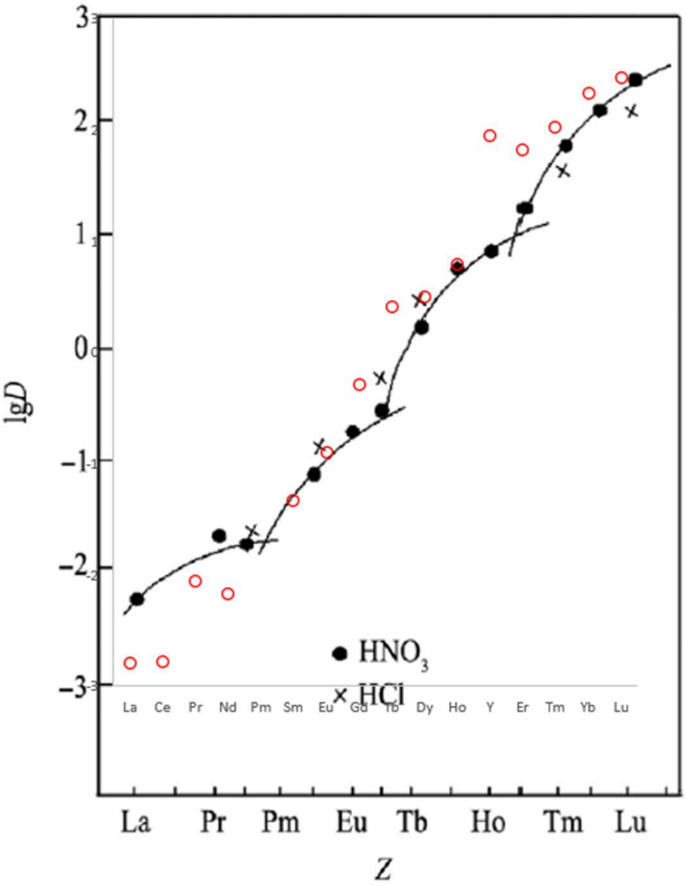


Figure 4 - Distribution ratio comparison for each RE. The open red circles are the predictions. The black lines, closed circles, and x's are the reported values.

Figure 5 is a plot of the partitioning isotherms for the fifteen REY as a function HEHEHP addition. Conditions were 0.01 mole of each rare earth element, 0.132 m HNO3, 1 L of tridecane, and 0 to 0.6 moles HEHEHP. Also plotted are Nd, Dy, and Y isotherm data reported by Mohammadi et al for same set of experiments but when using HCl[v]. The plot shows the similar groupings of elements shown in Figure 4 and as reported in the literature. The lowest grouping La, Ce, Pr, and Nd have weaker isotherms than reported for Nd with HCl, and although this is a different complex with different stabilities, the weaker isotherms are consistent with the lower than reported LogD shown in Figure 4. This is the result the slope and curve match work shown in Figure 1. The isotherms for Dy and Y are similar to Mohammadi et al, and this is also consistent with Figure 2 where we calculated that the dominant complex is the $RE(HA_2)_3$, a complex that is independent of the electrolyte used.

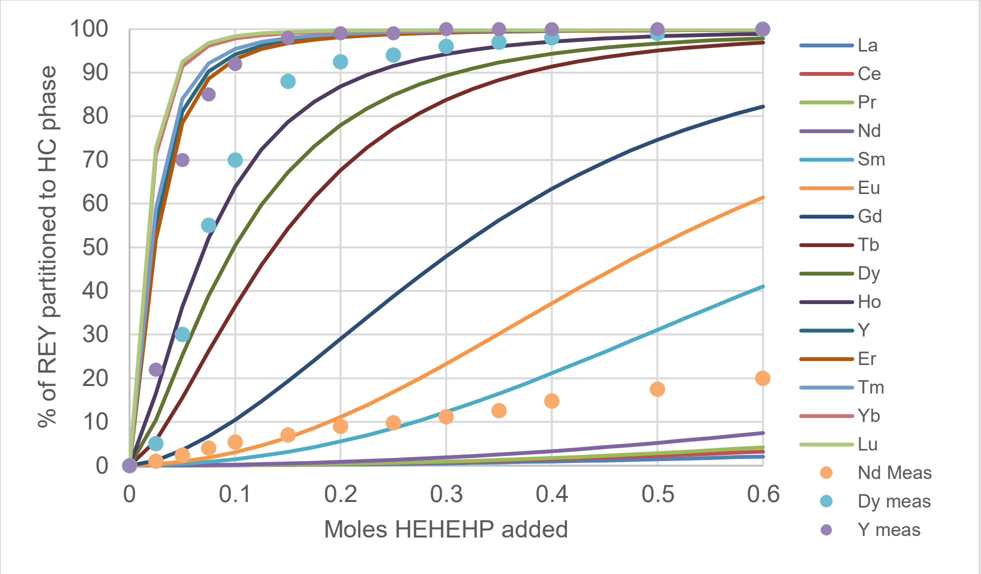
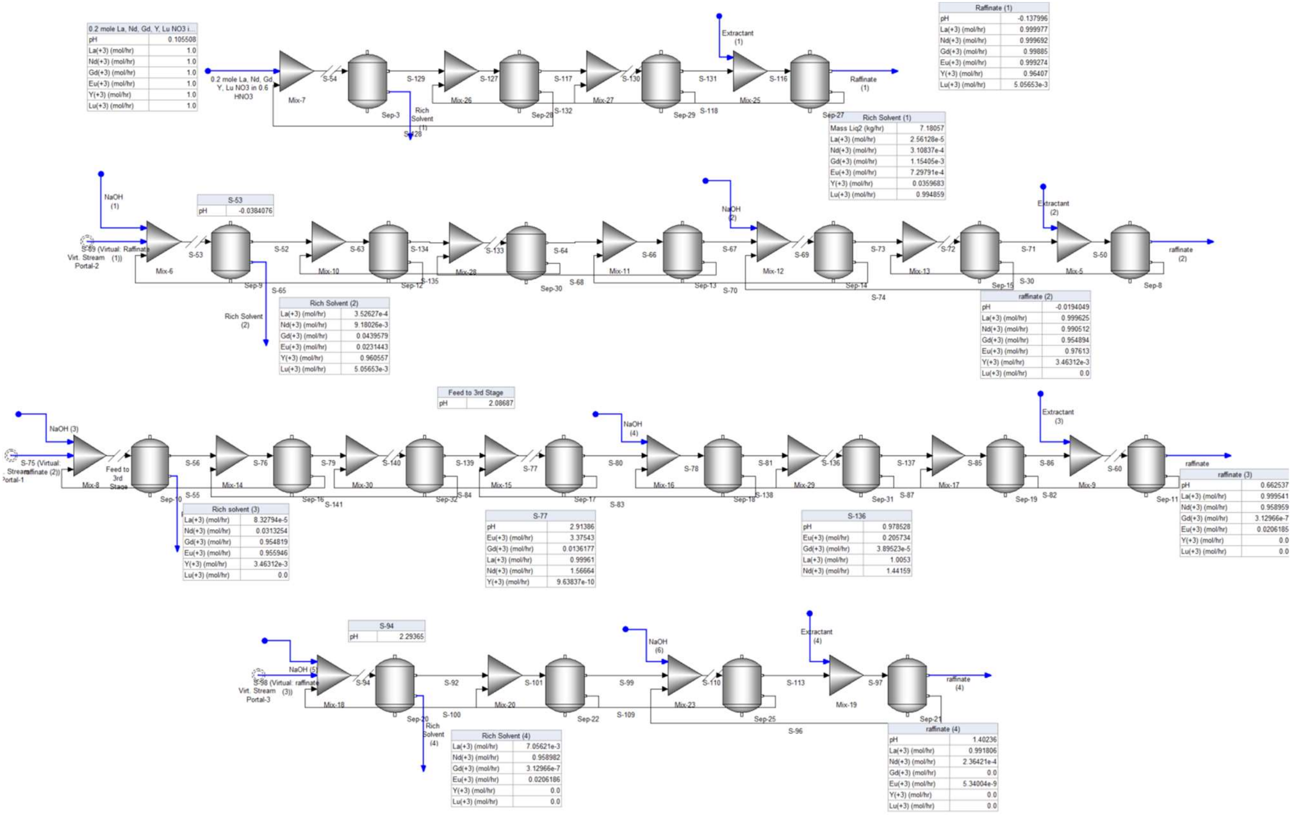


Figure 5 – Plot of the calculated isotherms for the fifteen rare earth metals.

APPLYING THE PREDICTIONS

Figure 6 is an image of a simulated solvent extraction process that separate Lu, Y, Gd, Eu, Nd, and La. It contains twenty-three separation stages divided into four sections. The first four stages (section #1) remove Lu, the next seven stages (section #2) remove Y, the next eight stages (section #3) remove Gd and Eu, and the final four stages (section #4) separates Nd from La. Each stage is modelled isothermally at 20 C. Phase separation (electrolyte from solvent) is complete – we did not simulate entrainment/inefficient separation effects. The loaded electrolyte stream flows through all twenty-three units. Fresh extractant is added in each separation section.



0.2 mole La, Nd, Gd, Y, Lu NO3 i...	
pH	0.105508
La(+3) (mol/hr)	1.0
Nd(+3) (mol/hr)	1.0
Gd(+3) (mol/hr)	1.0
Eu(+3) (mol/hr)	1.0
Y(+3) (mol/hr)	1.0
Lu(+3) (mol/hr)	1.0

Raffinate (1)	
pH	-0.137996
La(+3) (mol/hr)	0.999977
Nd(+3) (mol/hr)	0.999692
Gd(+3) (mol/hr)	0.99885
Eu(+3) (mol/hr)	0.999274
Y(+3) (mol/hr)	0.96407
Lu(+3) (mol/hr)	5.05653e-3

Rich Solvent (1)	
Mass Liq2 (kg/hr)	7.18057
La(+3) (mol/hr)	2.56128e-5
Nd(+3) (mol/hr)	3.10837e-4
Gd(+3) (mol/hr)	1.15405e-3
Eu(+3) (mol/hr)	7.29791e-4
Y(+3) (mol/hr)	0.0359683
Lu(+3) (mol/hr)	0.994859

S-53	
pH	-0.0384076

Rich Solvent (2)	
La(+3) (mol/hr)	3.52627e-4
Nd(+3) (mol/hr)	9.18026e-3
Gd(+3) (mol/hr)	0.0439579
Eu(+3) (mol/hr)	0.0231443
Y(+3) (mol/hr)	0.960557
Lu(+3) (mol/hr)	5.05653e-3

raffinate (2)	
pH	-0.0194049
La(+3) (mol/hr)	0.999625
Nd(+3) (mol/hr)	0.990512
Gd(+3) (mol/hr)	0.954894
Eu(+3) (mol/hr)	0.97613
Y(+3) (mol/hr)	3.46312e-3
Lu(+3) (mol/hr)	0.0

Feed to 3rd Stage	
pH	2.08687

Rich solvent (3)	
La(+3) (mol/hr)	8.32794e-5
Nd(+3) (mol/hr)	0.0313254
Gd(+3) (mol/hr)	0.954819
Eu(+3) (mol/hr)	0.955946
Y(+3) (mol/hr)	3.46312e-3
Lu(+3) (mol/hr)	0.0

S-77	
pH	2.91386
Eu(+3) (mol/hr)	3.37543
Gd(+3) (mol/hr)	0.0136177
La(+3) (mol/hr)	0.99961
Nd(+3) (mol/hr)	1.56664
Y(+3) (mol/hr)	9.63837e-10

S-136	
pH	0.978528
Eu(+3) (mol/hr)	0.205734
Gd(+3) (mol/hr)	3.89523e-5
La(+3) (mol/hr)	1.0053
Nd(+3) (mol/hr)	1.44159

raffinate (3)	
pH	0.662537
La(+3) (mol/hr)	0.999541
Nd(+3) (mol/hr)	0.958959
Gd(+3) (mol/hr)	3.12966e-7
Eu(+3) (mol/hr)	0.0206185
Y(+3) (mol/hr)	0.0
Lu(+3) (mol/hr)	0.0

S-94	
pH	2.29365

Rich Solvent (4)	
La(+3) (mol/hr)	7.05621e-3
Nd(+3) (mol/hr)	0.958982
Gd(+3) (mol/hr)	3.12966e-7
Eu(+3) (mol/hr)	0.0206186
Y(+3) (mol/hr)	0.0
Lu(+3) (mol/hr)	0.0

raffinate (4)	
pH	1.40236
La(+3) (mol/hr)	0.991806
Nd(+3) (mol/hr)	2.36421e-4
Gd(+3) (mol/hr)	0.0
Eu(+3) (mol/hr)	5.34004e-9
Y(+3) (mol/hr)	0.0
Lu(+3) (mol/hr)	0.0

Figure 6 – Simulating four-step extraction of six rare-earth elements

The loaded electrolyte flows into the process at 8 kg/hr (6.2 L/hr). It contains 1 mole each of $Lu(NO_3)_3$, $Y(NO_3)_3$, $Gd(NO_3)_3$, $Eu(NO_3)_3$, $Nd(NO_3)_3$, and La $(NO_3)_3$, 4 moles of HNO_3, and 320 moles (5765.8 g) of H_2O. The electrolyte pH is 0.1 and the feed temperature is 20 C. The extractant (HEHEHP+diluent) composition is 19.6 mol% HEHEHP, 21.6 mol% n-C_{10}, 39.2 mol% n-C_{13}, and 19.6 mol% n-C_{16}. The extractant flows into the process at four locations, one for each separation section. It flows at 7, 21, 6.4, and 4 kg/hr for Sections 1, 2, 3, and 4, respectively. That is 39.4 kg/hr solvent for 8 kg/hr electrolyte or 36.3 moles of HEHEHP per 6 moles of rare earths (6:1 mole ratio).

The caustic stream is 10 m NaOH and enters at six locations, none in section #1, twice in section #2, twice in section #3 and twice in section #4. A total of 1.83 kg/hr (45.75 mole) NaOH is added. We fixed the caustic feed in sections #2 and #4 to reach an average pH of ~0 and ~1.7, respectively. We used an equation-based tool to find the optimal extraction pH in section #3. The optimization objective was defined to maximize Gd and Eu removal while minimizing Nd loss. The optimal pH in Section #3 was between 0.9 and 1.5, depending on the stage.

We then performed a caustic feed sensitivity study in section #3 to test the pH effects on Gd, Eu, and Nd removal efficiency. Lastly, we varied section #3 stages between 5 and 15 while optimizing caustic addition to separate Gd from Eu.

Results

Table 1 contains the simulation results for the rich solvent stream exiting the process after optimizing the caustic feed to section #3. Each column represents the rare earth metal recovery after each section. The first column shows that 99.5% of Lu that enters the process is recovered in this section #1. Also, 3.6% of the Y and 0.12% of Gd is removed. Section #2 removes 96.1% of the added Y into the rich solvent. This solvent is also computed to extract 4.4% of Gd and 2.3% of Eu. It is very likely that with additional separation stages (eight are used in this section) a purer Y-rich solvent would be computed.

Table 1 - Element recovery in the rich solvent following each separation section.

Element	Section #1	Section #2	Section #3	Section #4
La(+3)	0.00%	0.04%	0.01%	0.71%
Nd(+3)	0.03%	0.92%	3.13%	95.90%
Eu(+3)	0.07%	2.31%	95.59%	2.06%
Gd(+3)	0.12%	4.40%	95.48%	0.00%
Y(+3)	3.60%	96.06%	0.35%	0.00%
Lu(+3)	99.49%	0.51%	0.00%	0.00%

Figure 7 is a plot showing the effects of section #3 raffinate pH on the Gd and Eu extraction efficiency. The section #3 raffinate pH is on the lower end of the pH value across the eight stages. Above 1.2 pH, about 90+% of Gd is recovered. Above 1.7 pH, both Gd and Eu are recovered at 95+%. Also, above 1.7 pH, Nd extraction starts to increase, which limits the optimal separation range.

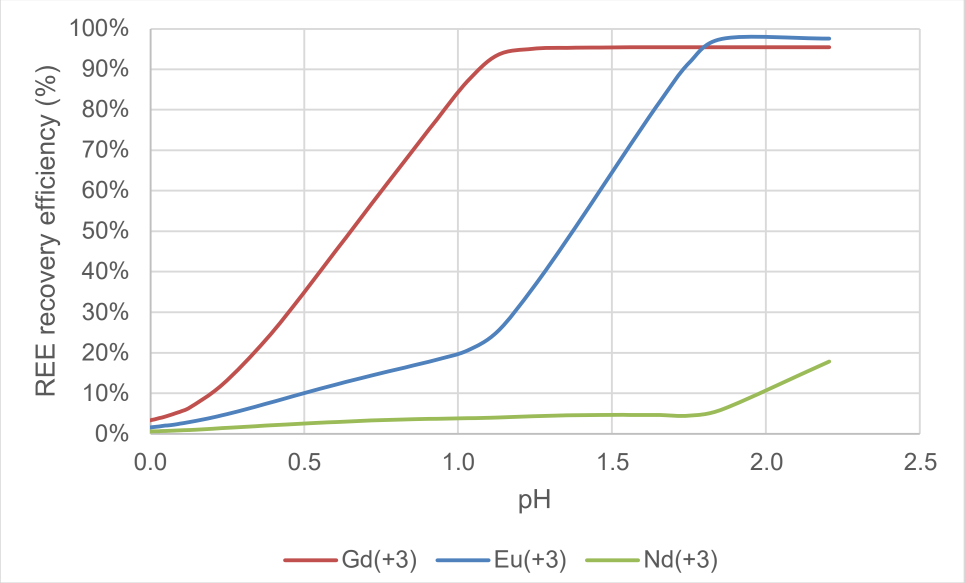


Figure 7 - Optimizing Gd/Eu separation from Nd using pH control.

Figure 8 is a plot of the Eu-Gd separation efficiency as the number of stages in Section #3 varies from 5 to 15. The caustic and extractant flow rates were optimized in a similar way described above, except that Gd is maximized in the loaded solvent and Eu is maximized in the raffinate. There is a sufficient gap between the Gd and Eu isotherms in Figure 7 that would indicate by adding more stages we can separate them. By optimizing the caustic and extractant flow rates and by increasing the number of separation stages, we were able to achieve a 4.5:1 ratio of Gd:Eu in the rich solvent. This effect is already known to the industry, and so the predictions are not new. Rather, we wanted to confirm that the speciation model could predict these observations. These results also indicate a diminishing separation performance with more stages.

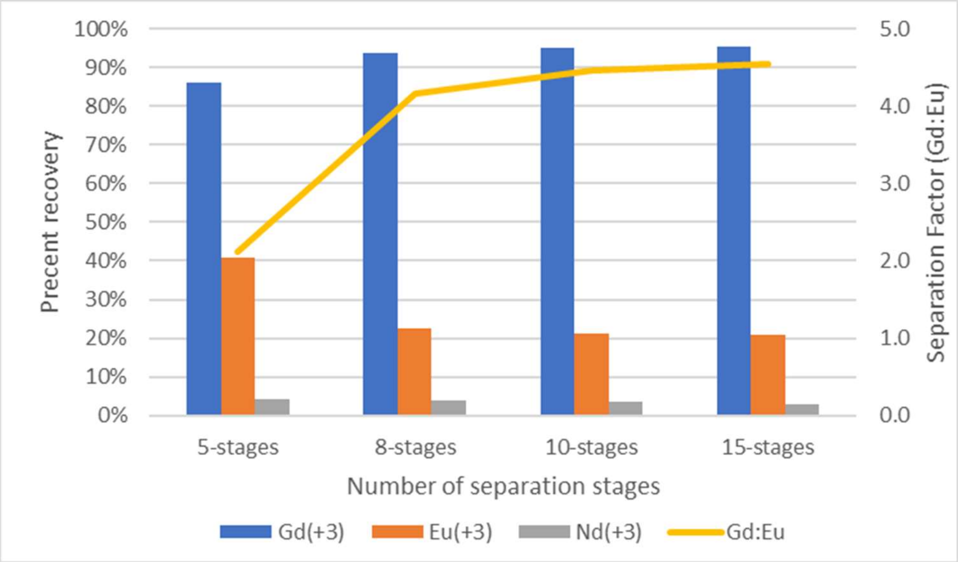


Figure 8 - Separation of Gd, Eu, and Nd as the number of separation stages vary.

SUMMARY/CONCLUSIONS

We developed a thermodynamic database of HEHEHP and its speciation with fifteen rare earth elements. We used available literature data to derive the various complexes and their partitioning between the aqueous and organic phases. We attempted to match literature data using as few interactions and species as possible. We needed a minimum of four HEHEHP-RE complexes to match the isotherms for all fifteen elements and to match the curvature shown in Figure 1. The mole ratio of HEHEHP:RE:NO3 in these complexes were 6:0:1, 3:0:1, 4:1:1 and 2:3:1. At least two are consistent with reported stoichiometries and two are inconsistent or mentioned as possible complexes.

When we used this database in a hypothetical separation process that used twenty-three separation stages. The results matched qualitatively and perhaps quantitatively the partitioning reported in the literature and the pH impact on separation. In all, the simulation achieved its intended purpose of testing the HEHEHP speciation database in a process simulation that is separating multiple elements.

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CHROMATOGRAPHIC SEPARATION OF RARE EARTH ELEMENTS AS ANIONIC COMPLEXES BY ION EXCHANGE

By

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ABSTRACT

Separation and purification of rare earth elements (REE) is known to be a troublesome issue. Reaching significant (> 99%) purities requires multiple steps. Mass production of purified REEs is often done by solvent extraction (SX) methods. Large number of consecutive steps in solvent extraction mean large quantities of SX chemicals and it also requires large number of mixer-settler units. Ion exchange (IX) methods are alternative option for REE production. Most research on IX methods in REE separation relies on HPLC technology. High pressure makes the scalability of the production expensive. REE separation by IX could be profitable if the separation could be done in a low-pressure system and with simple chemistry. IX as separation method allows collection of multiple different product fractions after the separation process by combining individual fractions after single step. With SX the collection of multiple (> 2) different products from single unit operation is not possible.

Phosphogypsum, waste material of phosphoric acid production, is known to contain trace amount of REEs. These precious metals can be extracted from this high calcium containing matrix by IX. Recovery of REE from the loaded resin can be done by alkaline complexing agents. Rare earth mixture (c(REE) ≈ 3 g/L) with high purity (98%) can be obtained as product. REEs are in form of metal-chelate complex in this alkaline mixture. Major REEs present in the mixture are La (15.2%), Ce (45.0%), Pr (5.9%) and Nd (23.5%). Ce can be removed from the solution by oxidating Ce(III) to Ce(IV) and adjusting pH to the suitable level. All the other REEs are present but in low concentrations compared to the others.

In this study, chromatographic REE separation is done by utilizing net negative charge of these REE-ligand complexes. Stationary phase in the separation process is a strong base anion (SBA) resin. REE-ligand complexation is known to enhance the affinity differences of individual elements in the REE series. Typically, with SBA resin in REE separation the mobile phase contains excess amount of free complexing agent or ligand. In these processes the elution order of REEs is often shown to be from Lu to La. This kind of approach requires usually large amounts of mobile phase since the REE-ligand complex affinities to stationary phase are strong. Strongest complex is first to exit the column carried by mobile phase. REE-ligand complexes remain negative throughout the whole process. In our research, the REE-ligand complex is fed to the column system as complexes and dilute HCl is used as mobile phase. Separation is still based on the differences on the complex strength but HCl as the mobile phase protonates weakest complexes first and thus elution order is reversed from La to Lu. This approach decreases the amount of eluent spent in the separation process.

Optimal conditions for REE separation were studied by using a synthetic REE mixture as the feed solution because the composition and properties could be varied systematically. The feed volume, flow rate, temperature, feed pH, mobile phase concentration (pH), and the selection of the acid and the resin were investigated to find most suitable conditions for the separation. With suitable feed composition and pH control the interactions of REE-ligand with SBA resin can be adjusted.

It was shown with an authentic feed mixture (from leaching of phosphogypsum) that the purity of individual REEs can be enhanced by means of IX process with dilute HCl as eluent. Product fractions of desired metal(s) ((Pr+)Nd) can be collected with enhanced purity and reprocessed to create new feed. In sequential separation cycles the purities can be furthermore enhanced. First cycle improved Nd purity from 46.5% to 75.5% (Yield 52.3%) and second cycle furthermore improved purity from 75.5% to 81.2% (Yield 86.9%). For Pr+Nd product fraction the purity is 95.5% after second cycle.

Keywords: rare earth element, ion exchange, MGDA, complex, separation

Background / Phosphogypsum

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
mg/kg (ppm)	31.8	260.2	735.4	102.2	422.6	64.0	15.8	37.0	3.4	13.4

- Rare earth content 1.7 grams per kilogram of phosphogypsum (Siilinjärvi, Finland)
- La-Nd being most important REEs

Phosphogypsum pile at fertilizer plant in Siilinjärvi, Finland. Source: YLE

- Globally available in large amounts (global production 100-280 Mt per year), metal content varies depending on the source. Apatite naturally contains rare earths
  - Most light rare earths are sorbed to the gypsum waste
  - Majority of heavy rare earths end up in the phosphoric acid

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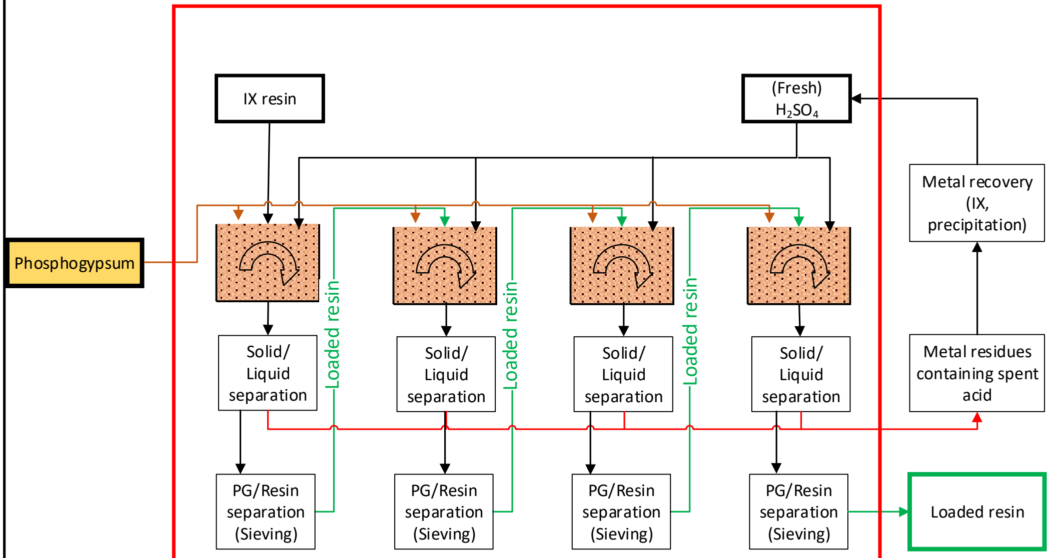
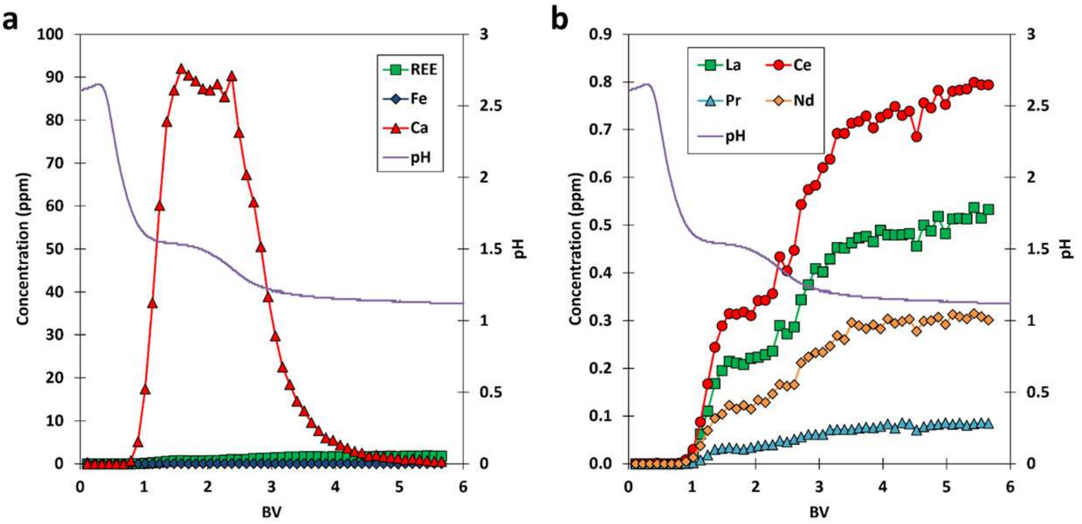
Resin-in-Leach (RIL)

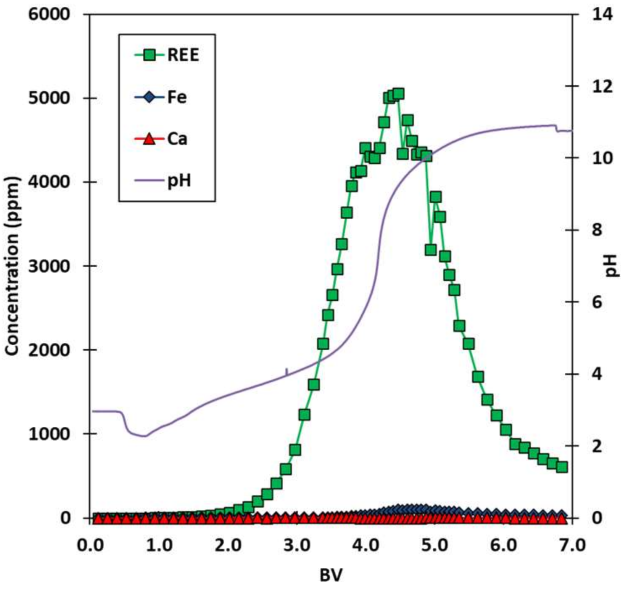


Ca	Fe	La	Ce	Pr	Nd
4.12	20.54	11.34	34.22	4.47	17.33

- REEs are extracted from phosphogypsum with multiple consecutive RIL steps.
- Resin remains the same. Loading increases every step.
- Fresh slurry (PG/acid mixture) is created for every cycle.

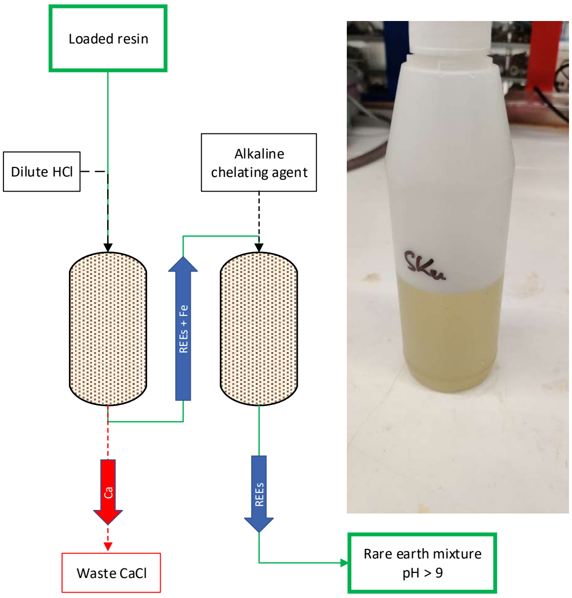


- Ca is washed from loaded resin with dilute HCl.
  - Fe is not affected by the dilute HCl
  - Minor REE leakage is observed which is insignificant.



- In the beginning of the graph, the heavier REEs (HREE) are more concentrated than La-Nd.
- It can be used to collect HREE fraction
  - Low concentration of 0.22 g/L
  - Sm-Lu 36.7% out of all REE
  - As comparison Sm-Lu make 6.9% of REEs in main fraction (3.1-6.0 BV).
- Fe is not effectively recovered from the resin with alkaline MGDA
  - Alkalinity causes $Fe(OH)_3$ precipitation on the resin surface → Regeneration issues

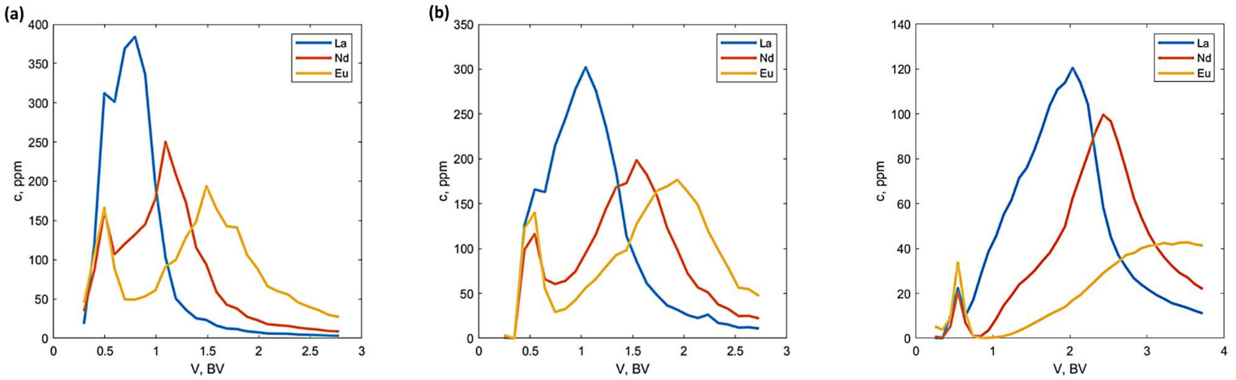
REE recovery



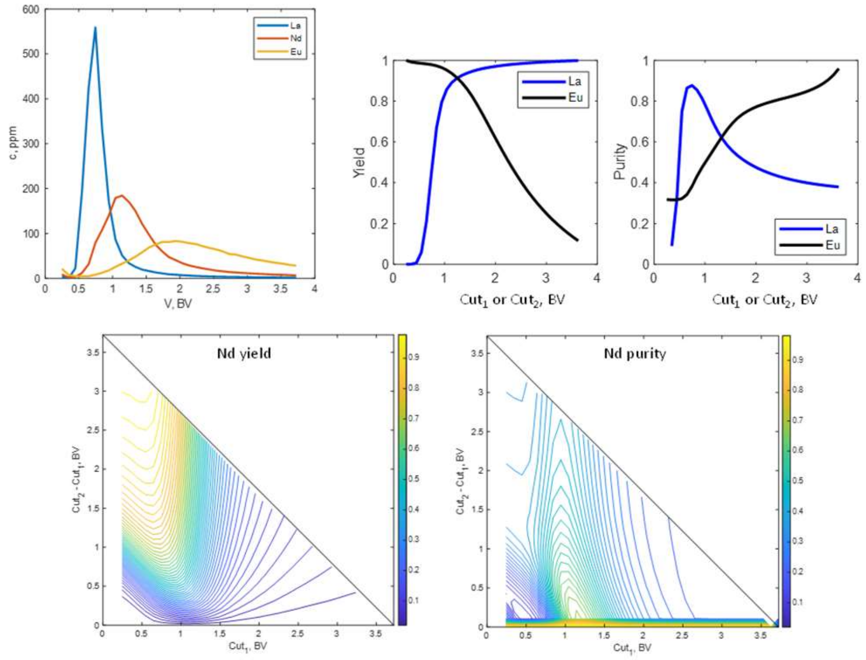
- Alkaline MGDA is used to recover REEs
- 3.2 g/L (REE) with purity of 98.27%

Element	(BV = 3.1–6.0); %	Element	(BV = 3.1–6.0); %
Ca	0.09	**Eu**	0.80
Sc	0.01	**Gd**	1.83
Fe	1.65	**Tb**	0.15
Sr	0.00	**Dy**	0.57
Y	1.79	**Ho**	0.07
La	15.19	**Er**	0.12
Ce	45.02	**Tm**	> 0.01
Pr	5.93	**Yb**	0.04
Nd	23.46	**Lu**	> 0.01
Sm	3.28		

- Chromatographic separation process was investigated first with synthetic MGDA-REE mixture.
    - Three REEs were selected: La, Nd, Eu
- Aim was to find suitable resin, mobile phase etc. other optimal conditions for separation.
- IRA-410 was chosen as separation material
    - Other resins were investigated but IRA-410 (type II SBA with 6% DVB)
- Dilute HCl is used as mobile phase
- Separation relies on stability differences between MGDA-REE complexes.
    - Dilute acid weakens (protonates) the weakest REE-MGDA complex first.
        - Order of elution is thus La, Nd, Eu.
    - Findings from the synthetic research were used with authentic material.

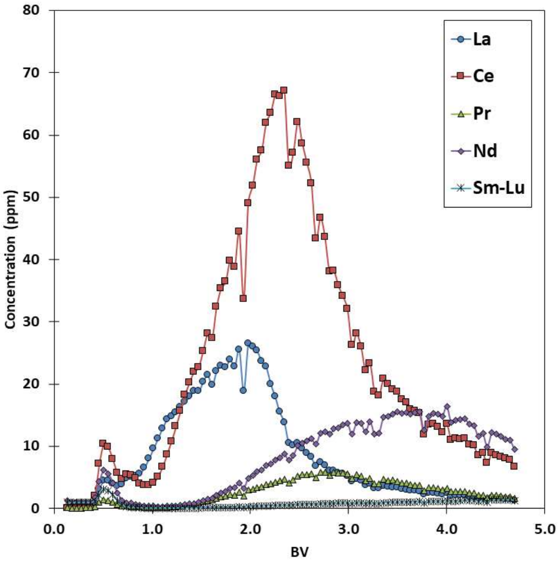


- Few examples with the synthetic feed

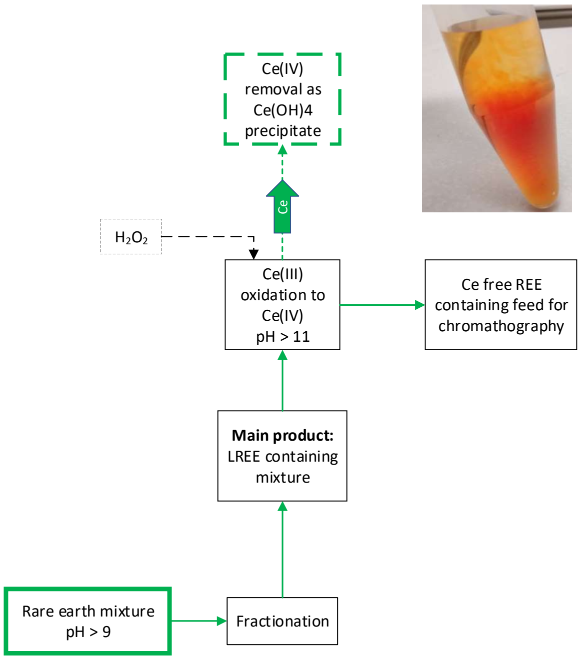


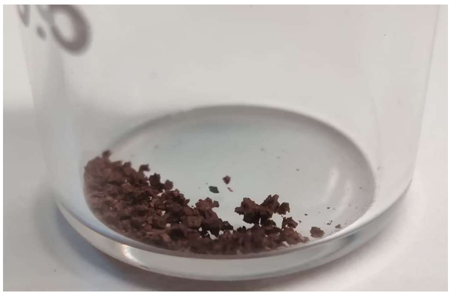
- With suitable conditions, the significant difference between REE-MGDA complexes can be achieved.
- From good separation, product fractions can be collected.

Chromatographic separation – Real feed

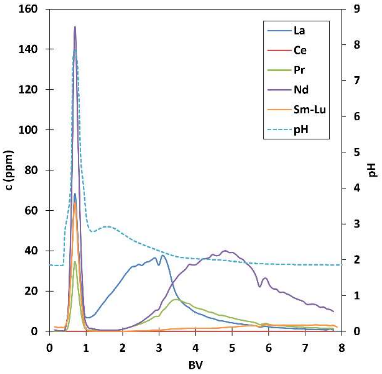


- One of the first experiments with authentic REE-MGDA product
- Systems follows same principles that were discovered with synthetic feed.
  - Trace impurities (mainly Ca and Fe) do not affect the separation.
- Ce excess affects the separation
- Without Ce the separation could be decent
- → Ce needs to be removed from the feed solution

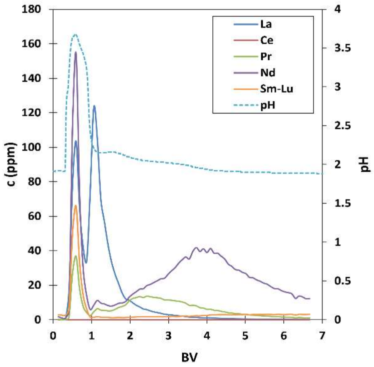




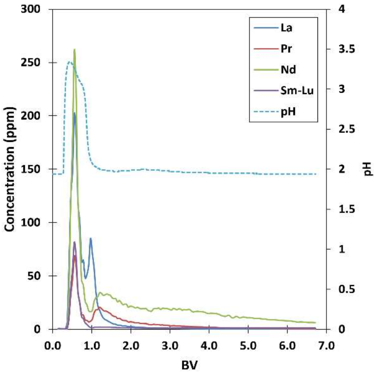
- Ce content 85,68%
- Other metals:
  - La: 8,53%
  - Fe: 2,66%
  - Pr: 0,91%
  - Nd: 1,37%
- Fe+Ce+La+Pr+Nd: 99,14%
- Better purities for Ce fraction are achieved ~93%



pH ~ 9



pH ~ 6

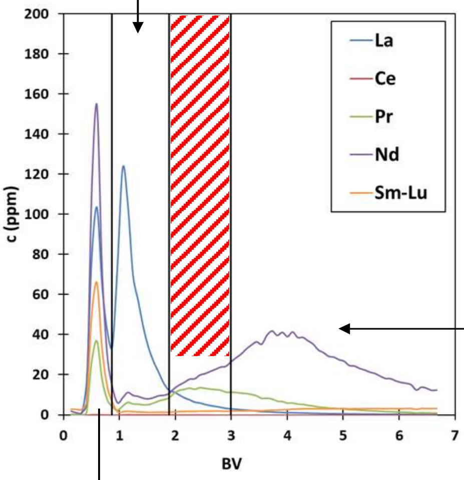


pH ~ 3

- Equal feed size
- Equal flow rate
- Same mobile phase
- Different feed pH

Chromatograms

La fraction; *Pu%*: 74.39% *Y%*: 54.01%

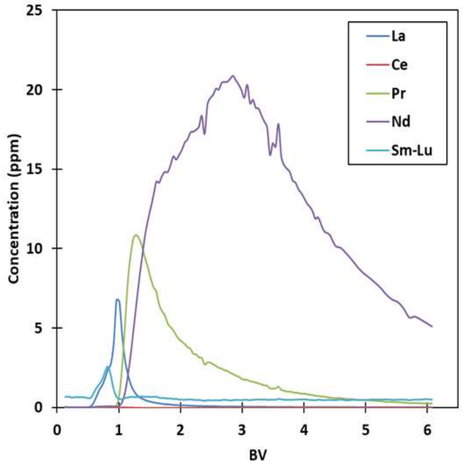


“Front peak” can be recycled

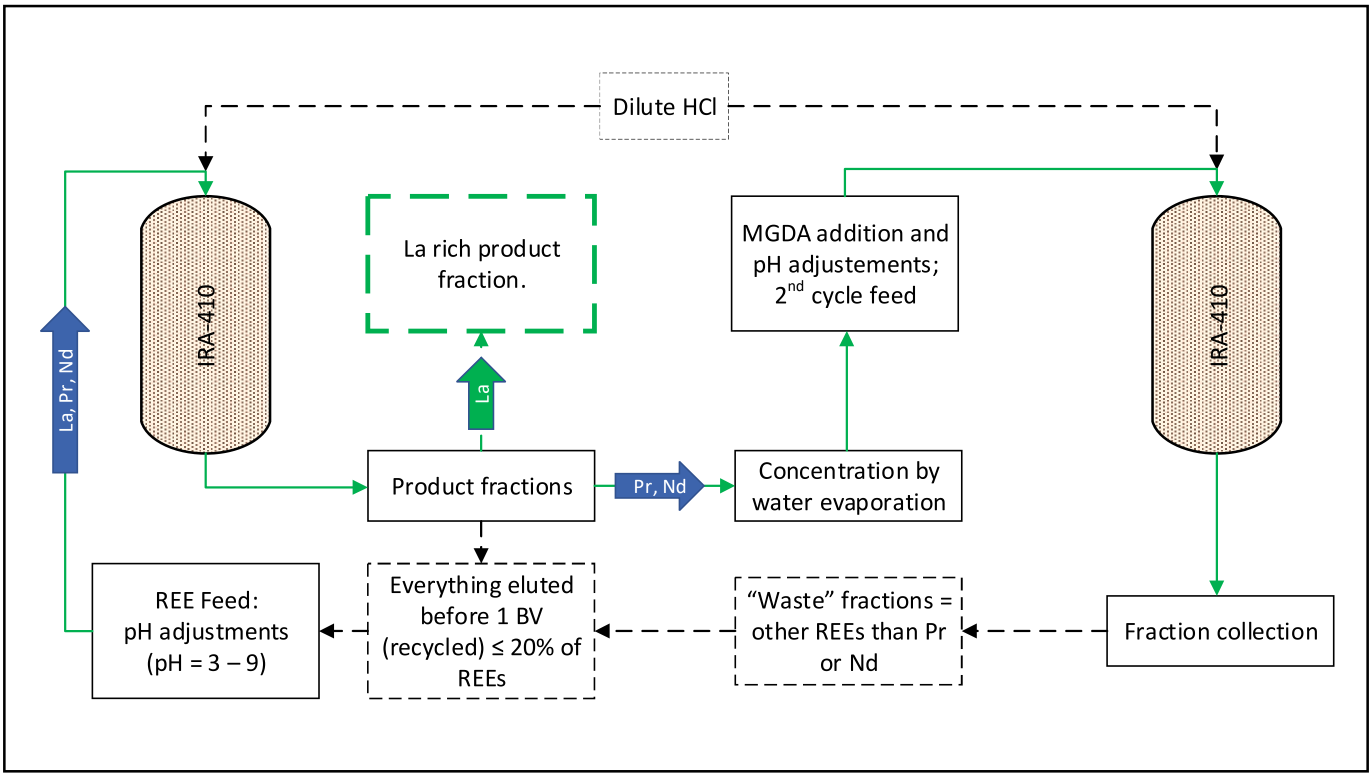
MGDA addition etc.

Condensation

Pr+Nd fraction



Pr+Nd product fraction (collected starting from 1.20 BV. Pr yield 91.3% and purity 14.3%. Nd yield 86.9% and purity 81.2%



Dilute HCl

IRA-410

La rich product fraction.

MGDA addition and pH adjustements; 2^{nd} cycle feed

IRA-410

La, Pr, Nd

La

Product fractions

Pr, Nd

Concentration by water evaporation

REE Feed: pH adjustments (pH = 3 – 9)

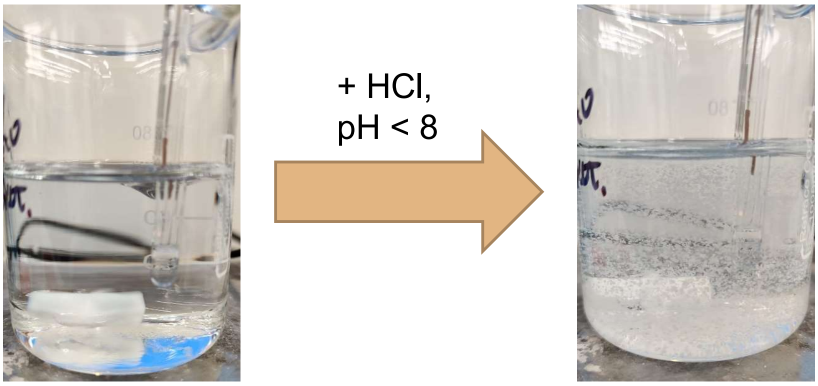
Everything eluted before 1 BV (recycled) ≤ 20% of REEs

"Waste" fractions = other REEs than Pr or Nd

Fraction collection

Oxalate precipitation

Synthetic Nd-MGDA + K-oxalate

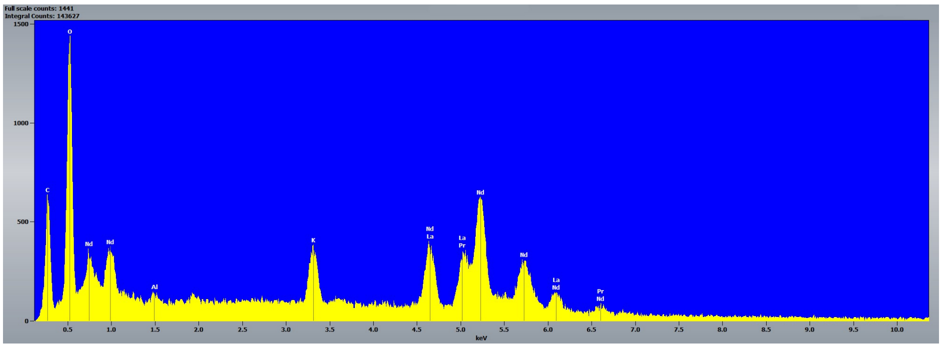


K-MGDA-REE precipitated from the process product. Mainly Pr-Nd oxalate.

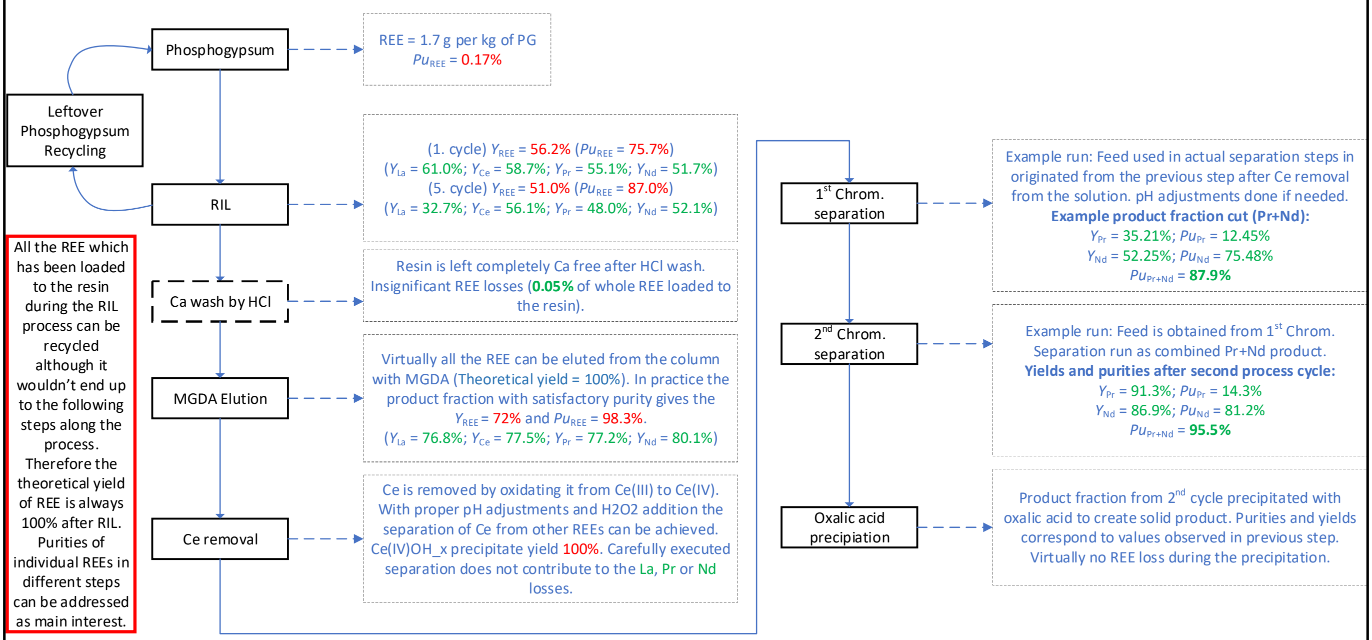
- Precipitation experiment with synthetic materials.
  - Precipitation does not occur if the pH > 9.
  - Decrease in pH (< 8) allows the precipitates to form.
  - Same applies to the authentic material.

No chemical modification needed after separation

Element	%
Pr	13.36
Nd	82.74
Ca, Sc, Fe, Sr	0.07
Other REEs	3.84



Element	w-%
C	6.8
O	9.1
K	4.5
La	18.4
Pr	12.0
Nd	48.8



All the REE which has been loaded to the resin during the RIL process can be recycled although it wouldn't end up to the following steps along the process. Therefore the theoretical yield of REE is always 100% after RIL. Purities of individual REEs in different steps can be addressed as main interest.

REE = 1.7 g per kg of PG
Pu_{REE} = 0.17%

(1. cycle) Y_{REE} = 56.2% (Pu_{REE} = 75.7%)
(Y_{La} = 61.0%; Y_{Ce} = 58.7%; Y_{Pr} = 55.1%; Y_{Nd} = 51.7%)
(5. cycle) Y_{REE} = 51.0% (Pu_{REE} = 87.0%)
(Y_{La} = 32.7%; Y_{Ce} = 56.1%; Y_{Pr} = 48.0%; Y_{Nd} = 52.1%)

Resin is left completely Ca free after HCl wash. Insignificant REE losses (**0.05%** of whole REE loaded to the resin).

Virtually all the REE can be eluted from the column with MGDA (Theoretical yield = 100%). In practice the product fraction with satisfactory purity gives the Y_{REE} = 72% and Pu_{REE} = 98.3%.
(Y_{La} = 76.8%; Y_{Ce} = 77.5%; Y_{Pr} = 77.2%; Y_{Nd} = 80.1%)

Ce is removed by oxidating it from Ce(III) to Ce(IV). With proper pH adjustments and H2O2 addition the separation of Ce from other REEs can be achieved. Ce(IV)OH_x precipitate yield 100%. Carefully executed separation does not contribute to the La, Pr or Nd losses.

Example run: Feed used in actual separation steps in originated from the previous step after Ce removal from the solution. pH adjustments done if needed.
Example product fraction cut (Pr+Nd):
Y_{Pr} = 35.21%; Pu_{Pr} = 12.45%
Y_{Nd} = 52.25%; Pu_{Nd} = 75.48%
Pu_{Pr+Nd} = **87.9%**

Example run: Feed is obtained from 1st Chrom. Separation run as combined Pr+Nd product.
Yields and purities after second process cycle:
Y_{Pr} = 91.3%; Pu_{Pr} = 14.3%
Y_{Nd} = 86.9%; Pu_{Nd} = 81.2%
Pu_{Pr+Nd} = **95.5%**

Product fraction from 2nd cycle precipitated with oxalic acid to create solid product. Purities and yields correspond to values observed in previous step. Virtually no REE loss during the precipitation.

NOLANS RARE EARTHS PROJECT: INNOVATIVE RECOVERY AND PURIFICATION OF PHOSPHORIC ACID BY VSEP NANOFILTRATION

By

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ABSTRACT

The Nolans Rare Earths Project (NRE) is one of the few advanced ore to oxide rare earths projects of scale in the western world to-date. The project is currently in detailed engineering phase and had started execution on enabling works in Q1 2023. It is designed to produce ~4 440 tpa NdPr oxide, 470 tpa SEG/HRE and 144,400 tpa of 54% w/w P_2O_5 MGA (Merchant Grade Phosphoric Acid) by-product on full operations.

The flowsheet involves an integrated processing of apatite and fluorapatite (major host minerals of rare earths elements) through flotation, pre-leaching, sulphation (cracking), water leaching, impurities removal, separation by solvent extraction and product recovery. Nolan's apatite and fluorapatite REE-base ore feed is the first of its kind in any known existing rare earths production plants and mature projects.

The leaching of these minerals with phosphoric and sulphuric acids produces excess phosphoric acid along with some thorium, uranium, iron, calcium, magnesium, and other cations, which are co-extracted during the process. The management of this process stream (to safely stabilise the acids and heavy metals) posed a challenge due to requirements for neutralisation, disposal, and containment.

Arafura had capitalised this challenge into an opportunity, using New Logic Research's (NLR) innovative VSEP (Vibratory Shear Enhanced Processing) nanofiltration technology. The VSEP nanofiltration membrane technology effectively recovers more than 70% of the phosphoric acid and rejects majority of the cations including thorium and uranium to meet the MGA specifications, using an acid-proof membrane. The technology is also used to control the recirculating load of impurities from recovered mixed phosphoric and sulphuric acids to the process plant. Unlike traditional (crossflow) spiral wound nanofiltration, VSEP can tolerate high suspended solids and calcium saturated feed, simplifying the circuit. Therefore, provides a more cost-effective solution than the traditional nanofiltration.

The recovery of phosphoric acid (as a saleable by-product) contributes to the economics of the project. On the other hand, the purification of the recycled mixed acid enables major operational flexibility, since it liberates the upstream pre-leach circuit from operating at a very tight range of major impurities from the fresh feed. This renders the purification circuit an integral and strategic part of the overall Nolans project flowsheet.

This paper aims to share some of the VSEP nanofiltration test work results and its translation to the engineering design of the Phosphoric Acid Recovery and Purification at Nolans. It also highlights the strategic importance of the circuit to the overall flowsheet, and therefore the technical and economic performance of the Nolans Rare Earths Project.

Keywords: Nolans Rare Earths Project, Rare earths elements (REE), NdPr, VSEP, nanofiltration, acid proof *membrane, NLR, thorium, uranium, merchant grade phosphoric acid, apatite, fluorapatite*

INTRODUCTION

The Nolans Rare Earths Project (NRE) is an advanced ore to oxide rare earths project of scale in the western world. The project is currently in detailed engineering phase and had started execution on enabling works in Q1 2023. It is designed to produce ~4 440 tpa NdPr oxide, 470 tpa SEG/HRE and 144,400 tpa of 54% w/w P_2O_5 MGA (Merchant Grade Phosphoric Acid) by-product on full operations[1].

The project is an integrated complex which includes a mine, concentrator (beneficiation plant), hydrometallurgical plant (extraction plant), refinery (separation plant and product handling), utilities (power plant, water treatment plant, sulphuric acid plant, gas separation plant) and major infrastructure (tailings dam, camp, off-site and on-site roads, bore water station etc). These facilities will be constructed and located in the Nolans site, 135 kilometres north of Alice Springs in Australia's Northern Territory. Alice Springs is well-serviced by modern existing infrastructure such as roads, rail, air, and telecommunication facilities, which largely enables the operation of the project in a single location[2].

The Nolans ore feed is a phosphate-based mineral, composed primarily of apatite and fluorapatite, which host the target rare earths elements. The ore also contains elevated amounts of thorium and uranium relative to the NORM (Naturally Occurring Radioactive Material). The processing of the ore generates mixed phosphoric acid and sulphuric acid (mixed acid), which is re-used in the plant and an excess phosphoric acid, with co-extracted impurities (including thorium and uranium) that must be managed by the project.

The Nolans Project incorporates the application of nanofiltration using New Logic Research's (NLR) innovative VSEP (Vibratory Shear Enhanced Processing) to remove majority of the impurities in these streams by membrane rejection. The VSEP nanofiltration recovers more than 90% of the phosphoric acid and mixed acid whilst rejecting more than 50% of thorium and uranium including other cations that are feeding into the flowsheet, using an acid proof membrane. This allows the Nolans project to:

(1) Generate a Merchant Grade Acid (54% w/w P_2O_5) that meets specification for sale, offsetting the requirement to neutralise the excess dirty phosphoric acid and additional volume for gypsum tailings containment and;

(2) Minimise the build-up of key impurities (Mg, Ca, Al, Fe, U, Th) from the regenerated mixed acid (particularly the phosphoric acid that is recycled upstream), in the system allowing for process flexibilities in the impurities composition of the incoming fresh ore (and concentrate) feed.

THE VSEP (VIBRATORY SHEAR ENHANCED PROCESSING) TECHNOLOGY

Membrane filtration in saltwater and wastewater have been widely demonstrated in desalination and mining industries. A key challenge to membrane filtration is fouling (scaling), which is caused by high TSS loading and increasing ion concentration build-up at the surface of the membrane. Fouling (scaling) not only leads to the decrease in flux but also in the loss of membrane's natural selectivity for rejection.

Conventional tangential or crossflow filtration reduced the solids loading to the membrane by pumping the feed at a high pressure and velocity, which creates a shear force at the surface the membrane. However, high feed velocity also results to a significant pressure drop from the inlet (high pressure) and the outlet (low pressure) end of the equipment, which increases the rate of fouling. Due to constraints in applicable forces, the conventional membrane filtration is only limited to low viscosity, low colloidal silica and low TSS feed material. Often, pre-conditioning or pre-treatment steps are necessary such as ultrafiltration and/or addition of anti-scalants / anti-fouling chemicals to meet the requirements of the downstream process[3].

In order to overcome these limitations (and provide operational flexibility and simplicity), NLR had developed an innovative vibrating membrane technology called VSEP (Vibratory Shear Enhanced Processing). In a VSEP system, the feed slurry is kept in a steady meandering flow between the parallel membrane leaf elements. Torsional vibration is induced to the membrane boundary layer via an oscillation created by the VSEP resonating drive system (Figure 1).

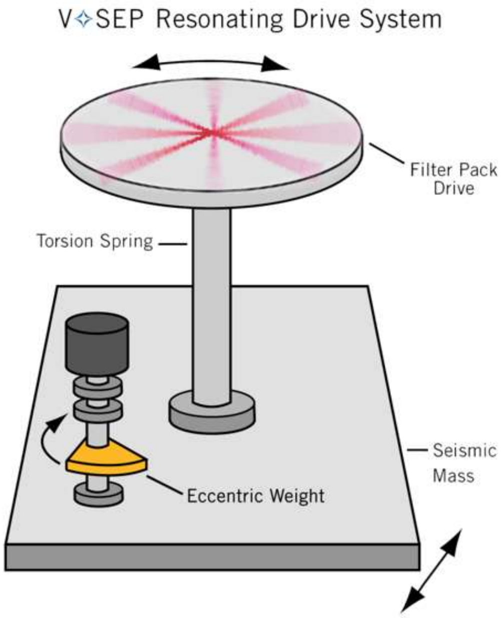


Figure 1 – VSEP Resonating Drive[4]

The membrane vibration produces shear waves that lift the solids, foulants / scales off the membrane surface and direct these to the centre of the flow (and remix with the bulk flow) in the membrane stack. This allows for the processing of high TSS and/or colloidal silica feed, eliminating the need for pre-treatments (hence, simplifying the flowsheet).

Figure 2 illustrates the comparison of fluid dynamics between a conventional crossflow and VSEP filtration.

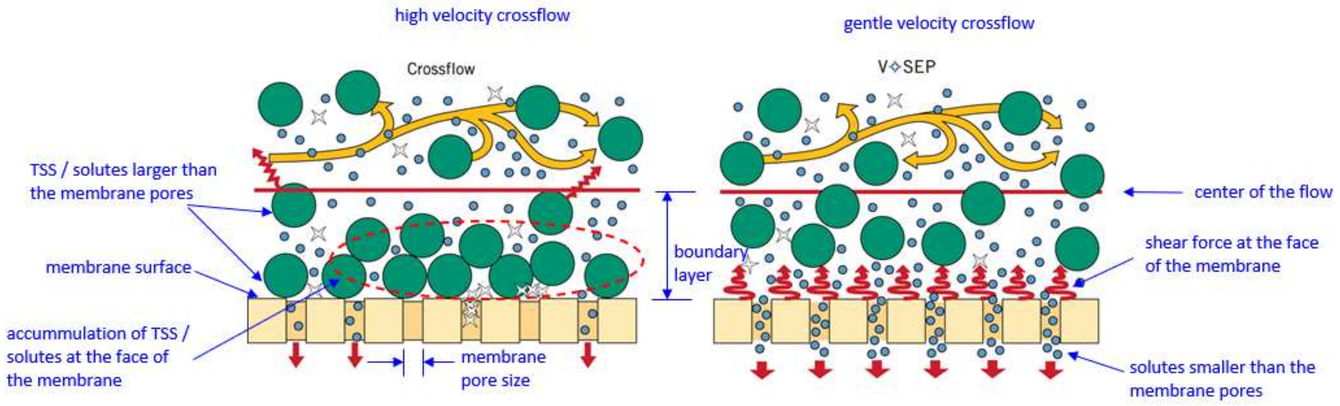


Figure 2 – Fluid Dynamics Comparison (Conventional Crossflow vs VSEP Filtration)[3]

A VSEP membrane filter pack assembly is illustrated in Figure 3. It is composed of:

- Filament-wound outer housing which encases the filter membrane elements.
- Membrane trays – which consists of a stainless-steel disc, drainage cloth and the membrane element.
- Metal spacers and rubber gaskets (o-rings) which separate the separates the tray and provide spacing for the feed to flow over the trays.

The assembly is compressed so that the gaskets form a seal to prevent process leaking. The standard modular size of a VSEP System is 9 to 139 square meters (100 to 1,500 square feet) composed of discs with a 19 inch (48 cm) active diameter[6].

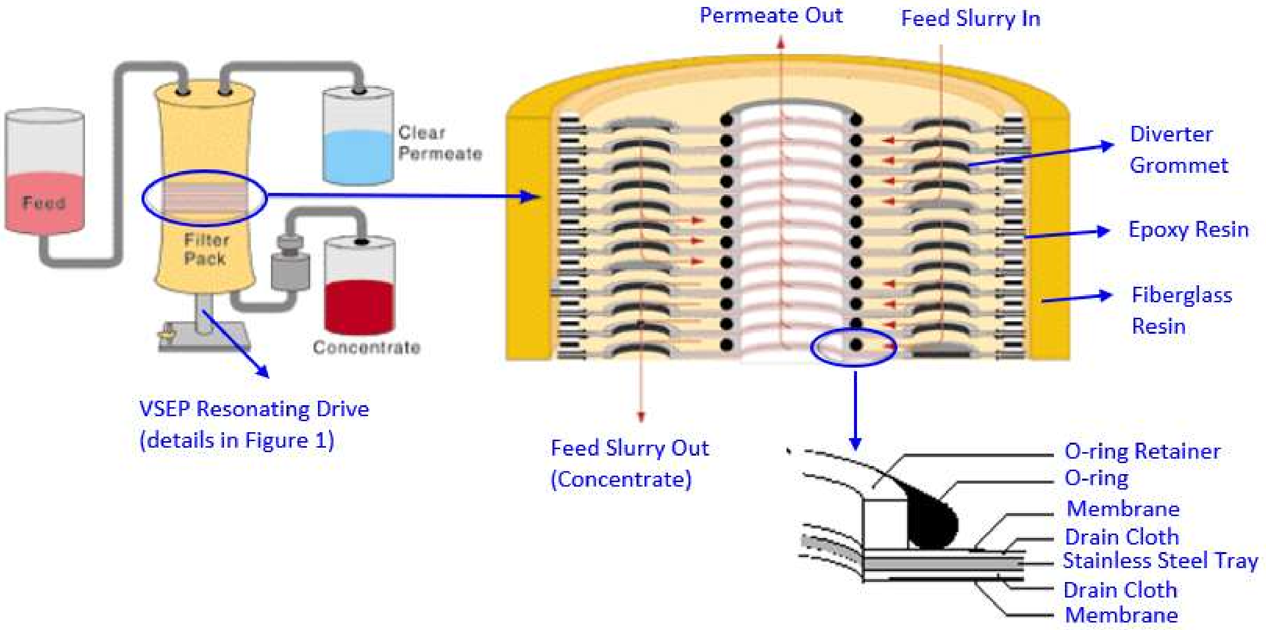


Figure 3 – VSEP Filter Pack Assembly[4]

A VSEP filter unit module is presented in Figure 4 and is made up of the following components:

- Filter Pack – as described and illustrated in Figure 3
- Drive System - as described and illustrated in Figure 1
- Supporting steel structure (frame)
- Feed, permeate and concentrate piping

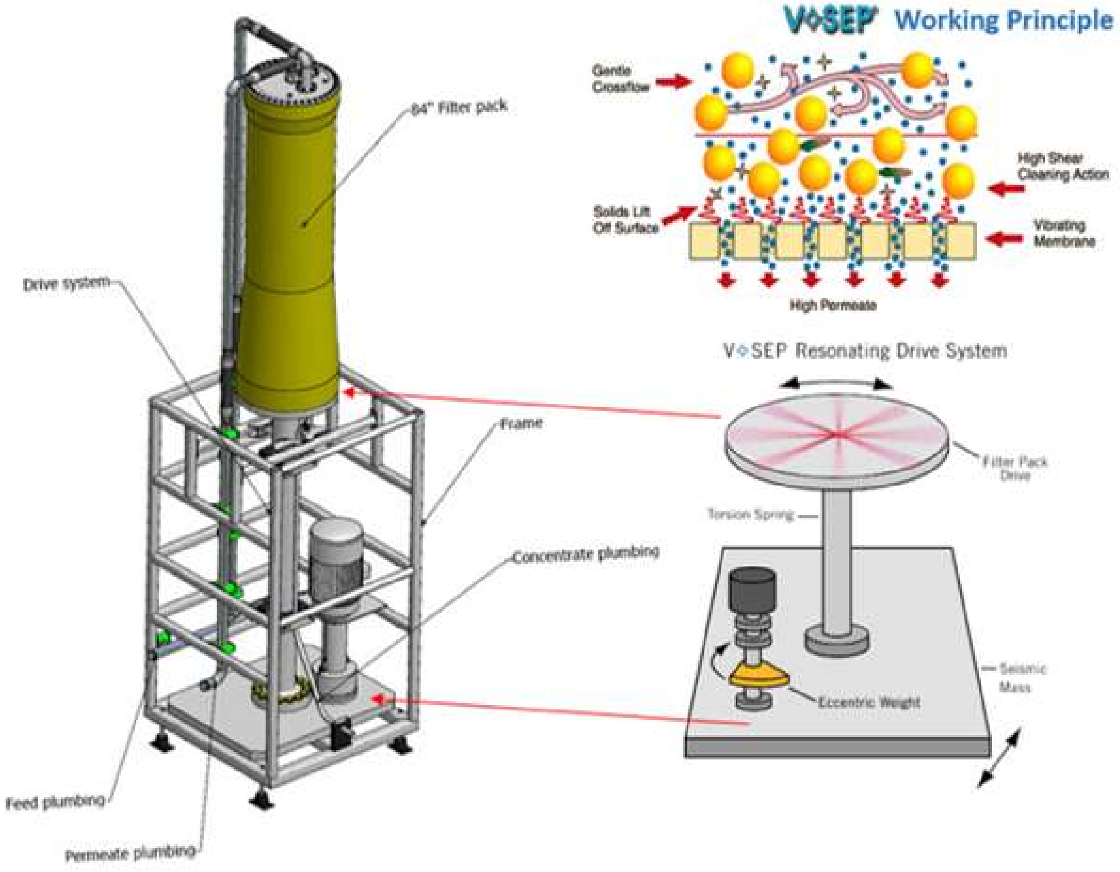


Figure 4 – VSEP Filter Unit Module[6]

NOLANS PROJECT HIGH LEVEL PROCESS DESCRIPTION

The Nolans Rare Earths Project is an integrated mine-to-metal oxide processing plant. The process plant is designed to process 1 Mtpa of ore throughput to produce 340,000 tpa of concentrate. This results to a mine life of 38 years and a nominal production of about 4 440 tpa NdPr oxide, 470 tpa SEG/HRE and 144 400 tpa of 54% w/w P_2O_5 MGA (Merchant Grade Phosphoric Acid) by-product.

A high-level schematic of the process flowsheet is presented in Figure 5.

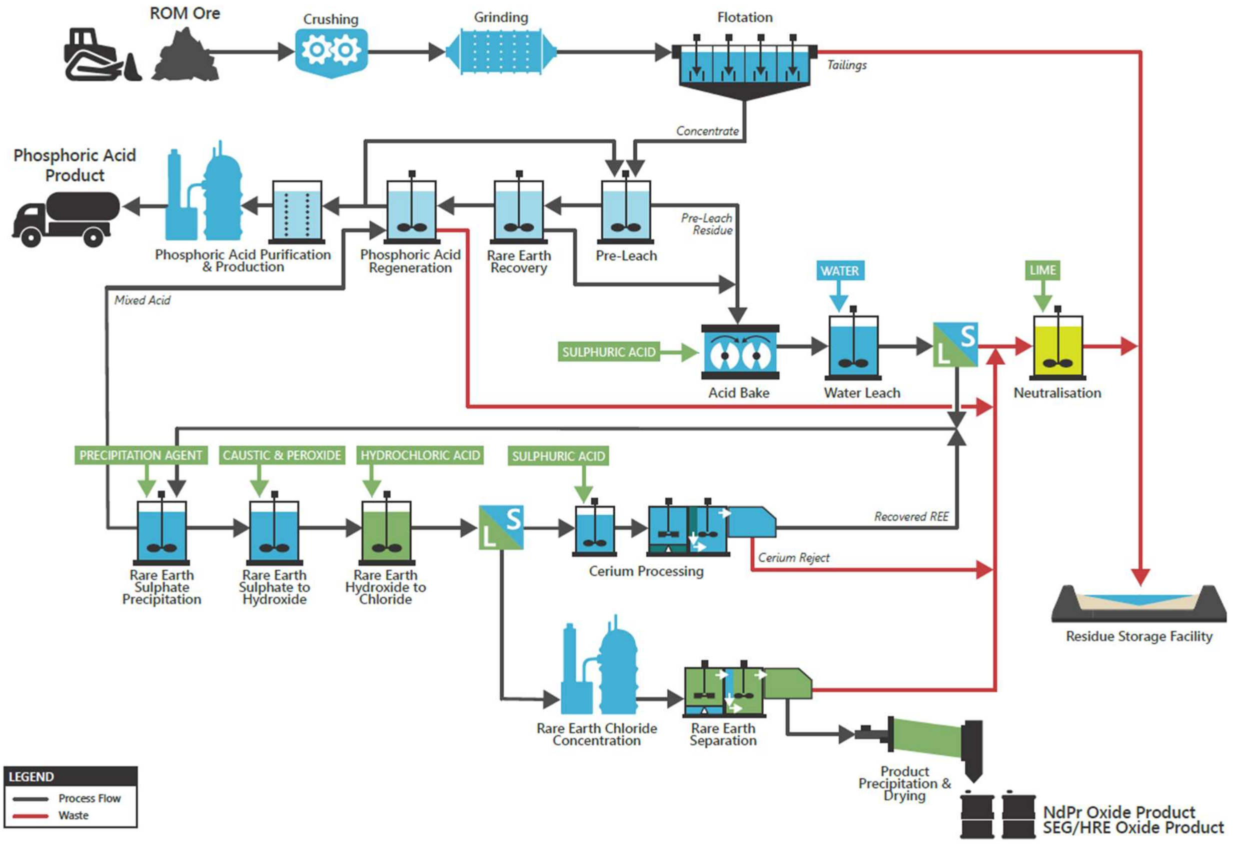


Figure 5 – Nolans Rare Earths Project High Level Flowsheet [1]

The Nolans ore feed is composed mainly of apatite and fluorapatite (REE host minerals), which is the first of its kind in REE processing. The ore is extracted from the deposit using open pit mining method. The ROM ore is transported to the processing plant (8.5 kilometres away from the mine) via haul trucks, where it is crushed, milled and beneficiated using flotation. The beneficiation plant separates majority of the gangue minerals (clays, non-phosphate minerals) from the REE-carrying phosphate minerals, increasing the REE contents from ~2.9% TREO (Total Rare Earths Oxide) in the ore to ~ 6% TREO in the concentrate. The ROM feed also contains elevated thorium (~2 800 ppm w/w%) and uranium (~200 ppm w/w%), of which ~30% is rejected in the beneficiation plant tailings.

The concentrate is pre-leached with regenerated phosphoric acid to selectively remove most of the calcium impurities in apatite / fluorapatite and reduce the solids mass for downstream sulphation. The leached calcium is solubilised as phosphate along with co-extracted REE and impurities such as Al, Mg, Ca, Fe, Th and U. The leach liquor is heated to an elevated temperature to selectively precipitate and recover the REE phosphates leaving behind most of the co-extracted impurities in the solution.

The solubilised calcium, which exists as monocalcium phosphate (MCP) is reacted with a mixed acid regenerated from the downstream water leach process. The mixed acid is composed of 26% w/w H_2SO_4 and 6% w/w H_3PO_4. The addition of sulphuric acid (from the mixed acid) to the MCP - rich liquor regenerates the phosphoric acid and precipitates the calcium as dihydrate gypsum. More than 90% of the phosphoric acid from this process is recycled back to pre-leach to leach the incoming fresh concentrate. The remaining excess regenerated acid is sent to the Phosphoric Acid Purification Area to remove the heavy metal impurities (particularly thorium and uranium) and reduce to trace levels. The gypsum precipitate is one of the final wastes of the process plant. This is treated and subsequently disposed to the Tailings Storage Facility (TSF).

The pre-leached residue and precipitated rare earths phosphates are then fed to the sulphation area, where the combined material is mixed with concentrated sulphuric acid (98% w/w H2SO4) and held for a period of time at 250^{o}C. The baking process effectively “cracks” the occluded refractory rare earths, so that it will be amenable to the subsequent water leaching. In water leaching, the baked material is mixed with water to solubilise the rare earths as sulphates. Phosphoric acid is also generated (from sulphuric acid leaching of the remaining apatite), along with the free sulphuric acid.

The rare earths sulphates are recovered from the liquor as sulphate precipitate through the addition of methanol before sending to impurity removal stages. The post-purification precipitate, virtually free of major impurities is dissolved with hydrochloric acid to selectively dissolve the target non-cerium rare earths (SEG/HRE, Nd, Pr), leaving the cerium behind in solids. The resulting solution is a target rare earths - rich chloride liquor ready for separation in the succeeding solvent extraction stages. The cerium which remains in the precipitate, is dissolved separately with sulphuric acid.

The resulting cerium-rich sulphate solution is sent to its dedicated solvent extraction to separate the cerium from the residual SEG/HRE, NdPr rare earths. The cerium, which is loaded in the organic is stripped with sulphuric acid and treated prior to tailings disposal. The target rare earths contained in the raffinate is recycled back to the water leach.

The SEG/HRE is separated from the NdPr through the first solvent extraction, where the former is loaded to the organic and stripped with hydrochloric acid. The raffinate, which contains the NdPr-rich solution is forwarded to the second solvent extraction where the NdPr are loaded into the organic and stripped with hydrochloric acid.

The different high purity product liquors (SEG/HRE and NdPr chloride solutions) are subsequently recovered as oxalate precipitates in their respective trains. The individual precipitates are calcined to convert the solids to SEG/HRE oxide and NdPr oxide final products.

PHOSPHORIC ACID PURIFICATION AREA IN DETAIL

In the Nolans flowsheet, phosphoric acid purification (PA Purification) is achieved by using nanofiltration technology, where molecules with large ionic size such as thorium and uranium are rejected by the membrane while small neutral molecules pass through the membrane. Nanofiltration technology is an established process for removing uranium and thorium in leach liquors and recovery of water in bitterns (RO concentrate).

The PA purification flowsheet employs VSEP nanofiltration (Vibratory Shear Enhanced Processing), where vibratory shear waves is directly applied in the membrane surface (as described in the previous section). In this manner, the VSEP is able to process raw acid feed from the PA regeneration and mixed acid circuits with relatively high TSS, high TDS and high acidity.

The VSEP nanofiltration has been proven in an industrial application of phosphoric acid recovery in a fertiliser plant in the US. Arafura had done a number of laboratory and pilot testworks including feed and membrane variability tests to establish its technical viability to the Nolans flowsheet.

The PA purification is comprised of two stage nanofiltration described as follows (refer to Figure 6 below):

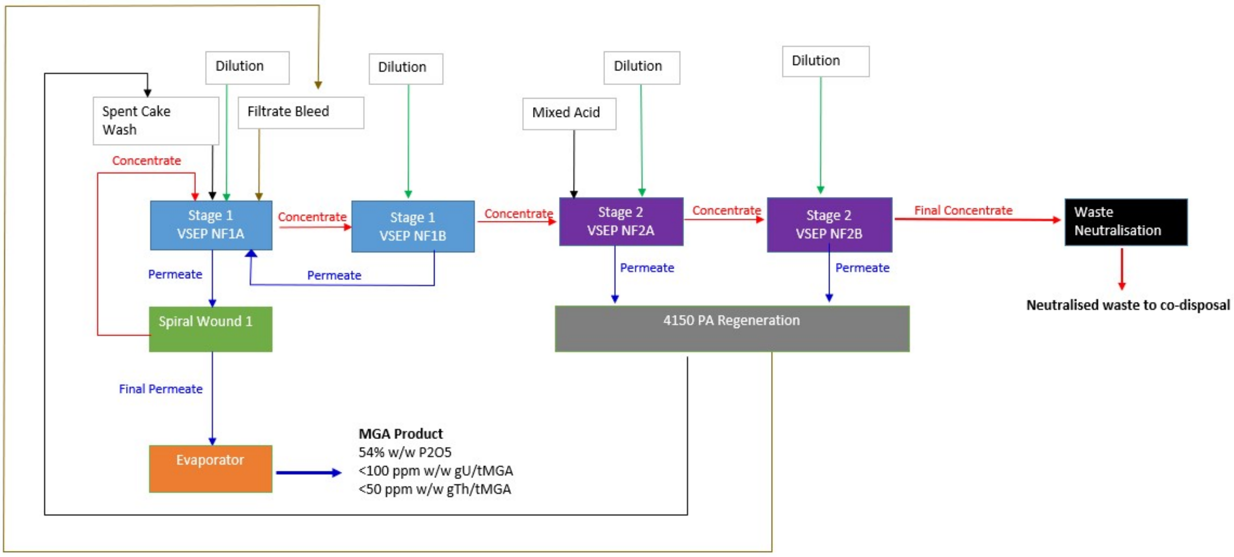


Figure 6 – Nolans Rare Earths Project Phosphoric Acid Purification Flowsheet

Stage 1 Nanofiltration - processes the excess phosphoric acid feed from the PA regeneration area, where the membrane rejects dissolved impurities, including U and Th to meet the phosphoric acid product specifications. Stage 1 uses two passes of nanofiltration for the permeate to maximise the phosphoric acid recovery within the constraints of impurity concentration. The concentrate (retentate) produced in Stage 1 flows in series to Stage 2 for further recovery of residual phosphoric acid.

Stage 2 Nanofiltration - processes the mixed acid recovered from the extraction area and Stage 1 concentrate. The membrane rejects dissolved impurities, including Al, Mg, Ca, U and Th to minimise the build-up of these impurities in the upstream circuit. The permeate collected from each pass (containing high concentrations of sulphuric acid and some phosphoric acid) is combined and recycled to the PA regeneration area for gypsum precipitation. The concentrate (retentate) produced in Stage 2 flows in series, with the final concentrate produced after the second pass.

Three parameters are key to the nanofiltration of the Nolans acid feeds:

- **Flux rate** – refers to the flowrate of the permeate and dictates the sizing or number of unit modules required. The Stage 1 VSEPs have flux rates ranging at 9-15 GFD (gallons of permeate per square feet/day) and Stage 2 have higher flux rates at 14-22 GFD

- **Rejection rate** – refers to the efficiency of molecule rejection by the membrane, which is typically around 15% phosphoric acid, >50 – 70 % uranium and thorium rejection in both stages.

- **Membrane life** – degradation resistance of the membrane from high acidity and high-pressure exposure

The final permeate leaving the polishing spiral wound nanofiltration contains about 15% w/w P_2O_5. This is sent to an evaporator, where the water is driven-off to achieve the 54% w/w P2O5 concentration for the merchant grade phosphoric acid (MGA) specification.

The final concentrate generated at the end of Stage 2 nanofiltration contains elevated levels of thorium and uranium (following the series of concentration). This is sent to waste neutralisation to stabilise and immobilise the dissolved metals (as hydroxide precipitate) prior to disposal to the RSF. Figure 7 illustrates the PA Purification circuit, with VSEP unit modules installation in the Nolans hydrometallurgical processing facility.

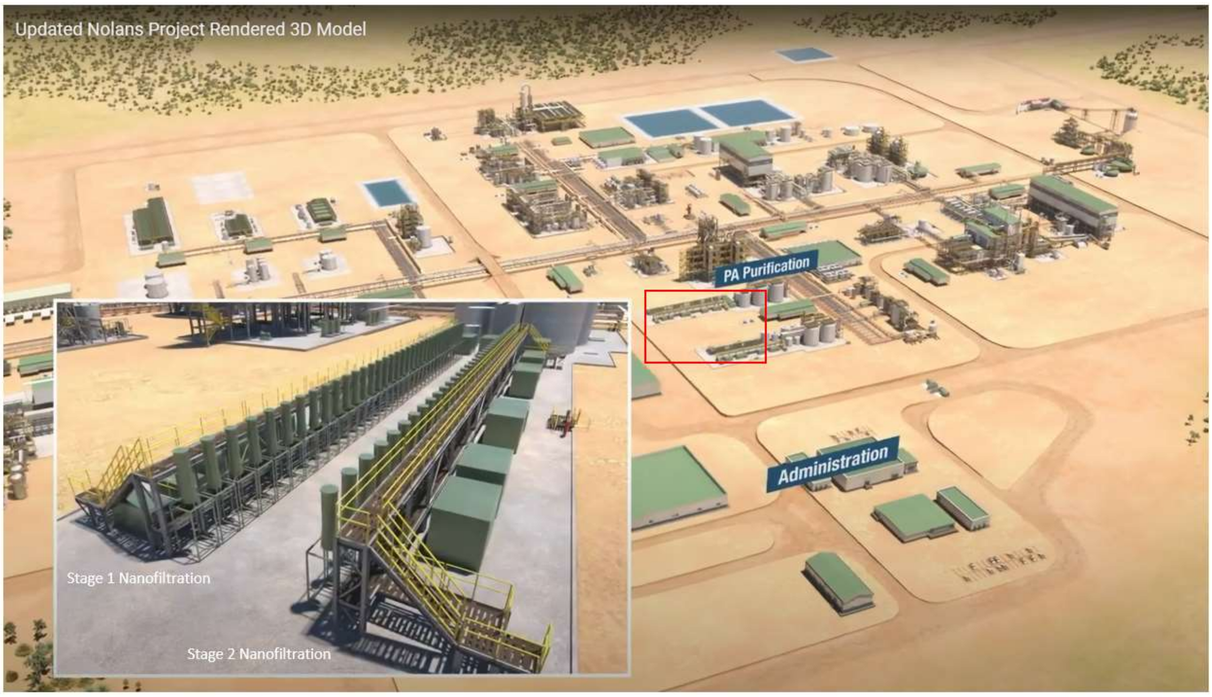


Figure 7 – PA Purification Circuit at Nolans Hydrometallurgical Processing Facility [7]

LABORATORY SCALE TESTWORK RESULTS

Overview

NLR and Arafura had begun working for the laboratory scale test work on Q1 2022. The testing was performed on synthetic solution of simulated acid streams with compositions nominated by Arafura. Initial work involved a thorough analysis of various nanofiltration membranes to ascertain instantaneous flux and rejection rates on the simulated acid streams. The most effective membranes were used to concentrate the simulated acid streams to produce clean permeated acid and concentrated reject acid streams. These concentration tests also allowed for the determination of average flux and clean permeated acid recovery rates. Simultaneously, long-term soak testing was performed on the entire suite of possible nanofiltration membranes to ensure that no significant loss flux or solute rejection would occur from continued exposure of the membranes to the acid solution.

The VSEP LP (Lab & Pilot) unit was used for the laboratory scale test work. The unit was set up in L-mode (Lab Mode) and utilized a single sheet of membrane surface area at 0.5 square feet (0.046 m^2). The surface area of a the full-scale industrial VSEP unit is 2,400 times the surface area of this unit, and thus would have 2,400 times the volume throughput. Figure 8 shows a typical set up for a VSEP LP in L-mode.

Figure 8 – VSEP LP in L-mode (left) with pump (center) and feed tank (right).

The system was operated in either recirculation mode (membrane selection) or batch mode (concentration studies), the only difference between the two being that in batch mode, the VSEP permeate is removed from the system as the acid concentrates, while in recirculation mode, the VSEP permeate is returned to the system. Recirculation mode is only used during the initial membrane selection, whereas batch mode is used in all other testing simulating the full-scale operation.

In batch mode, a finite volume of feed is processed. The concentrate, or reject, is sent back to the feed tank and the permeate, or filtrate, is sent to a separate destination. As the permeate is removed, the feed tank volume is decreased and becomes concentrated until an end point based on flow or other desired set point. The concentrate flow is held constant to maximize crossflow, and, in combination with vibration, will reduce the overall rate of fouling. The advantages of batch mode are slightly higher flux rates and slightly lower cleaning frequency. Figure 9 below shows a diagram of batch mode operation.

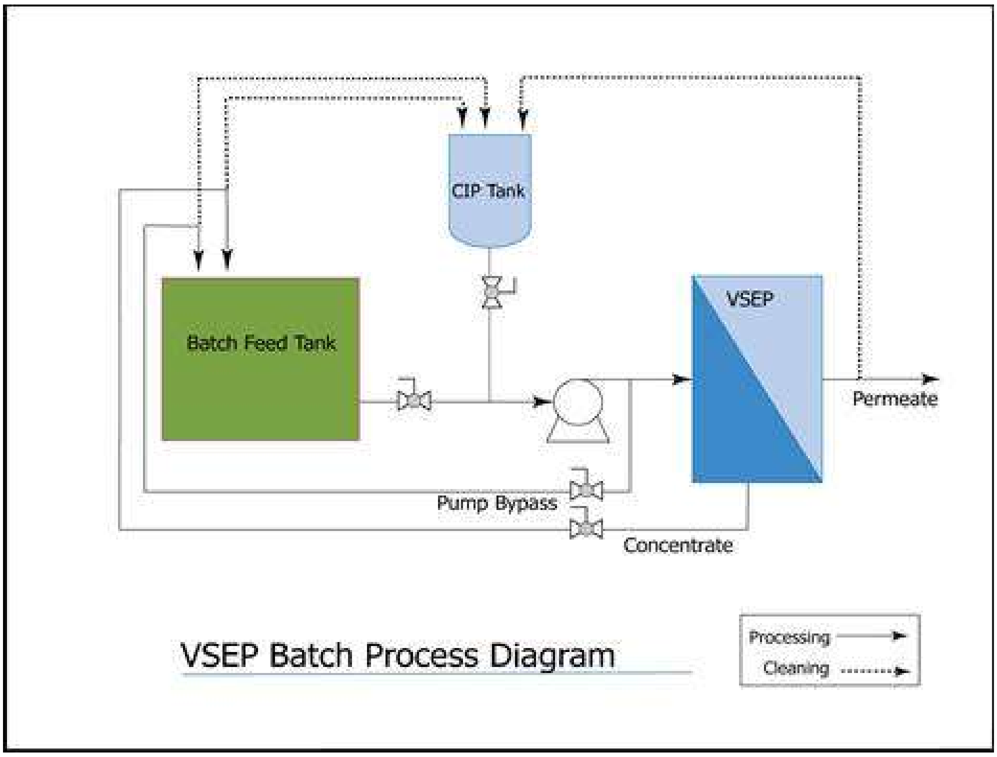


Figure 9 – VSEP Batch Mode Operation

Membrane Selection

A suite of nanofiltration membranes was tested with the simulated acid streams to determine which membranes had the highest permeate flux and solute rejection. The pore size of the membranes tested ranged from a molecular weight cut off (MWCO) of 100 to 800. A lower MWCO indicates higher solute rejection, while a higher MWCO indicates lower solute rejection. Typically, magnesium sulphate is the standard used to evaluate rejection for nanofiltration membranes. As uranium and thorium are the key contaminants in the acid streams, surrogates for tracking their partitioning were needed. Uranium rejection tracks relatively close to magnesium rejection, while thorium rejection tracks relatively close to lanthanum rejection, so these were the main solutes followed in the simulated acid streams. Each membrane was tested on an identical acid solution in the VSEP system at 40°C and the results were compared.

Table 1 shows the standard manufacturer information for the membranes tested.

Table 1 – Standard Manufacturer Membrane Data

Membrane	Pore Size	Max Temp	pH Tolerance	Water Flux[1,2]	Material
NF-1	100 da	80°C	0 to 12	13 GFD	Thin-film Non-polyamide
NF-2	200 da	80°C	0 to 12	17 GFD	Thin-film Non-polyamide
NF-3	300 da	70°C	1 to 14	62 GFD	Thin-film Non-polyamide
NF-4	300 da	90°C	1 to 14	18 GFD	Polyethersulfone on PP
NF-5	500 da	70°C	1 to 14	95 GFD	Thin-film Non-polyamide
NF-6	800 da	90°C	1 to 14	107 GFD	Polyethersulfone on PP

1. Average Batch Cell Test Results in GFD on new membrane @ 25ºC
2. GFD = Gallons of permeate produced per square foot of membrane per day. 1 GFD = 1.7 LMH (liters per square meters per day).

The membranes were compared using the permeate flux and the solute rejection. In general, the flux rates and rejection rates tracked well with the pore size (MWCO) of the membranes. Membranes with lower MWCO had lower flux rates and higher rejection, while membranes with higher MWCO had higher flux rates and lower rejection. To ensure that the quality of the permeate was satisfactory with respect to lanthanum and magnesium, only NF-1, NF-2, and NF-3 were progressed for further testing.

Table 2 shows the instantaneous flux and rejection data for the membranes tested.

Table 2 – Instantaneous Flux and Rejection Data

Membrane	Permeate Flux[1]	Pressure	Conductivity	pH	%Solids[2]	Lanthanum	Magnesium
Feed	-	-	108,000 µS/cm	1.9	18.79%	164 ppm	473 ppm
NF-1	1.0	500 psi	76,800 µS/cm	2.0	12.77%	4.6 ppm	11.6 ppm
NF-2	2.1	500 psi	78,800 µS/cm	1.9	13.16%	12.8 ppm	26.7 ppm
NF-3	1.2	500 psi	98,800 µS/cm	1.7	17.86%	62.5 ppm	184 ppm
NF-4	1.2	500 psi	96,800 µS/cm	1.7	17.27%	72.7 ppm	256 ppm
NF-5	3.3	500 psi	96,000 µS/cm	1.8	17.65%	118 ppm	337 ppm
NF-6	8.2	500 psi	91,700 µS/cm	1.8	18.51%	155 ppm	447 ppm

1. Permeate Flux is given as a ratio of permeate flux of the membrane to the lowest observed flux.
2. % Solids means total TSS + TDS

Membrane Soak Testing

In parallel to the membrane selection testing, soak testing of the membranes was taking place. The membranes were soaked in identical phosphoric acid solutions (same to that of the test concentration) and periodically removed from the solution and tested on clean water to track changes in flux and magnesium sulphate rejection over time. Within a few months it was observed that only NF-3 and NF-5 membranes were capable of being exposed to the acid solutions and not have significant changes in flux or rejection. Notably, the best rejecting membranes, NF-1 and NF-2, quickly lost rejection and gained flux, indicating that damage to the membranes from the acid was significant. As NF-5 membrane did not satisfy permeate quality limitations during the membrane selection, NF-3 membrane was the only membrane that was acceptable for long-term acid filtration. The NF-3 membrane was used for the remainder of the testing.

Figure 10 below shows the flux rates for each of the membranes over time, soaked in the phosphoric acid solution. Figure 11 shows the magnesium sulphate rejection for each of the membranes over time soaked in the phosphoric acid solution. After it was determined that only NF-3 would be appropriate to use, the NF-3 membrane was also put through a soak test with a sulfuric acid-based solution simulating the mixed acid feed. Figure 12 below shows the flux rates and magnesium sulphate rejection rates over time for the NF-3 membrane soaked in the sulfuric acid-based solution.

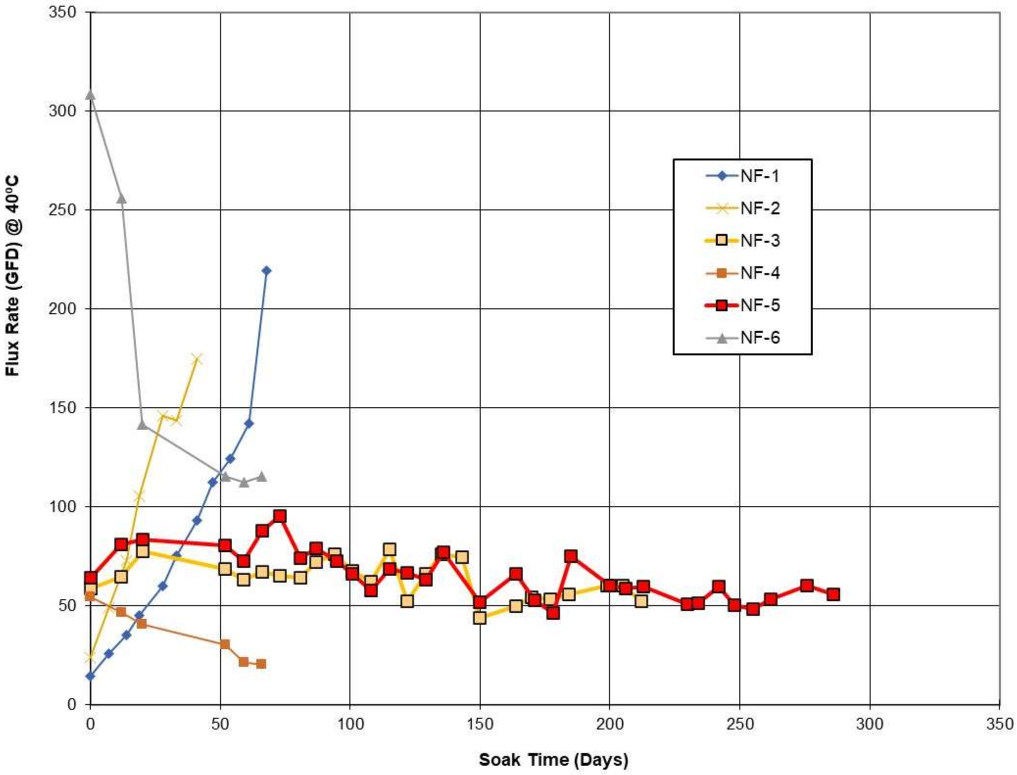


Figure 10 – Phosphoric Acid Soak Test Flux Rates

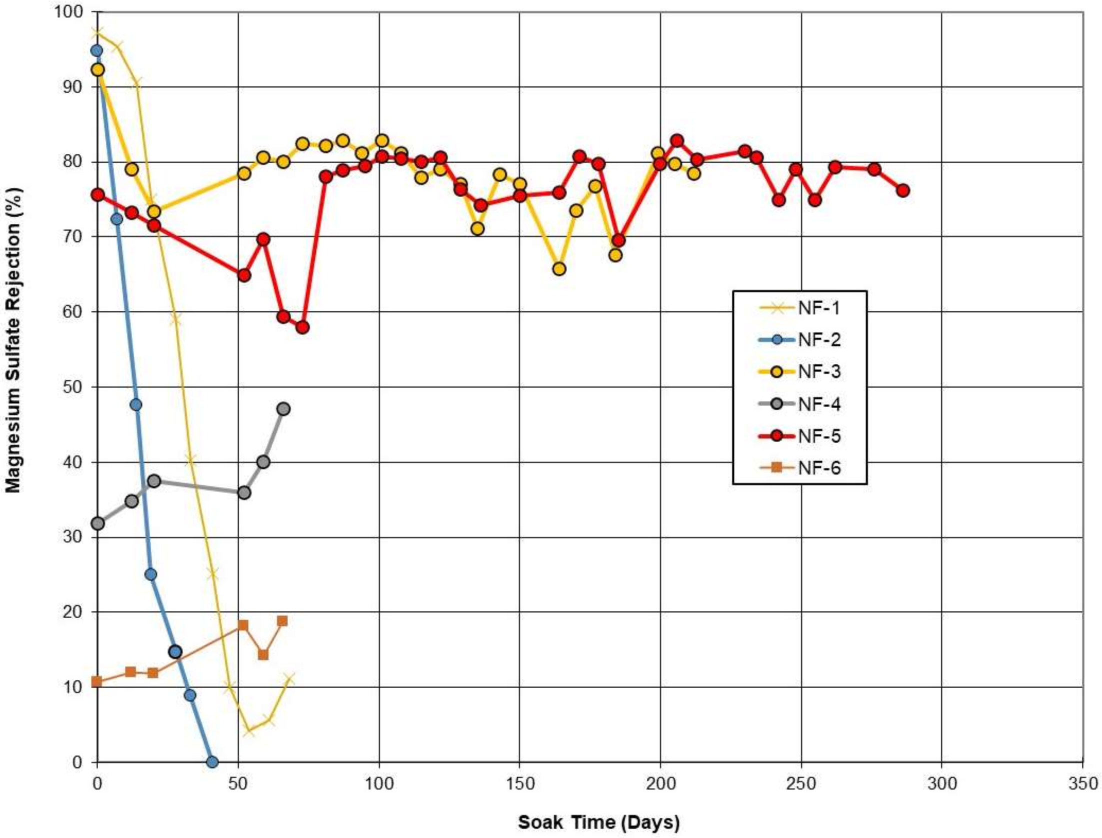


Figure 11 – Phosphoric Acid Soak Test Magnesium Sulphate Rejection Rates

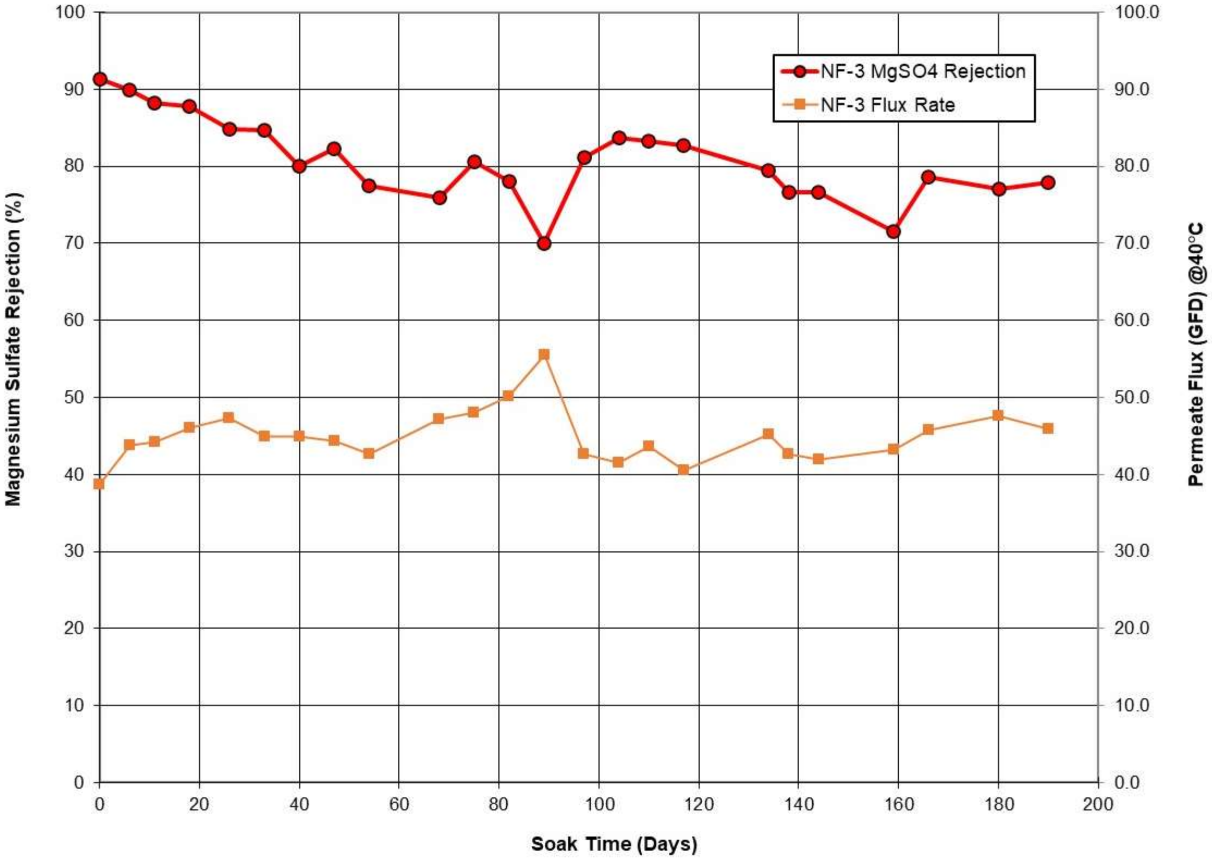


Figure 12 – Sulfuric Acid NF-3 Soak Test Flux and Magnesium Sulphate Rejection Rates

NF-3 L-Mode Concentration Testing

The NF-3 membrane was used to concentrate the phosphoric and sulphuric acid-based streams in the overall acid purification process flow sheet. The flow sheet is shown in Figure 13 below. Incoming phosphoric acid-based material was diluted with water and spent flush water and fed into NF1A. The concentrate from this stage is diluted with water and fed into NF1B. The permeate from these two stages feeds the evaporator to produce saleable MGA product.

The concentrate from NF1B is blended with sulphuric acid based mixed acid, diluted with water, and fed to NF2A. The concentrate from NF2A is diluted with water and fed to NF2B. The permeate from NF2A and NF2B is recycled back into the refining process, while the concentrate from NF2B is neutralized for disposal. Dilution rates at the beginning of each stage targets 180 g/L phosphorus plus sulphur (180 g/L P+S) to keep viscosity at a reasonable level for adequate filtration rates. Volumetric recovery rates were targeted at 80% +/- 5% for each stage as higher recovery with nanofiltration membranes can lead to significant bleed of undesirable contaminants to the permeate. In addition, unnecessarily high permeate recovery can also cause decreasing acidity and lead to thorium phosphate precipitation in NF1B, and excessive gypsum precipitation in NF2A and NF2B due to the presence of sulphuric acid mixed with the monocalcium phosphate-rich concentrate from NF1B. While the vibration of the VSEP system can minimize the effects of precipitation on the membrane system itself, excessive precipitation could eventually cause pumping issues and damage to downstream equipment.

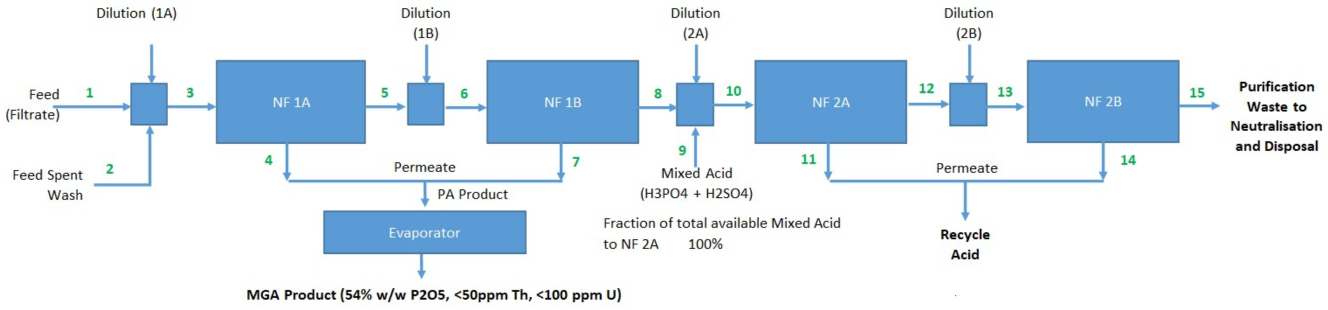


Figure 13 – Laboratory Scale Testwork Flowsheet

With so many recirculating streams, isolation of each stage was necessary. Thus, the testing was run in an open-loop fashion, in which each stage was independent of the other stages. Iterative modelling based on the initial rejection from the membrane selection informed the composition of the solutions for the concentration studies performed on each stage. The results of the four concentrations are shown in Table 3 below. Images of the samples from each stage are shown in Figures 14 through 17.

Table 3 – NF-3 L-Mode Concentration Testing Average Flux, Permeate Recovery & Analytical

Sample	Average Flux[1]	%Recovery	Conductivity	pH	%Total Solids[2]	Lanthanum	Magnesium
NF1A Feed	-	100%	81100 μS/cm	1.5	16.82%	127 ppm	388 ppm
Composite Perm.	1.6	74.3%	86100 μS/cm	2.1	14.19%	30.8 ppm	142 ppm
Final Concentrate	-	25.7%	88100 μS/cm	2.2	23.77%	459 ppm	1260 ppm
NF1B Feed	-	100%	55400 μS/cm	2.2	16.69%	135 ppm	694 ppm
Composite Perm.	2.0	79.9%	56800 μS/cm	1.9	11.92%	81.4 ppm	438 ppm
Final Concentrate	-	20.1%	57900 μS/cm	2.0	27.06%	186 ppm	1510 ppm
NF2A Feed	-	100%	443000 μS/cm	1.3	16.92%	259 ppm	43.8 ppm
Composite Perm.	2.5	77.5%	395000 μS/cm	1.5	14.20%	57.5 ppm	15.7 ppm
Final Concentrate	-	22.5%	422000 μS/cm	1.4	17.59%	788 ppm	121 ppm
NF2B Feed	-	100%	425000 μS/cm	1.7	17.17%	885 ppm	625 ppm
Composite Perm.	1.0	79.7%	383000 μS/cm	1.5	12.31%	423 ppm	322 ppm
Final Concentrate	-	20.3%	437000 μS/cm	1.2	19.60%	2360 ppm	1670 ppm

1. Permeate Flux is given as a ratio of permeate flux of the membrane to the lowest observed flux.
2. % Solids means total TSS + TDS

Figure 14 – NF-3 L-Mode NF1A Feed, Permeate, and Concentrate (left to right)

Figure 15 – NF-3 L-Mode NF1B Feed, Concentrate, and Permeate (left to right)

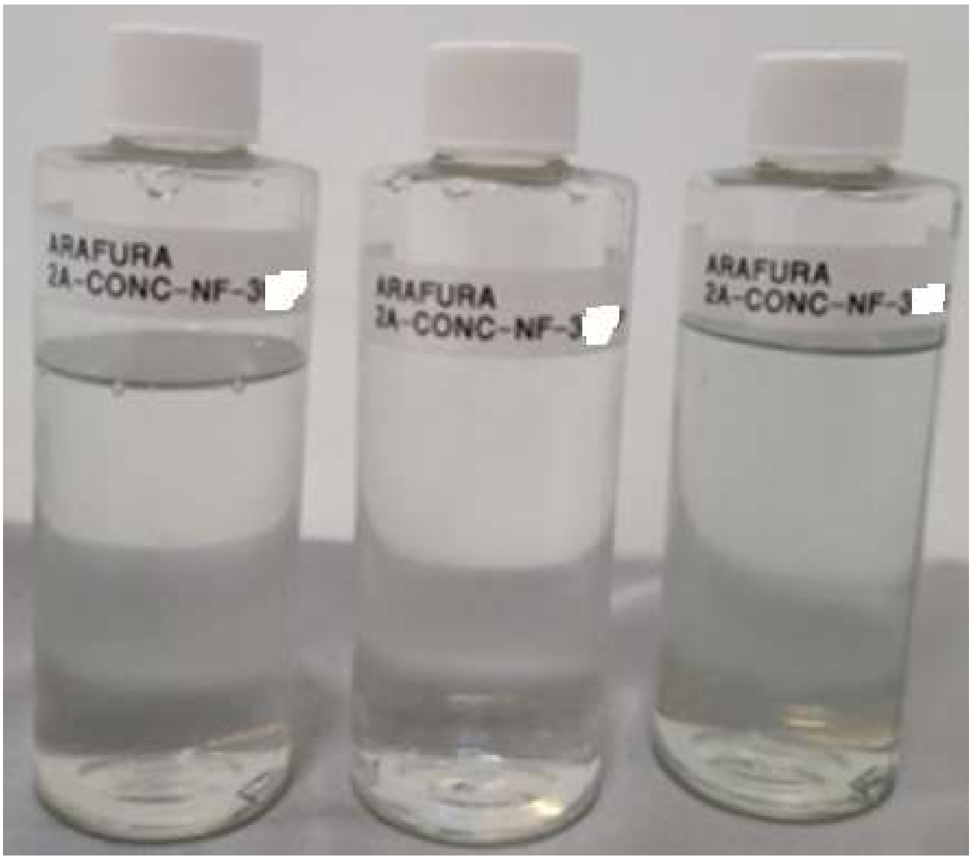


Figure 16 – NF-3 L-Mode NF2A Feed, Permeate, and Concentrate

Figure 17 – NF-3 L-Mode NF2B Feed, Concentrate and Permeate (left to right)

PILOT SCALE TESTWORK RESULTS

Overview

Laboratory scale test work was completed in October of 2022, the results of which informed the optimum flowsheet for pilot scale test work (refer to Figure 6 above). The optimised flowsheet incorporates both VSEP and traditional spiral-wound nanofiltration (both utilizing the NF-3 membrane). Testing began in January 2023 and is ongoing. Testing was performed with simulated acid streams with compositions designated by Arafura based on the optimum flowsheet.

The VSEP LP (Lab & Pilot) unit was used for the pilot scale test work. The unit was set up in P-mode (Pilot Mode) and utilized 19 double-sided trays of membrane surface area at 16.7 square feet (1.55 m^2). The surface area of a the full-scale industrial VSEP unit is 72 times the surface area of this unit, and thus would have approximately 72 times the volume throughput. Figure 18 shows a typical set up for a VSEP LP in P-mode.

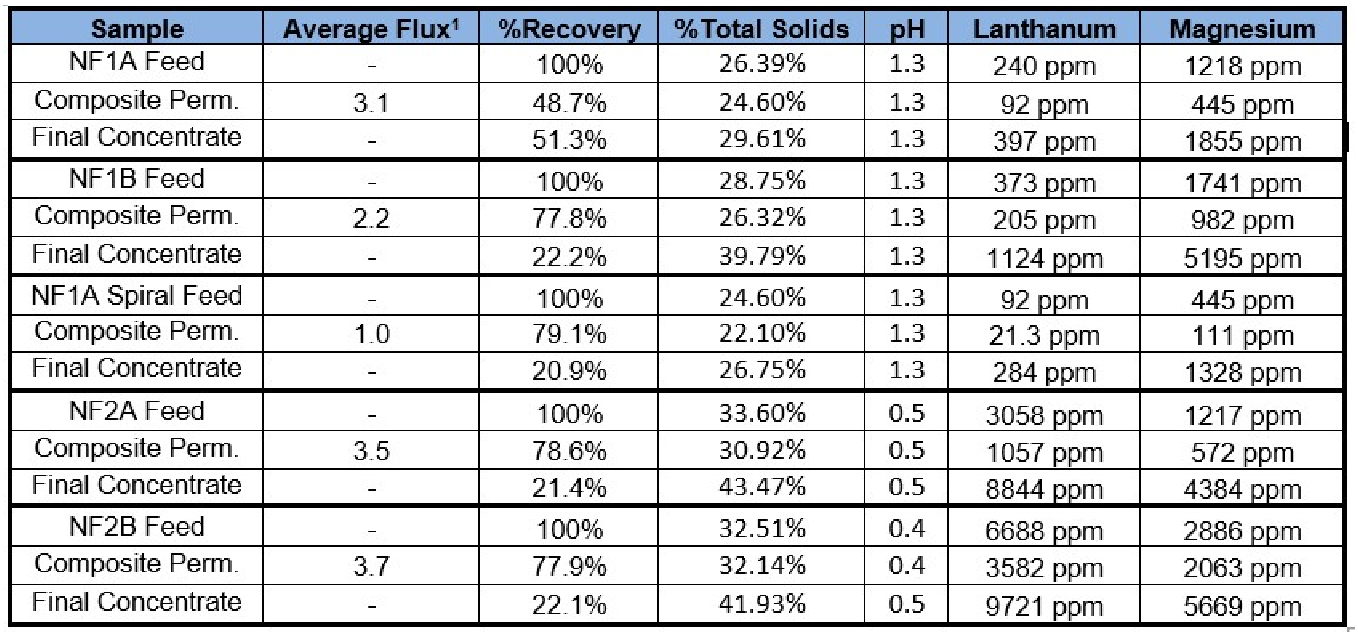
Figure 18 – VSEP LP in P-mode (left) with pump (center) and feed tank (right)

NF-3 P-Mode Concentration Testing

The NF-3 membrane was used to concentrate the phosphoric and sulfuric acid-based streams in the pilot flowsheet (Figure 6). Extensive modelling was performed to allow for Stage 1 and Stage 2 to be run independent of each other, but unlike the L-Mode testing, the products within each stage were carried over to the next step within the stage to better simulate actual operation.

Multiple repeat runs were performed on different NF-3 membrane stacks to ensure proper flux and analytical averages are covered. The results of the VSEP and spiral concentrations are shown in Table 4 below. Images of the samples from each stage are shown in Figures 19 through 23 below. The significant amounts of precipitated salts in the photos highlights the need for VSEP's vibration to ensure no plugging and higher throughput compared to traditional spiral wound systems.

Table 4 – NF-3 P-Mode Concentration Testing Average Flux, Permeate Recovery & Analytical



Sample	Average Flux[1]	%Recovery	%Total Solids	pH	Lanthanum	Magnesium
NF1A Feed	-	100%	26.39%	1.3	240 ppm	1218 ppm
Composite Perm.	3.1	48.7%	24.60%	1.3	92 ppm	445 ppm
Final Concentrate	-	51.3%	29.61%	1.3	397 ppm	1855 ppm
NF1B Feed	-	100%	28.75%	1.3	373 ppm	1741 ppm
Composite Perm.	2.2	77.8%	26.32%	1.3	205 ppm	982 ppm
Final Concentrate	-	22.2%	39.79%	1.3	1124 ppm	5195 ppm
NF1A Spiral Feed	-	100%	24.60%	1.3	92 ppm	445 ppm
Composite Perm.	1.0	79.1%	22.10%	1.3	21.3 ppm	111 ppm
Final Concentrate	-	20.9%	26.75%	1.3	284 ppm	1328 ppm
NF2A Feed	-	100%	33.60%	0.5	3058 ppm	1217 ppm
Composite Perm.	3.5	78.6%	30.92%	0.5	1057 ppm	572 ppm
Final Concentrate	-	21.4%	43.47%	0.5	8844 ppm	4384 ppm
NF2B Feed	-	100%	32.51%	0.4	6688 ppm	2886 ppm
Composite Perm.	3.7	77.9%	32.14%	0.4	3582 ppm	2063 ppm
Final Concentrate	-	22.1%	41.93%	0.5	9721 ppm	5669 ppm

1. Permeate Flux is given as a ratio of permeate flux of the membrane to the lowest observed flux.
2. % Solids means total TSS + TDS

While the pilot testwork is still in progress, it was observed that key rejection rates are well within the range of the averages of the laboratory results. Additionally, the average flux at increased feed concentration in the pilot testwork (150% more than the L-mode feed concentration) is also within the range of predicted limits. By concentrating the feed and pushing the limits the membrane to an optimum point, dilution water requirement for each stage is minimised. This results to the reduction of water make-up to the circuit and reduction of evaporative requirements in the phosphoric acid evaporator. By far, the optimised conditions of the pilot testing established the flexibility of the PA purification flowsheet to manage feed variabilities and room for further optimisation during actual operations.

Figure 19 – NF-3 P-Mode NF1A Feed, Concentrate and Permeate (left to right)

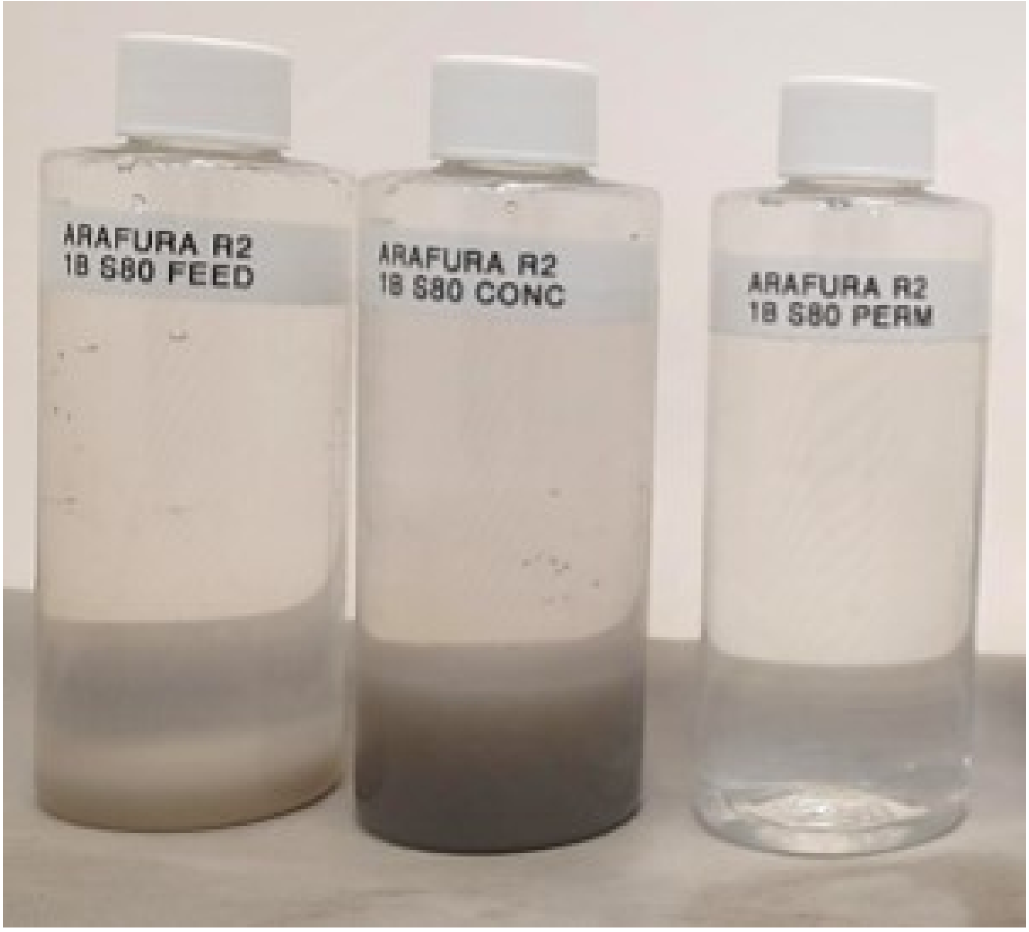


Figure 20 – NF-3 P-Mode NF1B Feed, Concentrate and Permeate (left to right)

Figure 21 – NF-3 P-Mode NF1 Spiral Feed, Concentrate and Permeate (left to right)

Figure 22 – NF-3 P-Mode NF2A Feed, Concentrate and Permeate (left to right)

Figure 23 – NF-3 P-Mode NF2B Feed, Concentrate and Permeate (left to right)

CONCLUSIONS

The PA Purification circuit is a strategic and integral part of the overall Nolans Rare Earths flowsheet. Following the results of laboratory and pilot testworks, it was established that nanofiltration process offers a viable technical solution to recover and purify the excess phosphoric acid and mixed acid (sulphuric + phosphoric acid) generated from the Nolans process. The wealth of data collected and analysed from the testworks established the ability of the flowsheet to manage variabilities and thus provides both Arafura and NLR a key confidence in the solution.

The application of NLR's innovative VSEP (Vibratory Shear Enhanced Processing) to the Nolans nanofiltration process provides operational flexibility and economic viability of the solution to the project.

The PA Purification circuit is now entering the detailed design engineering phase. As the project progresses, it is envisaged that the collaborative work of NLR and Arafura will go beyond the delivery of the Nolans project. The aim is to continuously improve the efficiency of the circuit with feed variability, along with the evolution in membrane filtration technology (i.e. new membrane, feed conditioning etc.).

ACKNOWLEDGEMENTS

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THE DEVELOPMENT OF SEARCH MINERALS' DIRECT EXTRACTION TECHNOLOGY FOR THE RECOVERY OF REE FROM ITS CRITICAL REE DISTRICT IN SE LABRADOR

By

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ABSTRACT

The Search Minerals Foxtrot project in Labrador represents a significant Canadian resource of critical rare earth elements rich in key magnet rare earth elements. A preliminary economic assessment of the project indicated that the project is technically feasible and economically attractive. Search is planning to validate its Direct Extraction technology in an 18-tonne hydrometallurgical demo plant at SGS Canada.

Since 2012, SGS has been working with Search Minerals to develop and optimize a simple and robust process flowsheet, proven during several pilot campaigns that operated from 2016 to 2022.

This paper will provide an overview of the testwork programs since 2012 and highlight how each program contributed to the process flowsheet from ore to final purified product options (Mixed RE Oxide or Mixed RE Carbonate). It will also focus on some of the challenges that were encountered and overcome along the way and will describe the current state of development.

Keywords: rare earth element, acid bake, thorium, process development, pilot plant

INTRODUCTION

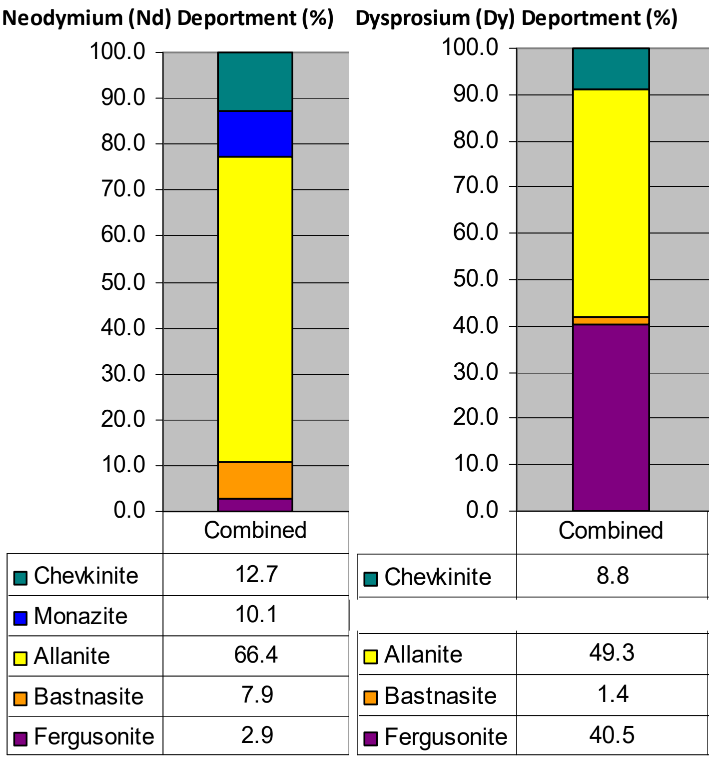
The demand for rare earth elements is increasing dramatically due to their growing use in advanced technology applications such as electric vehicles, smart phones and wind turbines. In order to meet increasing demand, new sources of rare earths must be identified. Goode(1) reported in 2022 that REE demand will double in the coming 7-11 years, mainly driven by magnet REE requirements. In 2021 the global REE production was 280,000 tonnes of rare earth oxide, and so to double in 10 years, 28,000 t/a of additional production is necessary each year. To put this in perspective, MP Materials produces 43,000 t/a at Mountain Pass and Lynas produces 22,000 t/a from its Mt Weld deposit.

Search Minerals has identified a Critical Rare Earth Element (CREE) district in south-eastern Labrador in the province of Newfoundland, Canada. The CREE district is ~64 km long and 8 km wide and contains two deposits that have been drilled for 43-101 resource definition (Foxtrot and Deep Fox) (2)(3)(4). In addition, three prospects have been sampled on surface by channeling (Fox Meadow, Fox Valley and Silver Fox) and approximately 20 exploration targets that will be progressively explored. An initial small drilling program was conducted at Fox Meadow in 2022 with assay results pending. In addition, each deposit contains significant grades of zirconium and hafnium. Zirconium and hafnium recovery is currently under investigation using conventional mineral processing techniques. Zircon flotation after REE WHIMS magnetic recovery has been explored with good results. A preliminary economic assessment of the project indicated that the project is technically feasible and economically attractive(4). Important infrastructure is already available; a deep water port, air strip, road and power infrastructure are pre-existing at Port Hope Simpson. The three communities of Port Hope Simpson, St. Lewis, and Mary's Harbour are in close proximity to the site.

Table 1 shows the resources and selected grades available at Foxtrot and Deep Fox(4). The major elements of value are the magnet making rare earths (Pr, Nd, Dy, and Tb). The predominant rare earth minerals identified at Foxtrot are allanite (LREE rich) and fergusonite (HREE rich). Figure 1 provides elemental deportments for neodymium and dysprosium. Allanite and fergusonite carry most of the Dy at 49.3% and 40.5%, respectively, followed by chevkinite (8.8%) and bastnasite (1.4%).

Table 1: Summary Mineral Resources Deep Fox and Foxtrot as of Dec 31, 2021

Classification	Tonnes	Pr (g/t)	Nd (g/t)	Dy (g/t)	Tb (g/t)
Open Pit					
Indicated	8,483,000	381	1,422	187	32
Inferred	1,441,000	329	1,231	179	30
Underground					
Indicated	6,611,000	368	1,376	182	31
Inferred	4,862,000	380	1,427	191	33
Totals					
Total Indicated	15,094,000	375	1,402	185	32
Total Inferred	6,303,000	369	1,382	188	32



Neodymium (Nd) Deportment (%)	Combined
🟩 Chevkinite	12.7
🟦 Monazite	10.1
🟨 Allanite	66.4
🟧 Bastnasite	7.9
🟪 Fergusonite	2.9

Dysprosium (Dy) Deportment (%)	Combined
🟩 Chevkinite	8.8
🟨 Allanite	49.3
🟧 Bastnasite	1.4
🟪 Fergusonite	40.5

Figure 1: Elemental Deportment of Neodymium (left) and Dysprosium (right)

Since 2012, SGS has been working with Search Minerals to develop and optimize a simple and robust process flowsheet, proven during several pilot campaigns that operated from 2016 to 2022. Metallurgical progress has been reported regularly(5)(6)(7)(8)(9)(10) leading up to the development of the Direct Extraction technology, which was patented in 2019(11). The key elements of the Direct Extraction Process are rock crushing, acid mixing and baking at 180–200°C, water leaching, iron precipitation, mixed rare earth carbonate precipitation, acid re-leaching of the mixed carbonate, purification of the releach solution for minor elements (including uranium, thorium, and zinc) and precipitation of a high purity final rare earth product.

Search is planning to validate its Direct Extraction technology in a 18-tonne hydrometallurgical demo plant at SGS Canada. The demo plant is supported by the Government of Canada who is contributing $5 million in non-dilutive support to Search Minerals via a Contribution Agreement, which will be used to fund the construction and operation of a demonstration plant for rare earth extraction and recovery. The total project cost is estimated at approximately $9.3 million with a further $1 million of funding under application from other sources. Search Minerals' contribution to the construction and operating costs is expected to be approximately $3.3 million(12).

HISTORIC PROCESS DEVELOPMENT

Preliminary metallurgical testing was initiated in 2012 and focused on beneficiation followed by acid baking and water leaching (5). While a modest concentration was achieved in the beneficiation, this was at the expense of REE losses to tailings. From 2014 to 2017, the approach switched to the development of the Search Minerals Direct Extraction Process (11). The key element of the Direct Extraction Technology is the elimination of the grinding and beneficiation circuits. Due to the low acid demand by gangue minerals and the ability for acid to soak into relatively coarse particles, a whole ore acid bake process was developed, leading to comparatively high overall recoveries while also displaying friendly material characteristics within the acid bake process.

From 2019 to 2020 several improvements to the Direct Extraction technology were incorporated, consisting of a re-arrangement of the acid-feed mixing step and changes to the uranium and thorium removal circuits(9). The following sections provide further detail about the various programs.

2012 Flowsheet (Crush/Grind, Beneficiation, Acid Bake)

The early metallurgical testwork on Foxtrot ore samples focused on mineralogy, beneficiation, concentrate sulphation, and water leaching followed by PLS purification and recovery of rare earths as a mixed oxalate precipitate (5). Gravity, magnetic separation, and flotation were applied to a bulk sample of Foxtrot ore to produce an upgraded mineral concentrate of around 2.5% TREO. The reported REE recovery averaged 83% to a concentrate containing 38.5% of the original mass.

The concentrate was then subjected to acid baking and water leaching to produce an acid leachate containing a 2.5 to 3 g/L TREE liquor. Testwork showed that 96% Nd and 94% Dy could be extracted into a water leach solution at 1000 kg/t H_2SO_4 addition and bake temperature of 200°C. The solution was then purified by pH adjustment using MgO to reject iron, thorium, and some degree of aluminum. Rare earths were subsequently precipitated with oxalic acid to make a mixed rare earth oxalate containing over 55% TREO content, but also containing 5 g/t U and 163 g/t Th.

The key issues and observations with respect to the 2012 flowsheet can be summarized as follows:

1. Complex beneficiation: The use of gravity, magnetic, and flotation separation to produce a high mass recovery concentrate with ~17% loss of rare earth values to tailings is costly in both capital and operating cost, and the loss of rare earth elements is a heavy penalty on potential mine revenue. Even at optimum acid bake leach conditions, overall recovery of REE from ore into a PLS was 80% Nd and 78% Dy. The use of three separate beneficiation techniques that have minimal benefit in overall concentration of value did not appear to be justified.
2. Potential challenging material handling in acid/feed mixing step due to fine grind and high acid addition relative to concentrate mass.
3. Optimization of reagent use: The use of sulphation and water leaching was highly effective at extracting the rare earth elements from the mineral concentrate. However, there was little opportunity for optimization of the sulphation conditions in the early work.
4. Impurity control: The use of simple pH adjustment to reject thorium followed by oxalate precipitation was effective in recovering a crude mixed rare earth oxalate. However, the levels of thorium (at 163 ppm in the oxalate precipitate) were considered too high to be acceptable to a rare earth refinery.

2014-2017 Development of Direct Extraction Technology

Bench Testwork – 2014/2015

In 2014, testwork resumed with an overall objective to simplify the process flowsheet by attempting to treat whole ore (avoiding the cost and metal loss associated with comminution and beneficiation), reduce the operating cost per unit of recovered rare earth oxide, and produce a premium quality product (mixed rare earth oxide) low in thorium for further refining. The direct treatment of Foxtrot ore was investigated through a series of studies on acid baking/water leaching, solution purification, RE precipitation, RE re-dissolution and purification to remove thorium, and finally RE precipitation with oxalic acid and calcination to make a mixed REO as per flowsheet shown in Figure 2. Details of this work were presented by Dreisinger et al.(7)

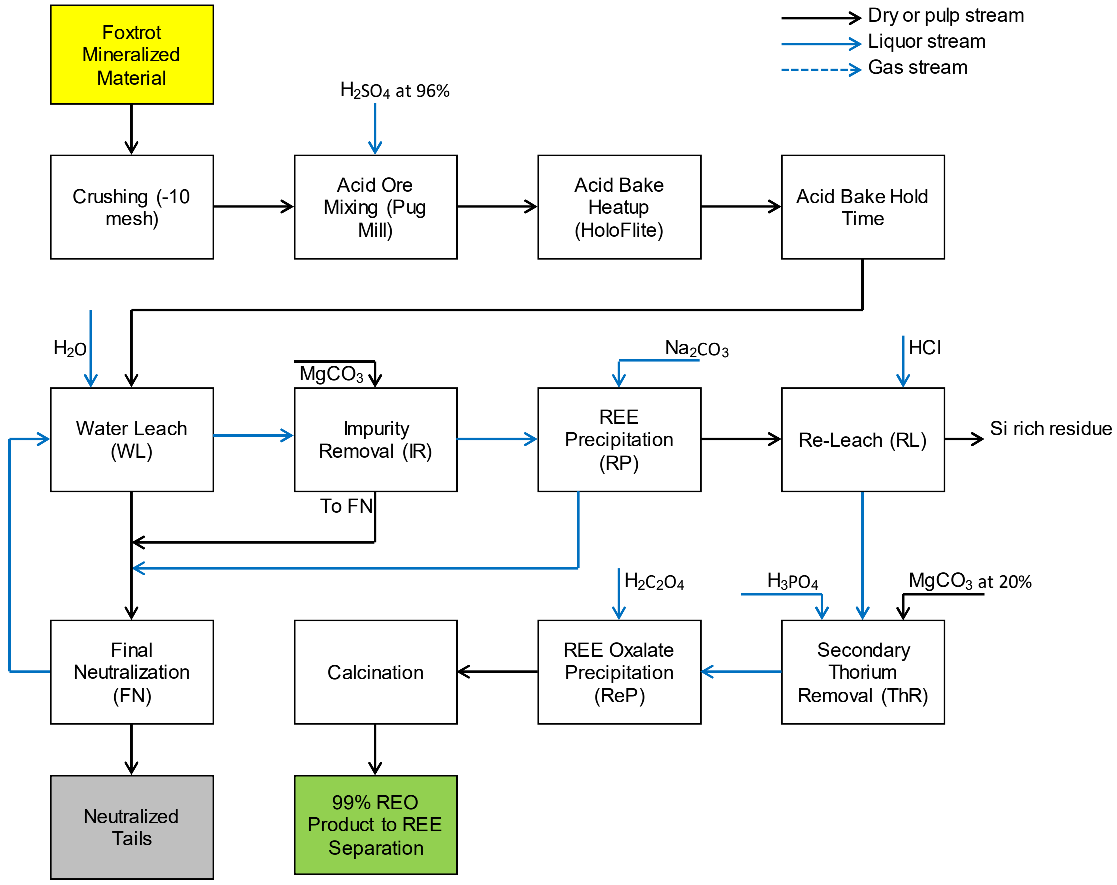


Figure 2: BFD - Direct Extraction - 2014

Acid bake testwork was conducted to investigate the effect of crush/grind size and acid addition. Figure 3 shows the results of the initial testing on the impact of crush size and acid addition. Ore test charges (100 g) were treated with 1500 kg/t of H_2SO_4 for 4 hours at 200ºC in a static bake and then water leached for 24 hours to extract the REE's into solution. The acid bake extraction of REE's from the minus 10 mesh material was almost the same as the original concentrate (also shown on the graph - left). The direct extraction of the light REE's approaches 95%. The impact of acid addition at 6 mesh is illustrated in the right graph in Figure 3. At acid additions in the range of 100-250 kg H_2SO_4/t, the REE extractions were still as high as ~ 85% for the light REE's. Additional tests (Figure 4) illustrated the effect of water leach temperature and time indicating that an extended hot water leach promotes increased REE extraction. Neodymium concentrations were still increasing after 24 hours indicating that longer than 24 hours may lead to additional extraction.

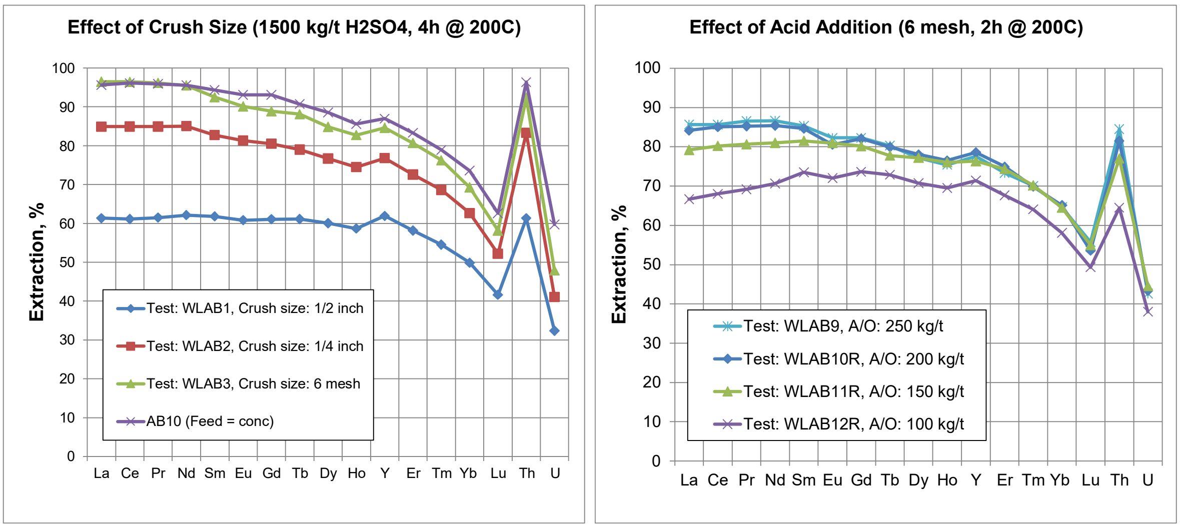


Figure 3: Acid Bake Testing: Effect of Crush Size (left) and Acid Addition (right)

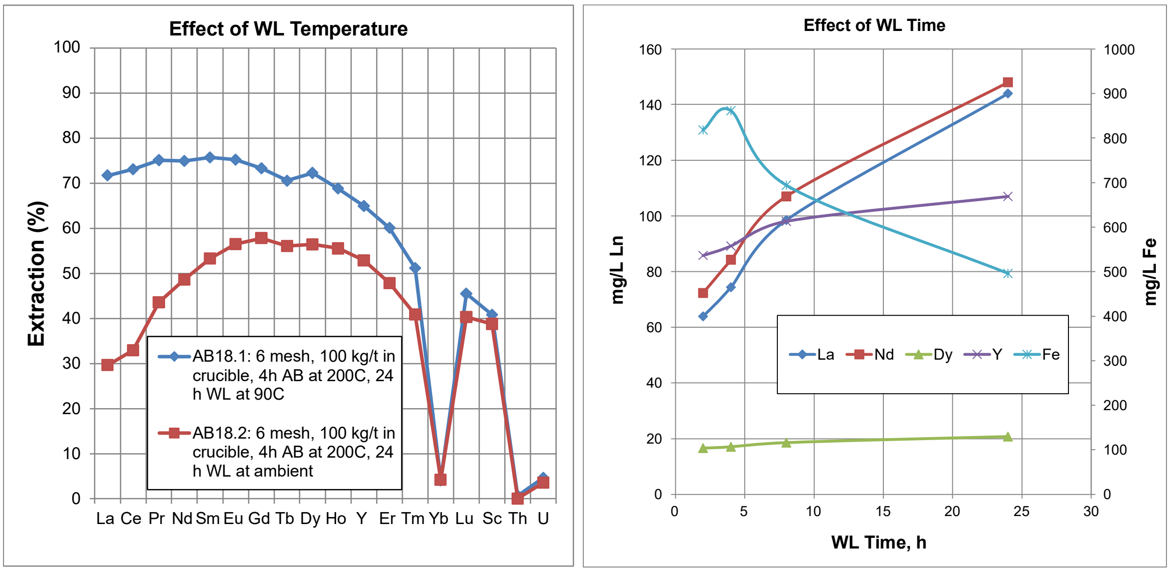


Figure 4: Acid Bake Testing: Effect of WL Temperature (left) and Retention Time (right)

Using a composite PLS, the removal of impurities was tested by pH adjustment and oxidation (for Fe removal). Three alkalis were tested including MgO, $MgCO_3$, and Na_2CO_3. For each test, the removal of impurities appeared to be maximized with minimum rare earth loss due to co-precipitation. All three alkalis were successful, with magnesium carbonate ($MgCO_3$) selected for further bulk testing at pH 3.75, 75°C, and ORP adjustment to 600 mV. More than 90% of the iron was eliminated along with 88.4% of the thorium. There was also significant rejection of Si, Al, Ti, and P. REE losses to the impurity removal precipitate ranged from 0.74 to 3.6% from La to Lu. Note that the final precipitate was analyzed at 0.018% Mg, indicating a high efficiency of $MgCO_3$ use.

The partial purified solution was treated with a soda ash solution (Na_2CO_3) to precipitate the REEs into a mixed carbonate product for further purification. This was a further change in procedure from the earlier work (5) where oxalic acid was added as the primary REE precipitant. A pH target of 7.25 at ambient temperature was set. The results are presented in Table 2 below, showing precipitation of REEs approaching 100%. The co-precipitation of Th, U, Fe, and Al is similarly very high.

The mixed carbonate product was subsequently re-leached with 37% HCl solution at pH 1 for 1 hour at 80°C. The chloride leach solution was then treated with 15% slurry of MgO in deionized water to pH 3.8 at 50°C for 1 hour to reprecipitate re-leached thorium. The re-leach process was virtually 100% effective in re-dissolving the REEs, and the re-leach residue and thorium removal residue would be returned to the water leach process to recover any lost REEs. The thorium depleted solution was treated with oxalic acid to selectively precipitate the REEs, followed by calcination at 750°C for 4 hours to produce a final mixed rare earth oxide product. The assay of the rare earth oxalate and the calcined rare earth oxide are shown in Table 2. Despite the significant selectivity of REE oxalate precipitation against uranium and zinc, these elements were still elevated in the final precipitate.

Table 2: Crude (left) and Final (right) Rare Earth Precipitation

Element	PPt Units	Crude REE Precipitation				Final REE Precipitation		
		Feed sol'n	Filtrate	Precipitate	PPT	RE Oxalate	PPT	RE Oxide
		Assay (mg/L, %, g/t)			%		%	
TREE	%			34.8		35.7		66.1
La	g/t	134	0.24	57700	100	58900	97	110000
Ce		315	0.39	129000	100	135000	100	250000
Pr		36.3	0.06	15600	100	16000	100	29500
Nd		136	0.18	58800	100	64900	100	119000
Sm		26.1	0.05	11000	100	10800	100	19900
Eu		1.39	0.03	584	98	573	100	1060
Gd		23	0.04	10900	100	10200	100	18300
Tb		3.62	0.03	1640	99	1570	100	2820
Dy		20.8	0.05	9270	100	8850	100	16100
Ho		4.08	0.02	1800	100	1730	100	3180
Y		107	0.3	42100	100	39500	98	75600
Er		11.1	0.04	4880	100	4670	99	8560
Tm		1.46	0.04	636	97	590	99	1070
Yb		7.92	0.03	3470	100	2910	99	5350
Lu		0.93	0.03	409	97	348	99	629
Sc		0.07	0.07	40	55	< 50	94	< 50
Th		0.85	0.04	422	96	3.6	73	6.5
U		1.07	0.13	467	88	21.1	7.5	48.5
Al	%	83.6	0.5	3.67	99	<0.01	3.1	<0.01
Fe		39.3	0.2	1.81	100	0.001	18	
Mg		1550	1560	0.505	0.7	0.020	0.2	0.03
Ca		616	583	1.95	6.6	0.15	6.9	0.26
Mn		77.4	68.8	0.131	3.9	<0.001	0.2	<0.001
Zn						0.08	3.1	0.15

Bench Testwork – 2016

The objectives of the 2016 testwork program were to:

- Prepare for the integrated pilot plant
- Optimize the flowsheet and improve impurity removal, particularly that of uranium and zinc
- Simplify the crude RP re-leach circuit by replacing hydrochloric acid with sulfuric acid.

While a number of bench scale acid bake and water leach tests were conducted, these were not large enough to provide sufficient filtrate to carry testwork forward to the impurity removal, REE precipitation, and other downstream processes. Bulk testwork was required to produce sufficient sample to test the downstream processes. A 6-inch diameter Bartlett-Snow rotary calciner/kiln was used in concert with a large walk-in Grieve oven to conduct a semi-continuous acid bake program, followed by bulk water leaching. Material handling within the rotary kiln operation was easy and the material flowed easily through the kiln without excessive caking. Photographs of the acid bake operation are shown in Figure 5. The material was free flowing at the acid/feed mixing, kiln feeding, and kiln discharge steps. Acid baked material was batch water leached and treated with $MgCO_3$ to reduce Fe/Th and Al levels.

Figure 5: Acid Bake Operation

To reduce uranium levels in the final REE oxide, conventional uranium IX (Purolite A660 resin) was introduced in-between the primary impurity removal (IR) and crude rare earth precipitation (RP). Test results showed that uranium removal was successful with >99% loading.

While hydrochloric acid re-leaching of primary rare earth precipitates worked well, sulfuric acid re-leaching was preferred due to lower reagent costs. Initial re-leaching targeted a 50-60 g/L TREE liquor, but such solutions set up as a gel overnight, leading to subsequent re-leach tests targeting a 25-30 g/L TREE liquor. Additional impurities included 0.9 mg/L Sc, 0.2 mg/L U, and 9.8 mg/L Th. Base metal impurities included 2.9 g/L Al, 1.3 g/L Fe, and 2.8 g/L Zn along with 114 mg/L Be and 460 mg/L Mn.

Selective removal of thorium, iron, and aluminum from both chloride and sulphate REE-rich releach liquor was studied. Iron in solution is converted to iron phosphate with addition of phosphoric acid; thereby lowering the pH at which iron will precipitate. Figure 6 includes select test results of secondary thorium removal testing. In the sulphate feed scenario, removal of 93% Th, 99% Fe, 43% Al, and 7% U was achieved at the expense of 5% Nd and 4% Dy. The final liquor contained 0.64 mg/L Th and 26.7 g/L TREE. The yellow-coloured solids produced contained 6.88% Fe, 7.09% Al, 3.60% P, and 474 g/t Th and 12.8% REE (1.53% Nd). These solids made up 1.5% of the overall test pulp and filtered relatively quickly. In the chloride feed scenario, removal of 100% Th, 100% Fe, 28% Al, and 27% U was achieved at the expense of 2% Nd and 2% Dy. The liquor product from the chloride test contained 0.04 mg/L Th and 31.6 g/L TREE. The cayenne-coloured solids produced contained 10.9% Fe, 7.04% Al, 4.93% P, and 712 g/t Th and 4.18% REE (0.79% Nd). These solids made up 1.1% of the overall test pulp. The wet solids were waxy and filtered slowly.

Precipitate from the sulphate-based secondary thorium removal test was acid-baked at 2001 kg/t sulphuric acid and 80°C, then water-leached to recover REE units into solution as a possible recycle stream. Full REE digestion was achieved, resulting in 26.5 g/L REE stream and 184 g/L H_2SO_4. This has shown that any REE “lost” in the thorium removal step can be fully recovered.

Sulphide precipitation of zinc was studied at 50°C. Based on a titration test, an ORP of -200 mV was selected for subsequent tests. In all tests, over 99% of Zn precipitated along with most of the copper and cadmium producing a zinc sulphide (65% Zn, 33% S, less than 0.1% REE).

Based on these results sulphuric acid re-leaching was shown to be feasible and was selected for the pilot plant flowsheet. A revised block flow diagram is included in Figure 7.

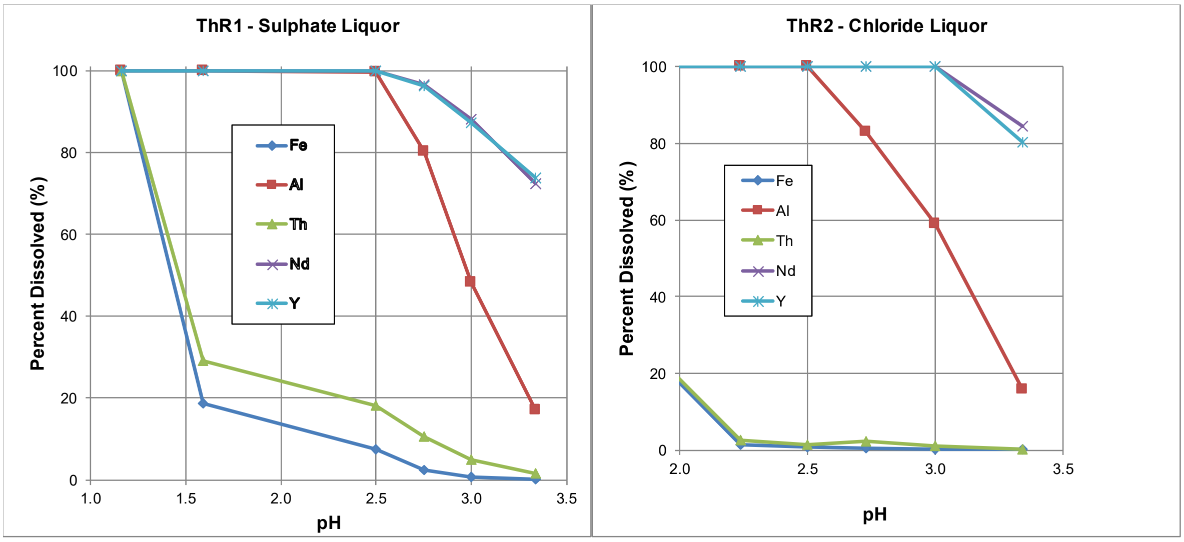


Figure 6: Secondary Thorium Removal

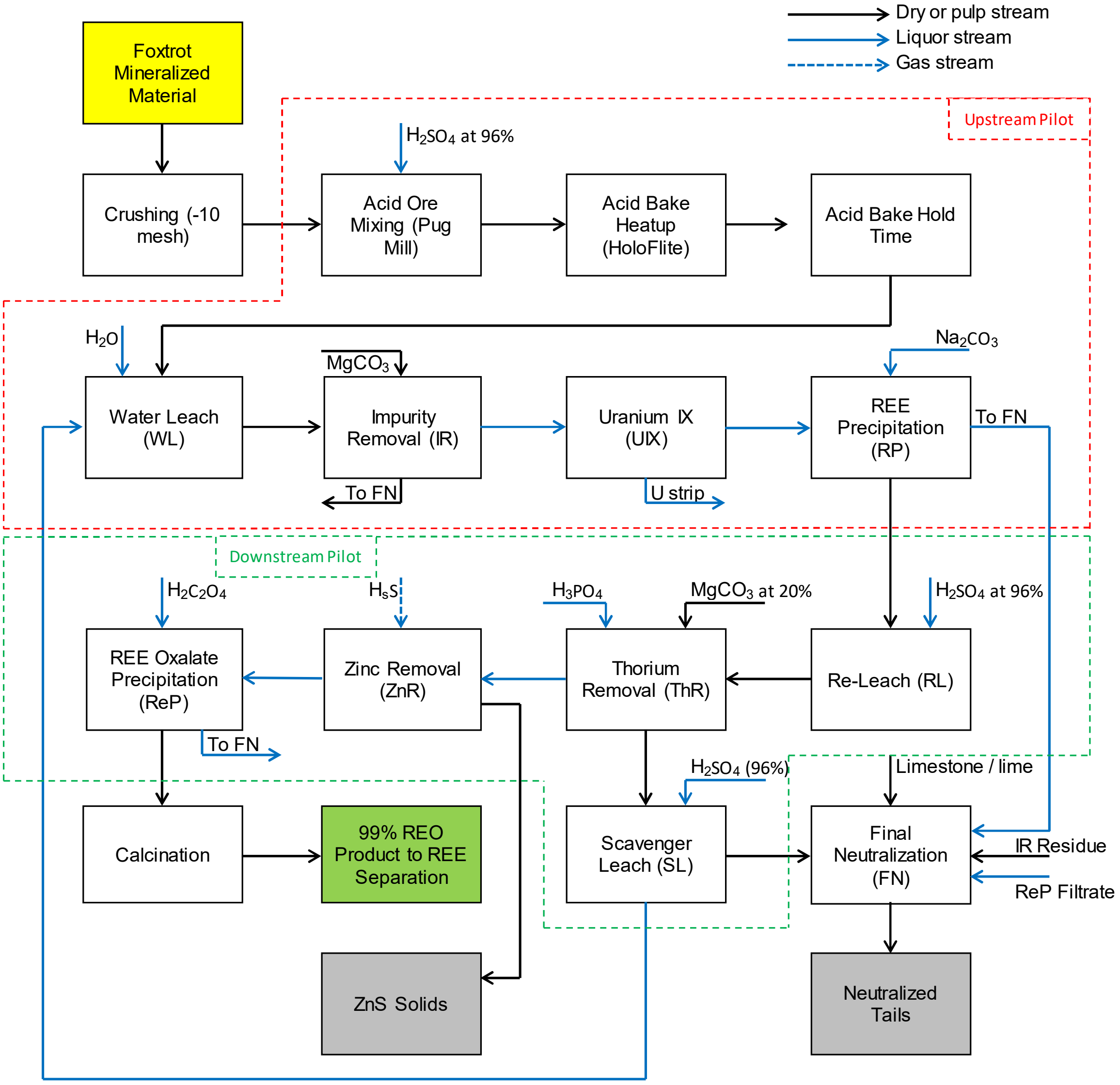


Figure 7: BFD - Direct Extraction - 2017

Pilot Plant Operations (2017)

Three pilot plant campaigns were conducted(8) to test the Search Minerals Process treating Foxtrot ore (0.90% TREE) from the Acid Bake circuit to the Rare Earth Element precipitation circuit. The "as piloted" flowsheet is depicted in Figure 7, with the pilot campaign battery limits indicated.

The overall flow sheet was split into two different pilot circuits, consisting of:

- Upstream circuits: Acid Bake (AB, consisting of Mixing, Heating and Holding Time), Water Leach (WL), Impurity Removal (IR), Uranium IX (UIX), and REE Precipitation (RP). Two separate campaigns (PP1 and PP2) were carried out for a total run time of 12 days. Product from RP was used in the downstream circuit;
- Downstream circuits: Re-leach (RL), Thorium Removal (ThR), and Zinc Removal (ZnR). One single campaign (PP3) of 4 days was carried out.

Upon completion of the pilot campaigns, the final rare earth oxalate precipitation, calcination, scavenger leach, and final neutralization were operated batch-wise.

Crushed ore (-10 mesh) was treated in a three-step acid bake process consisting of acid/ore mixing (at a sulphuric acid dosage of 144 kg/t) in a pug mill, followed by heating the acid/ore mixture in a HoloFlite to approximately 190°C. The heated material was then maintained at the target temperature in a static walk-in oven. While this circuit operated well for periods of time, significant wear and tear of the HoloFlite screws interfered with its capability to transfer material adequately. Photographs of the setup are shown in Figure 8 and in Figure 9.

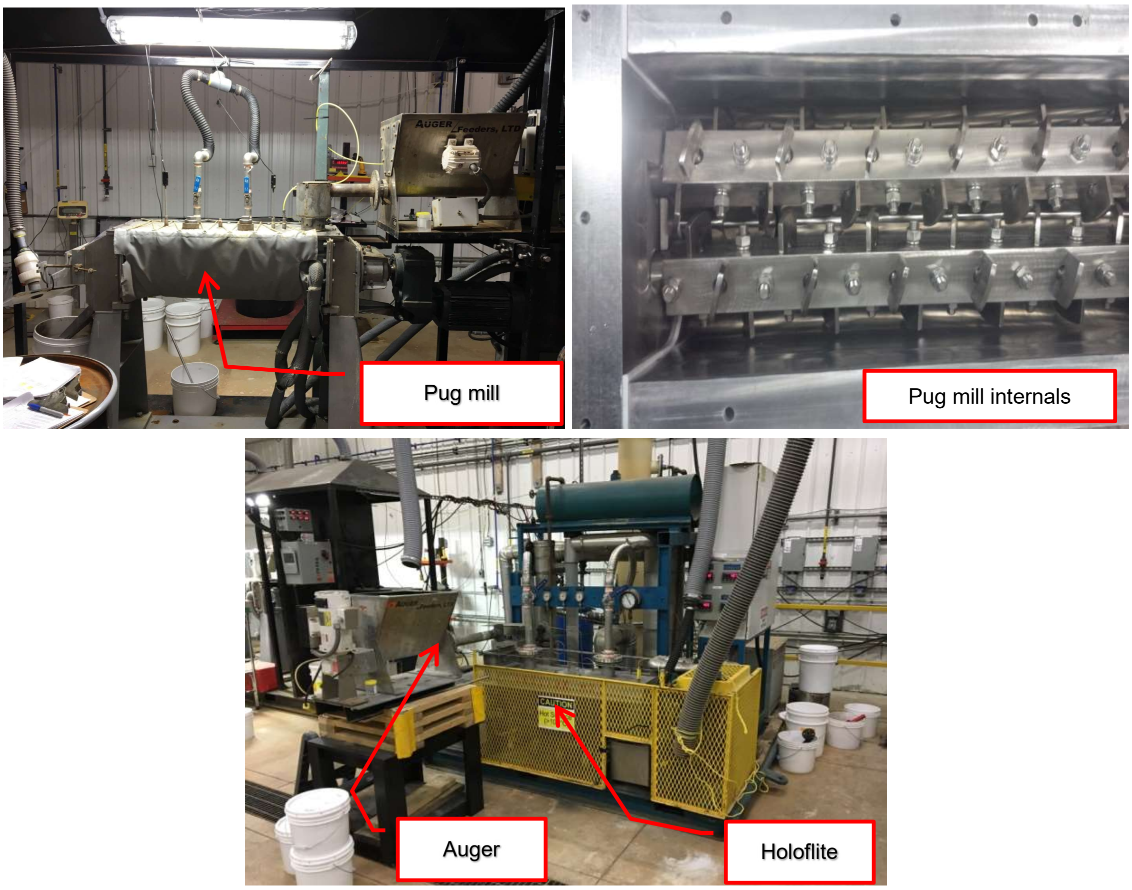


Figure 8: Acid Feed Mixing and Heating Pilot Equipment

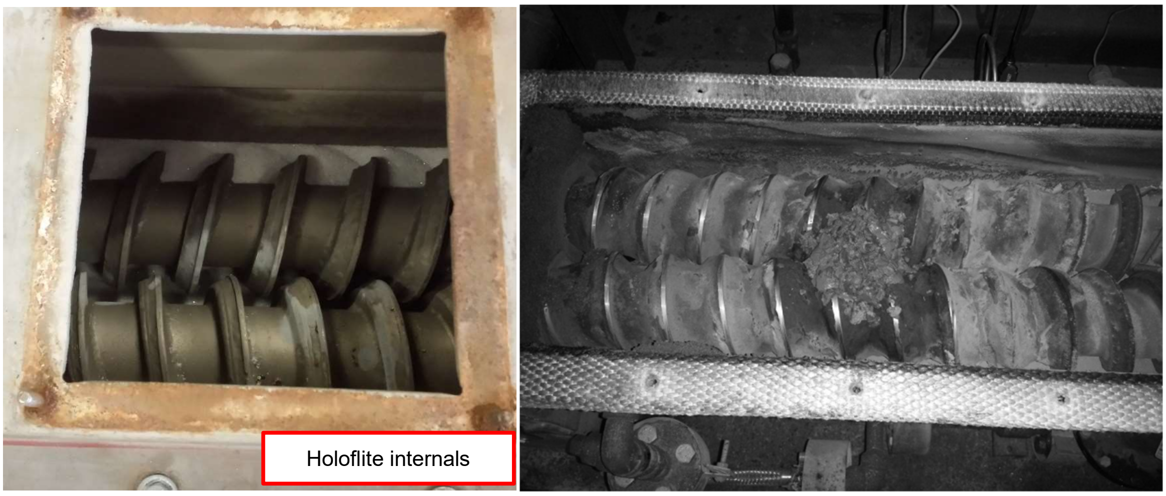


Figure 9: Pilot Holoflite Internals (Left: before pilot. Right: after pilot)

The calcined material was removed from the walk-in oven and processed in a water leach tank train to selectively dissolve REE. Figure 10 shows photographs of this operation before and after piloting. Due to the coarse size of the solids, challenges were encountered around advancing the solids from tank to tank. Using a pump to transfer pulp between tanks solved much of this problem. Measured extractions were high, with neodymium extraction ranging between 82 and 89% and dysprosium extraction ranging between 63 and 73%. Water leach pulp was treated with hydrogen peroxide and magnesium carbonate in an impurity removal circuit, which precipitated 92% of the dissolved thorium as well as close to 100% of the iron. Rare earth losses were below 2% under optimized conditions, leading to an overall extraction of 83% Nd and 66% dysprosium. The combined water leach/impurity removal pulp filtered well on a filter press, producing a PLS of around 0.75 g/L TREE.

Figure 10: Calcine Holding Oven and WL Circuit

Uranium was successfully extracted using two ion exchange columns (lead and lag) filled with a strong base anion resin (the pilot plant used Purolite A660). Uranium extraction was virtually quantitative (>98%) while REE co-extraction was negligible (<0.1%). The circuit did not run long enough to reach maximum loading capacity on the column and no elution testwork was carried out.

Raffinate from UIX was reacted with sodium carbonate to produce an impure (crude) intermediate rare earth carbonate precipitate of around 30% TREE. Key impurities in this stream included thorium (400-500 g/t), silicon (~6%), aluminum (6.8%), and iron (0.35%) as well as around 3% zinc. The downstream circuit was designed to separate REE from these impurities.

The intermediate rare earth precipitate was re-leached in pH 1 sulphuric acid to form a ~25 g/L TREE leach solution which was subsequently treated using phosphoric acid and magnesium carbonate to remove the remaining levels of thorium.

Due to the low allowable limit on thorium in the final product, this circuit was required to operate at a relatively high pH of ~4.8, and REE co-precipitation was significant (40-50%) as illustrated in Figure 11. Co-precipitated REE were subsequently recovered in a standalone scavenger leach process, which was capable of re-dissolving (99.8%) the contained REE and Th which in a commercial operation would be returned to the upstream impurity removal circuit. While the overall REE losses were negligible in these circuits, the operation was not efficient and very sensitive to pH fluctuation. Moreover, the required scavenger operation led to additional reagent consumption. A post pilot plant series of bench tests aimed to improve this part of the flowsheet.

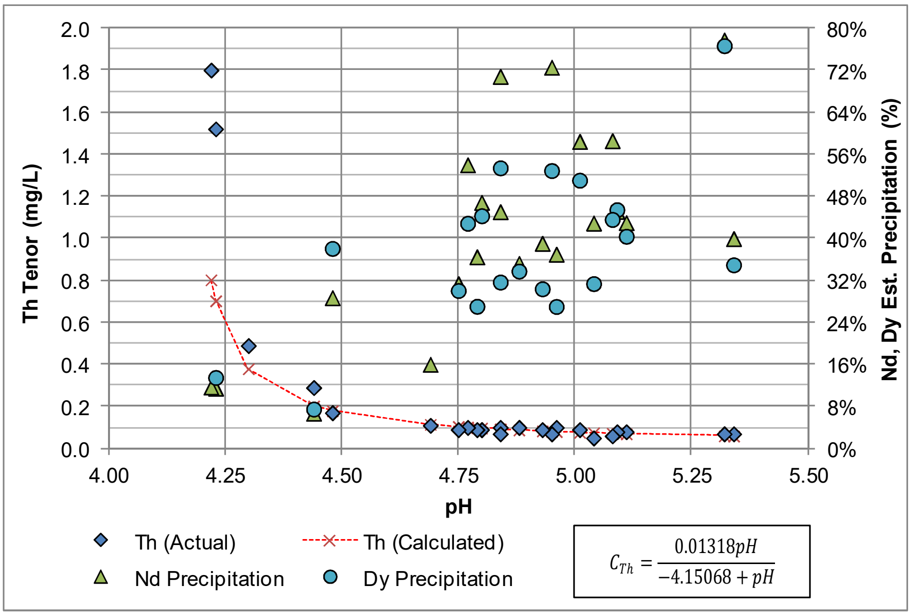


Figure 11: Relation between Th levels and Nd/Dy Co-precipitation

Thorium free filtrate was subsequently treated in a zinc removal circuit with gaseous hydrogen sulphide to selectively precipitate zinc sulphide. Operation of this circuit was found to be relatively straightforward with high zinc precipitation efficiency of 98% and low REE losses of <0.02%. Zinc removal filtrate was stored during the pilot plant for batch off-line rare earth oxalate precipitation testing.

2019-2020 Improvements to Direct Extraction Technology

In 2019, further refinements to the Direct Extraction Technology were investigated, focusing on three aspects:

1) Mixing of preheated acid and whole ore, rather than cold mixing and subsequent heating
2) Rearrangement of the process to incorporate uranium removal (UIX) after releaching of the intermediate REE precipitate
3) Removal of residual thorium after releach via solvent extraction, rather than selective precipitation

Preheated Ore and Acid Mixing

Mixing of preheated acid and whole ore offered no discernable change in the chemical performance of the acid bake and water leach step, with 85-90% LREE extraction and 70-80% HREE extraction still achieved. This was successfully scaled up and tested continuously using a screw heater for the ore and a heated tank for the acid, mixing the two in a pug mill before holding statically at temperature in a box furnace (heaters and pug mill pictured in Figure 12). While chemical performance was the same, so too was the abrasiveness observed during the initial continuous pilot plant testing. The stainless steel (SS316) paddles of the pug mixer were eventually worn down (through combined corrosion and erosion) and unable to properly advance material through the pug mill (seen in Figure 13), leading to significant material buildup. While this is partially attributed to materials of construction of the pilot plant, it also indicates that the nature of the material does not change whether the heat is supplied in advance of mixing or during. It is assumed that more resistant metal alloys will be required for heated mixing of the acid and ore at scale.

Figure 12: Screw Feeder and Pug Mill Utilized for Acid/Ore Heat and Mixing

Figure 13: Pug Mill Interior After Shutdown

Uranium Removal on Releach Solution

In a similar vein, moving the UIX from before to after intermediate REE precipitation and re-leaching was successful. Intermediate REE precipitate containing uranium was re-leached with sulphuric acid at pH 1, followed by a pH adjustment to 3.5 using magnesium carbonate to reject major contaminates (Si, Fe, and partial removal of Al), and then passed through a lead-lag ion exchange configuration using Purolite A660. Uranium was reduced from ~32 mg/L to <0.02 mg/L, demonstrating that the UIX can be operated on a more concentrated liquor instead of directly after water leaching and impurity removal when uranium concentrations are 1-2 mg/L.

Thorium Removal via Solvent Extraction

To investigate alternative thorium removal, a specific solvent extraction process was developed using Primene JMT (primary amine) as the extractant, based on historic published data(13)(14). Solvent extraction was developed first at bench scale and then confirmed in a continuous pilot plant that operated for five days.

The best results were obtained when using a dilute organic, with 1% Primene JMT and 2.5% tridecanol (modifier) by volume in Aromatic 150ND diluent. Thorium extraction was found to improve with a lower aqueous feed pH, necessitating a reacidification to pH 1.5 after the releach and pH adjustment to 3.5 to reject Si/Fe/Al. With these conditions, bench extraction tests routinely produced raffinates with <0.1 mg/L Th, the expected level required to ensure <5 g/t Th in the final product.

Thorium stripping from the loaded organic initially investigated the use of sodium chloride; this was partially successful at 1/1 phase ratios when 1 M NaCl was used, with 58% Th stripping achieved. Soda ash stripping was also tested to much greater success (>97% stripping) but the resulting separated phases were cloudy with suspected precipitation of residual REE carried forward through co-extraction and entrainment in the organic. To avoid potential three-phase systems from forming, the focus shifted back to using a combination of sodium chloride and hydrochloric acid, as well as either sulphuric or hydrochloric acid alone. It was found that chloride-based stripping (either with or without sodium) was successful, while sulphuric acid failed to strip thorium. However, it did result in removal of some of the co-loaded REE. Through further testing, it was also found that thorium stripping was much more effective under a controlled atmosphere (either a sealed separatory funnel or a mixer/settler with an inert gas purging the head space.

After developing the SX process at bench scale, it was operated continuously over a five-day pilot plant campaign. The configuration is shown in Figure 14, consisting of two counter-current stages each for extraction, scrubbing, and stripping. Extraction ran at 45°C with an advance phase ratio of 5/1 A/O, while the scrub stages were treated with 0.25 M H_2SO_4 at an advance phase ratio of 0.5 A/O (with an internal aqueous recycle to force a 1/1 ratio in the mixer). Scrub solution was directed to the extraction stages, mixing with the extraction feed solution. Stripping used 0.5 M HCl, added at a phase ratio of 1.25/1 A/O, also with an internal aqueous recycle. While extraction was operated warm, both scrubbing and stripping were at ambient temperature.

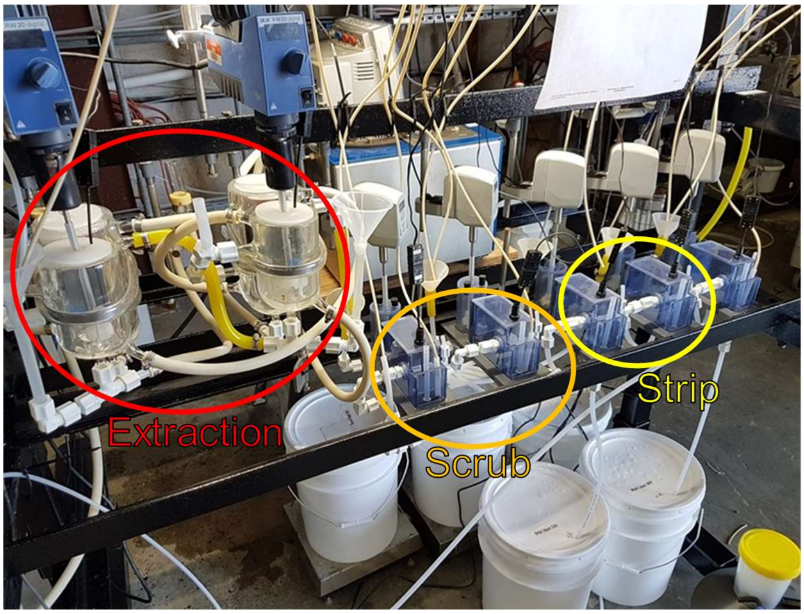


Figure 14: Solvent Extraction Pilot Apparatus for Th Removal

Feeding at ~5 mg/L Th, the process routinely provided raffinate concentrations of <0.03 mg/L Th, or >99% extraction. This exceeded the target limit of <0.1 mg/L. Co-extraction of REE was typically <1% throughout the campaign, partially recovered in the scrubbing stages and recirculated back to extraction. What is not recovered in scrubbing is recovered with thorium in stripping, which can be returned to the upstream leach unit operation for REE recovery and combining the thorium streams for a single outlet.

The solvent extraction circuit was stable and well behaved throughout the continuous pilot plant. The organic solution was continuously recycled throughout operation and showed no signs of chemical degradation or fouling by any chemical species building up through insufficient stripping. The implementation of thorium solvent extraction is a major enhancement to the process when compared to the pH adjustment/precipitation method used in the originally developed process that was tested in 2016 and has been adapted into future process designs for the Search Minerals Direct Extraction Process.

RECENT PROCESS DEVELOPMENTS

2021-2022 Production of Mineral Concentrate (Lab and Pilot Tests)

In 2021, four composite samples from Silver Fox, Fox Trot, Deep Fox, and Fox Meadow, respectively, were received and prepared for magnetic separation. The beneficiation potential to produce a rare earth concentrate by magnetic separation was evaluated using a low-intensity magnetic separator (LIMS) and a wet high-intensity magnetic separator (WHIMS). Each sample was stage-ground to 100% passing 53 µm, chosen as good liberation (>90%) of rare earth minerals was expected based on the mineralogy analysis.

Representative samples of each Composite were processed by LIMS to reject magnetite, followed by WHIMS testing on the LIMS non-magnetic product using Eriez L-4-20 laboratory unit. The WHIMS test was performed at 5,000 Gauss, and the non-magnetic product was re-passed at 10,000 Gauss, followed by 15,000 Gauss. Table 3 shows the summary of the magnetic separation results on the four samples.

Significant REE upgrading with good recovery was observed in each of the WHIMS magnetic concentrates in all four samples. The TREO/Y recovery of WHIMS magnetic concentrate (up to 15,000 Gauss) for Silver Fox sample was the highest (~86%) while the TREO/Y recoveries of Deep Fox, Fox Trot, and Fox Meadow were slightly lower, in the range of 78-82%. The TREO/Y upgrade of Silver Fox was also the highest, at 8.3 times and a grade of 8.4% TREO/Y. The upgrade of Deep Fox, Fox Trot, and Fox Meadow was lower, at 4.3 to 4.8 times and a grade of 3.3 to 4.8% TREO/Y.

Table 3: WHIMS Magnetic Separation Results Summary

Product	Sample ID	Silver Fox	Deep Fox	Foxtrot	Fox Meadow
WHIMS Mags Concentrate up to 15,000G	Mass Pull, %	10.3	16.0	19.3	18.2
	TREO/Y Grade, %	8.42	4.61	4.81	3.25
	TREO/Y Recovery, %	85.7	78.3	78.3	81.8
	TREO/Y Head Grade, %	1.02	0.96	1.13	0.76
	Upgrade Ratio	8.25	4.80	4.26	4.28
LIMS Mags	Mass Pull, %	9.00	6.50	6.80	6.20
	TREO/Y Grade, %	-	0.17	0.19	0.15
	TREO/Y Recovery, %	-	1.13	1.20	1.24
	Fe_2O_3 Grade,%	86.8	94.6	97.1	91.9
	Fe_2O_3 Recovery,%	73.9	54.1	54.8	51.9

Table 3 also showed a larger portion of iron (~20% more) was rejected by LIMS for Silver Fox, compared to the other three samples. The mineralogy results of the four samples revealed that there was more iron-bearing silicates (such as amphibole/pyroxene, biotite, and chlorite) contained in Deep Fox, Foxtrot, and Fox Meadow compared to Silver Fox, as shown in Table 4. This is consistent with what was shown in Table 3, where the amount of iron-bearing silicates in Deep Fox, Foxtrot, Fox Meadow was ~8-16% higher than that in Silver Fox. These iron-bearing silicates are likely not able to be rejected by LIMS and instead report to the WHIMS magnetic concentrate, which might cause a higher mass pull and the dilution of WHIMS magnetic concentrate.

Table 4: Mineralogy Summary of Iron Bearing Minerals

Sample ID	Silver Fox	Deep Fox	Foxtrot	Fox Meadow
Fe-Oxides	8.66	7.37	4.40	6.41
Biotite	0.17	4.48	3.90	0.37
Chlorite	0.51	2.29	-	1.22
Amphibole/Pyroxene	0.10	2.20	13.7	12.8
Sum of Iron-bearing Silicates	0.78	8.97	17.6	14.4

The Outotec SLon-100 is another popular WHIMS laboratory unit, which is known as a Vertically Pulsating High Gradient Magnetic Separator. The Foxtrot LIMS non-magnetic product was processed by SLon-100 at slightly different conditions, see Table 5. The SLon-100 combined with Eriez WHIMS achieved 5-15% higher TREO/Y recovery than using WHIMS alone, despite a slightly higher mass pull.

Table 5: Summary of SLon Test Results on Foxtrot Sample

	Test ID	SLon-1	SLon-2	SLon-3	WHIMS Test
	Rod Matrix, mm	1.5	1.5	2.0	-
Magnetic Intensity, Gauss	1st Pass	2,000	1,000	12,000	5,000
	2nd Pass	10,000	12,000	12,000	10,000
	3rd Pass	12,000	12,000	15,000*	15,000
	4th Pass	15,000*	15,000*	-	-
Comb. Mag Conc up to 15,000 Gauss	Mass Pull, %	25.0	27.7	22.5	19.3
	TREO/Y Grade, %	3.62	4.52	4.17	4.81
	TREO Recovery, %	85.7	93.4	89.7	78.3
	Upgrade	3.2	4.0	3.7	4.3

*15,000 Gauss was performed by Eriez WHIMS

With the encouraging laboratory results, two new bulk samples, Comp 2 weighing 53 tonnes from Deep Fox deposit and Comp 1 weighing 20 tonnes from Foxtrot deposit, were received at SGS Lakefield for a magnetic separation pilot plant in late 2021. The objective was to evaluate the developed flowsheet in a continuous pilot plant.

The magnetic separation pilot plant was conducted on the two new bulk samples at an average throughput of ~550 kg/h, for a total of 134 hours of operation. The samples were crushed to -1/4" before feeding the magnetic separation pilot plant. The pilot plant included a grinding circuit, a size classification circuit, a LIMS circuit including one rougher and one cleaner, and a WHIMS circuit including one LONGi wet belt magnetic separator and one SLon-750 II. A simplified flowsheet is presented in Figure 15.

The benchmark tests using SLon-100 (SLon-6, SLon-7) were performed using a sample feed F_{80} of ~80 µm. However, the Derrick screen efficiency was poor at an aperture of ≤125 µm at the operating throughput, resulting in a high recirculation load in the ball mill in the first few pilot plant shifts. Significant improvement was achieved by changing to the screen aperture of 150 µm (F_{80} ~100 µm). The REO recovery of the combined REE magnetic concentrate was ~88-90% for Deep Fox and ~83-85% for Foxtrot, grading ~3.1-3.5% TREO+Y for Deep Fox and 3.6-3.9% TREO+Y for Foxtrot, with a mass pull of ~31-33% for Deep Fox and ~27% for Foxtrot. The metallurgical performance was steady across most of the pilot plant testing (Figure 17). The pilot plant testing successfully demonstrated magnetic separation performance at a coarser primary grind size (P_{80} ~100 µm) than that of the batch tests, which will ensure grinding cost savings.

A total of ~13,792 kg of Deep Fox REE concentrate and a total of ~5,145 kg of Foxtrot REE concentrate were produced from the pilot plant campaign, with an average grade of 3.3% and 3.8% TREO+Y, respectively.

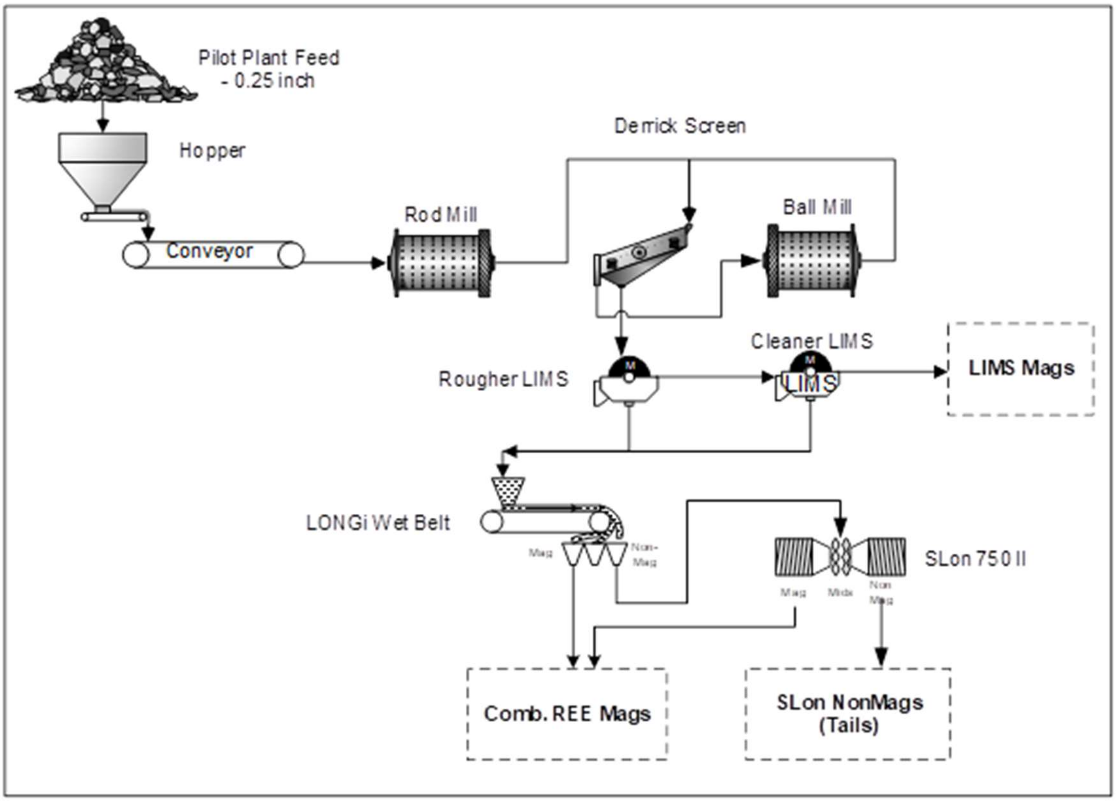


Figure 15: Magnetic Separation Pilot Plant Simplified Flowsheet

Figure 16: Pilot Plant Testing Key Equipment (from Left to Right: LIMS, LONGi Wet Belt, and SLon 750II)

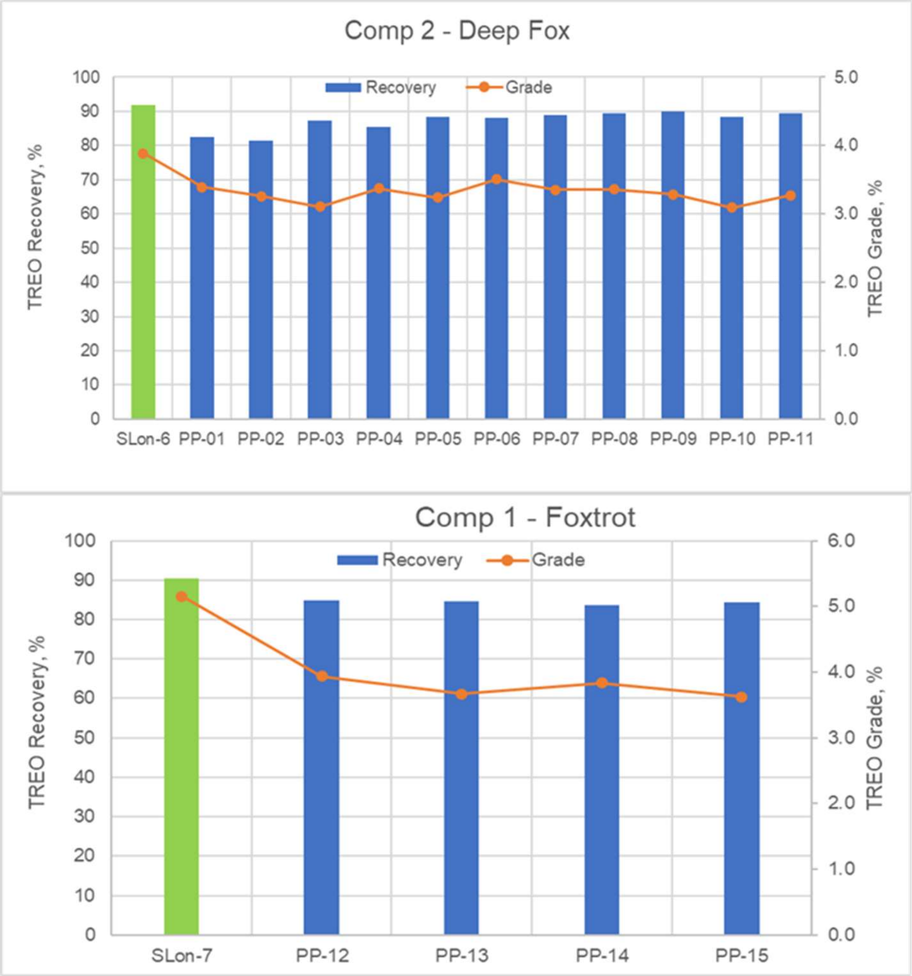


Figure 17: Pilot Plant Results Summary (vs Laboratory Tests SLon-6 and SLon-7)

2022 Acid Baking of Mineral Concentrate

Following the successful production of mineral concentrates from both Deep Fox and Foxtrot ores, comparison acid baking tests were conducted to confirm rare earth extractions from such a concentrate were comparable to the previous beneficiation products. The initial experiments focused on determining the impact of acid addition using the Deep Fox concentrate, investigating a range of additions from 300-800 kg/t. To match historical testwork, the concentrate was mixed with sulphuric acid and then roasted at 200°C for four hours before cooling. The resulting calcine was then water leached at 90°C for 24 hours to ensure sufficient time to react, much like the whole ore processing.

As expected, it was found that the extractions improved proportionally with the acid addition, with LREE (represented by Nd) tending to offer better leaching than HREE (represented by Dy). The relationship between extraction and acid addition is shown in Figure 18, using a 10% solids basis (relative to concentrate) in the water leach. To achieve >95% Nd extraction, acid additions of 800 kg/t or higher are required, matching the theoretical demand based on the concentrate composition (~820 kg/t required for REE and gangue content).

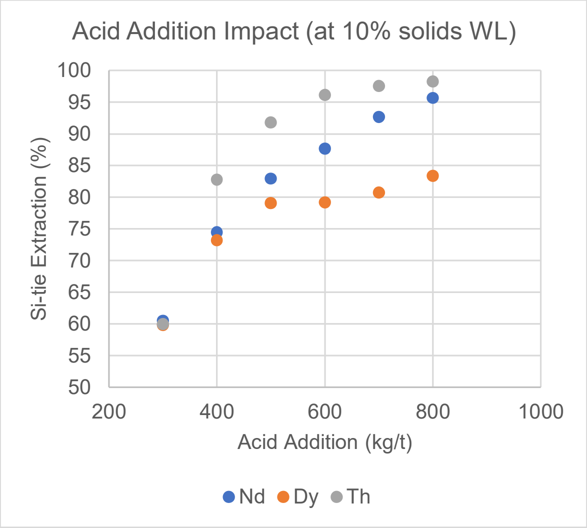


Figure 18: Extraction vs. Acid Addition for Deep Fox Concentrate

Concentrate from the Foxtrot ore was also tested, and high extractions (≥95%) were observed at 700-800 kg/t acid additions, also matching the theoretical acid demands (REE/gangue) of that material, which was ~700 kg/t. While the acid requirements for both concentrates were found to be higher than that of the concentrate produced in 2012, it was determined that the new concentrates contain higher levels of magnesium (10-12x more by grade) in addition to the increased REE grades (1-1.7x more) which resulted in higher acid consumption.

A breakdown of the relative acid demand is shown in Figure 19, highlighting that of the acid consumers in each material, the concentrates see a higher relative contribution from magnesium and calcium, whereas the whole ore is predominately driven by iron and aluminum. While whole ore processing was able to offer acceptable REE recoveries with an acid addition less than the theoretical requirement for the Foxtrot ore, that is not the case with the concentrates. It appears that together with REE bearing minerals, acid consuming gangue minerals are concentrated in the mineral concentrate.

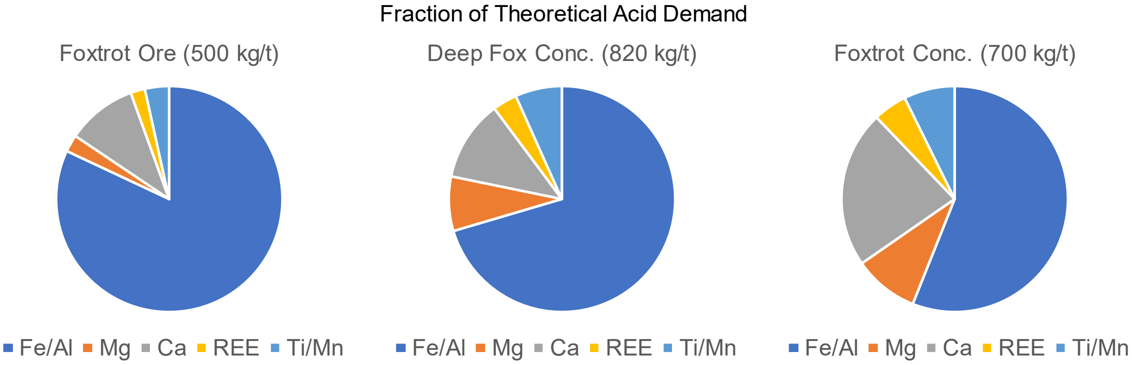


Figure 19: Theoretical Acid Demand Breakdown for Foxtrot Ore and Deep Fox/Foxtrot Concentrates

Further investigation is planned to refine the optimal conditions when processing the new concentrates; this is expected to consider water leach pulp density to manage saturated calcium/sulphur in solution, as well as determining any impacts on the downstream processing steps as a result of the different liquor chemistry that can be expected. Additionally, changes to the physical handling characteristics that come from using a higher acid/solids ratio than in whole ore processing are expected and will be considered. That said, it is believed that the original process developed for whole ore can be adjusted to accommodate concentrate with further optimization.

2023 Overall Flowsheet

Taking into account all process improvement as discussed above, the revised flowsheet is presented in Figure 20.

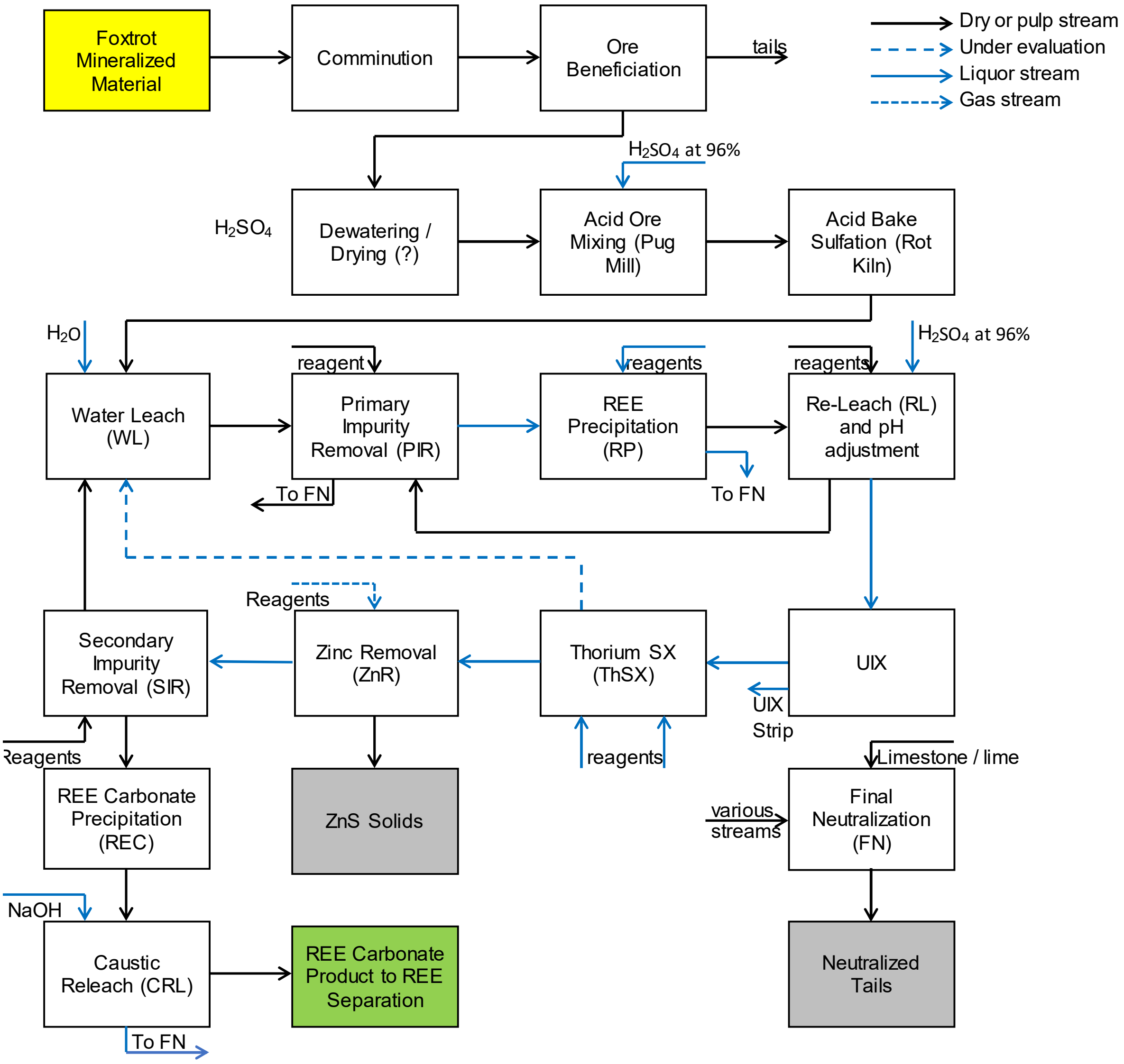


Figure 20: BFD - Direct Extraction - 2023

PROJECT UPDATE

2023 Preparation for Demonstration Pilot Plant

On March 7, 2023(12), Search Minerals announced that the Government of Canada is contributing $5 million in nondilutive support to Search Minerals via a Contribution Agreement which will be used to fund the construction and operation of a demonstration plant for rare earth extraction and recovery. The total project cost is estimated at approximately $9.3 million with a further $1 million of funding under application from other sources. Search Minerals' contribution to the construction costs is expected to be approximately $3.3 million. The demonstration plant will process ~18 tonnes of rare earth concentrate prepared from 72 tonnes of Deep Fox and Foxtrot mineralization using Wet High Intensity Magnetic Separation. The work will be completed by SGS Canada and completion of the program is expected in 2024. The funding of the demonstration plant helps Search Minerals to:

- Confirm application of the Direct Extraction Process to the rare earth concentrate materials
- Obtain engineering data for feasibility study completion, expected in 2024
- Prepare ~1 tonne of high purity mixed rare earth carbonate precipitate to be used to validate separation of individual rare earth products

ACKNOWLEDGMENTS

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Rare Earth project and thank Search and SGS Management for allowing publishing of this data.

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RARE EARTH PRODUCTION FROM AN AUSTRALIAN CLAY HOSTED DEPOSIT

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ABSTRACT

Australian Rare Earths (AR3) is progressing inputs to feasibility studies and approvals for their Koppamurra Project in South Australia, rich in clay hosted rare earth elements (REE) that are critical to producing renewable energy technologies and de-carbonising the world's energy landscape. The Project is led by a highly credentialled team, supported by world class consultants and advisors with proven expertise in the rare earths and mining industries.

AR3, in collaboration with Wallbridge Gilbert Aztec (WGA) metallurgists and process engineers, and experts from ANSTO, SGS Lakefield and University of Toronto, have substantially progressed a comprehensive metallurgical test work program to evaluate and select a process for economic recovery of the REEs from the deposit. The flowsheet evaluation is supported by robust data collection and storage by the WGA Data Analytics team, who have securely consolidated drilling and test work data, and identified geometallurgical relationships through machine learning applications.

Understanding the ore's metallurgical response is critical for developing an economic process flowsheet. Through mineralogical studies, bench-scale beneficiation and extraction tests and a recent large-scale test work program, a preliminary process flowsheet has been developed and continually updated based on insights derived from test work. The following insights have recently been derived:

- Leach optimisation test work conducted at ANSTO and University of Toronto demonstrated an average recovery of 65%, up to 77% of the four key magnet REEs, being Nd, Pr, Dy and Tb, in the pH range 1.5 to 2.0 at ambient conditions. This recovery was maintained whilst significantly reducing acid consumption from the dissolution of the gangue minerals, iron and aluminium, by 50%. Further leach tests on samples from spatially diverse locations within the deposit, provided consistent metallurgical response to varied pH, leach time and solids density, despite the geographic spread.

- Solid-liquid separation experts, Metso Outotec and GBL / IFS have progressed test work to develop process technology selection and determine optimal separation conditions.

- Bench-scale size separation test work at SGS showed early potential for >30% mass rejection and >50% gangue mineral rejection in a coarse waste stream, whilst maintaining REE grade in the product stream. This may provide both an opportunity to reduce material throughput and acid consumption, leading to commercially attractive equipment sizing and reagent requirements.

- An 850 kg composite sample extracted from the Koppamurra Trial Pit was processed by ANSTO in December 2022 for generation of a mixed rare earth carbonate and product specification analysis. This significant step change in the scale of test work, covering the entirety of the process flowsheet, will inform design and operational criteria for testing of a 500-tonne bulk sample at an even larger pilot scale.

These insights provide both an environmentally sound and commercially attractive process pathway to economic production of a high-quality specification REE product. Pipeline test work in further optimising particle size separation, solid-liquid separation, impurity removal and carbonate precipitation will contribute to finalising the process flowsheet and provide key inputs to both the mining lease application and a scoping study.

Keywords: Rare Earth Elements, Clay Hosted, Renewable Energy Technologies, Mining Lease Application

INTRODUCTION

Rare earth elements (REE) play a vital and increasing role in numerous everyday devices and are critical to renewable energy technologies for decarbonising the world's energy landscape. The REE industry is driven by the demand for rare earth containing high strength permanent magnets (REPM), as components in renewable energy technologies.

The projected five-fold increase in demand for REE by 2030 underscores their importance. Nevertheless, supply is volatile due to China's dominance in the industry and dwindling reserves, with the country currently accounting for approximately 70% of global annual mined production(1). Furthermore, China is the exclusive producer of the the two heavy rare earth elements (HREE), dysprosium and terbium, which enable REPMs to function at high temperature(2). Currently only two mines outside of China are operational, namely Mountain Pass in the US and Mount Weld in Australia. Hence, diversifying the rare earth supply chain is now a pressing concern for the industry.

This pre-eminent position of China can be attributed, in part, to their tenure of ionic clay hosted deposits, as opposed to the hard rock variety. The former deposits tend to exhibit shallower depths and do not necessitate energy-intensive techniques such as blasting, milling, or crushing. Additionally, they typically do not generate radioactive tailings, thereby making the mining and processing of these deposits more simple and economically favourable in comparison to the hard rock deposits.

Australian Rare Earths (AR3) flagship Koppamurra deposit represents one of only three advanced ionic clay hosted REE deposits outside China(3). AR3, in collaboration with Wallbridge Gilbert Aztec (WGA) metallurgists and process engineers, together with experts from ANSTO, SGS Lakefield and the University of Toronto, have substantially progressed a comprehensive metallurgical test work program for Koppamurra. The program, having now encompassed 142 (unique) samples and 24 composites with a range of spatial and mineralogical diversity, has undergone 11 phases of test work, including mineralogy, rare earth element extraction extents and minerals processing methods. Through these efforts, a comprehensive understanding of the ore's metallurgical behaviour has been attained, which is essential in the development of an environmentally sustainable and commercially attractive process flowsheet.

As a first in Australia for an ionic clay hosted rare earth resource, AR3 recently produced a mixed rare earth carbonate (MREC) at pilot scale, under ambient temperatures and pressures. This significant step change in the scale of test work, covering the entirety of the process flowsheet, will inform design and operational criteria for larger scale testing of a 500-tonne bulk sample.

DEPOSIT DESCRIPTION

Resource

AR3 currently hold multiple exploration licenses across southeast South Australia and western Victoria, as presented in Figure 1. A substantial JORC Resource (ASX March 2023) of 101 Mt at 818 ppm Total Rare Earth Oxide (TREO), incorporates the results from two completed drilling programs, with another program currently underway. The Resource defined to date is <5% of the total 4,000 km^2 of granted exploration tenure.

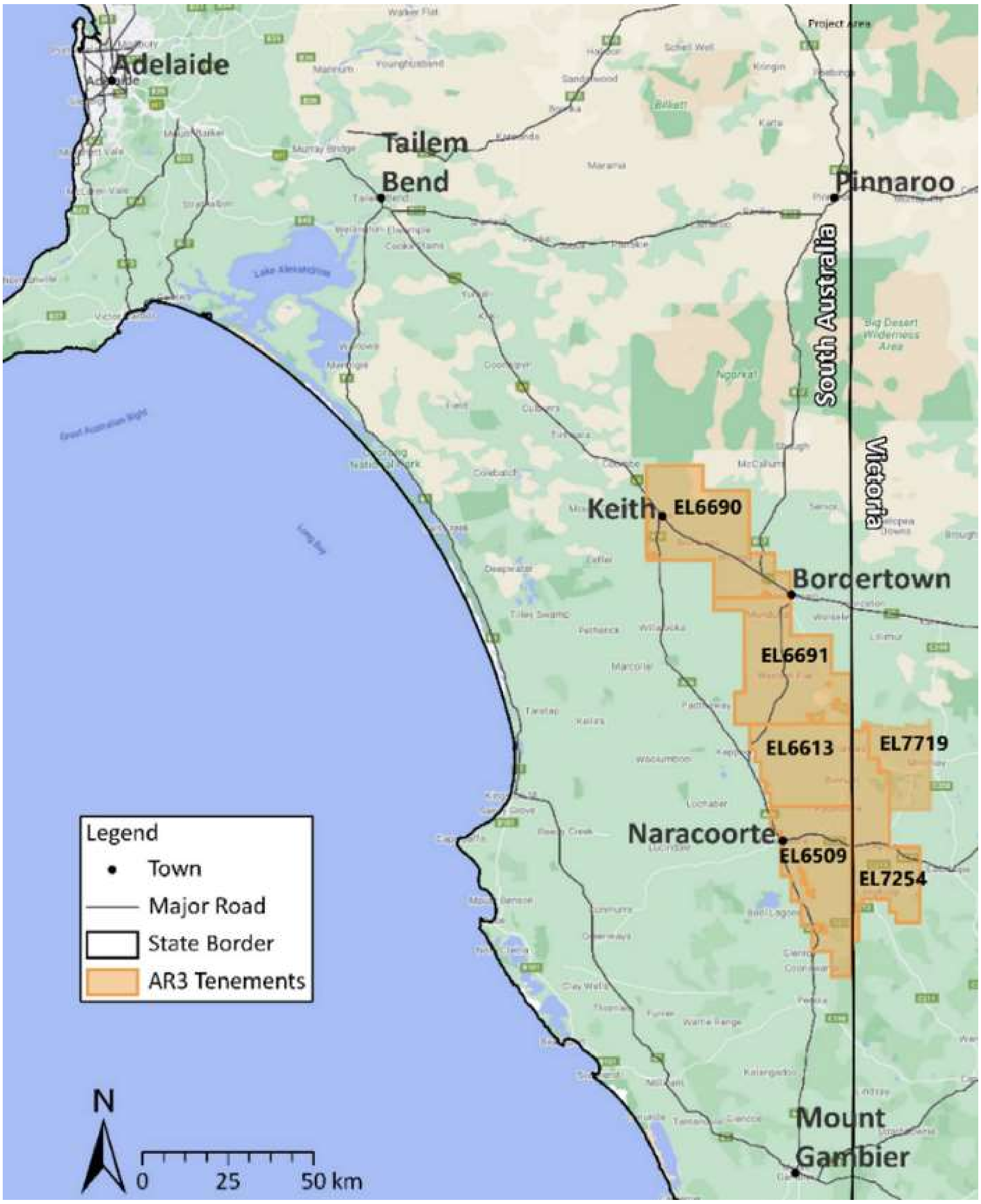

Figure 1: AR3 tenement areas across southeast South Australia and western Victoria.

Koppamurra is characterised by a shallow, REE mineralised clay sediment, <10 m from surface, deposited above the Gambier limestone base, as presented in Figure 2.

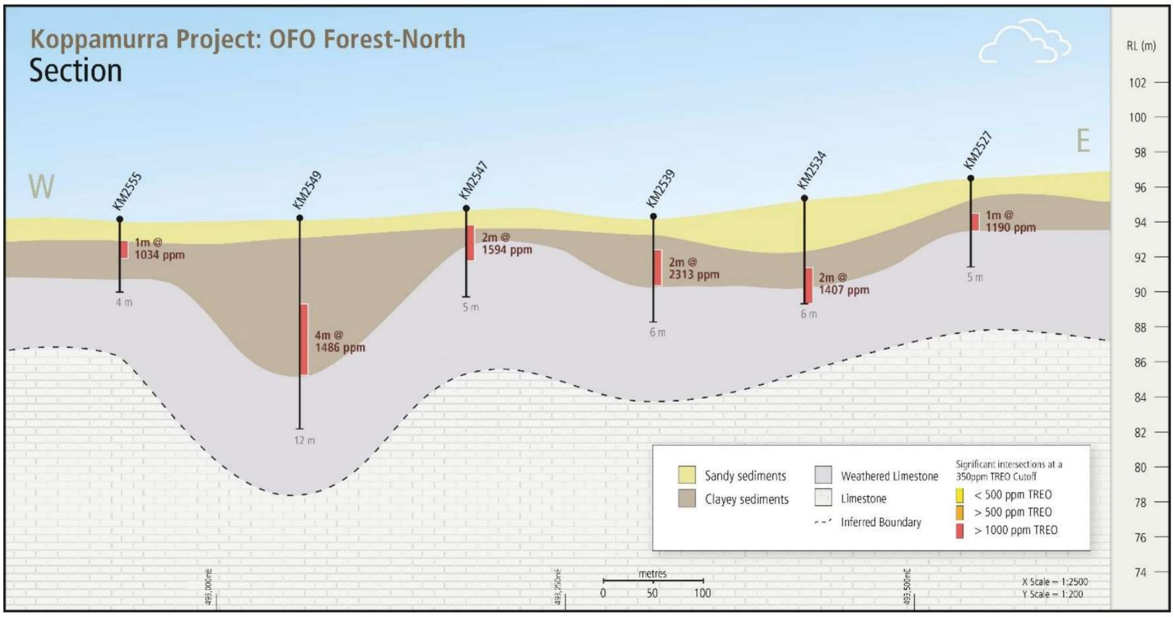

Figure 2: Cross sectional lithology of OFO Forest-North, demonstrating the shallow nature of the Koppamurra REE mineralisation.

Mineralogy

Mineralogical studies were conducted on a composite sample of 74 spatially diverse samples across the Koppamurra deposit, which identified the presence of eight REE bearing minerals. Among these minerals, the carbonate mineral Lanthanite-(Ce), was found to primarily contain the four valuable magnet REE, Neodymium (Nd), Praseodymium (Pr), Dysprosium (Dy) and Terbium (Tb). These four high-value REE bearing minerals were predominantly concentrated in the <20 µm fraction.

The Koppamurra deposit is characterised as an ionic clay deposit, similar to those exploited throughout southern China. Subsequent characterisation has revealed the presence of three distinct phases of REE in the Deposit, in varying proportions.

The ionic (ion-adsorbed) phase of REE is formed through the chemical weathering of REE bearing primary minerals, and subsequent weak adsorption of liberated ions to the surface of secondary minerals. Accordingly, extraction of these REE is achieved through rapid ion exchange desorption, facilitated by pH adjustment using dilute salt solutions, under ambient conditions.

An additional strongly ionically bonded phase of REE is present, which is formed through the chemical weathering or hydrothermal alteration of REE bearing primary minerals. During formation, liberated ions become strongly adsorbed to the surface of secondary minerals, or isomorphous substitution enables the REE to be deposited into the crystal lattice structure of secondary minerals. Accordingly, extraction of these REE is achieved through a weak acidic leach.

A third additional REE phase, the mineral phase is present, in which the REE are naturally present in the crystal lattice structure of primary minerals that are resistant to weathering and alteration. Accordingly, extraction of these REE can only be achieved through energy-intensive cracking or roasting before acidic leaching.

Metallurgical response test work to date on composite samples from the Koppamurra deposit showed up to 77% extraction of the four valuable magnet REE, for a pH 1 leach at ambient conditions. This indicates that processing operations for ion-adsorbed and strongly ionically bonded REE phases can be applied to economically recover REE from the Deposit. Having an understanding of the type and proportion of REE phase/s present in a deposit, as well as their metallurgical behaviour under varying operating conditions, is critical for comprehending the economic and environmental implications of processing operations.

PROCESSING PLANT OPERATIONS

Proposed Flowsheet

A simplified depiction of the proposed flowsheet for the economic production of a high-quality specification MREC product is presented in Figure 3. The proposed process initiates with the mechanical mining of shallow mineralised clay, followed by slurry pumping to the processing plant. Due to the fine nature of the ore and the predominant presence of ion-adsorbed and strongly ionically bonded REE phases, the energy intensive methods of cracking and roasting of the ore are not required to enable extraction of the REE. Post slurry pumping, beneficiation is employed to reject gangue minerals and coarse material deficient in REE, leading to an inherent upgrade of the fine material. This fine material undergoes REE extraction via controlled addition of a lixiviant to facilitate desorption of the REE from the clay host. The REE entrained in the liquor are recovered from the solid clay host via solid-liquid separation, followed by neutralisation of the resultant leach residue solids. The resultant liquor, containing the entrained REE, undergoes impurity removal in which the pH of the solution is raised to precipitate out predominantly iron and aluminium. Another solid-liquid separation stage is employed to separate the precipitated solid impurities from the liquor. The resultant solids are consolidated with the neutralised leach residue solids. The pH of the resultant liquor is again raised, to precipitate the REE as a mixed rare earth carbonate solid. Another solid-liquid separation stage is employed to recover the MREC solids, with the recovered liquor recycled as process water, and the MREC solids dried and packaged for shipment to downstream processors.

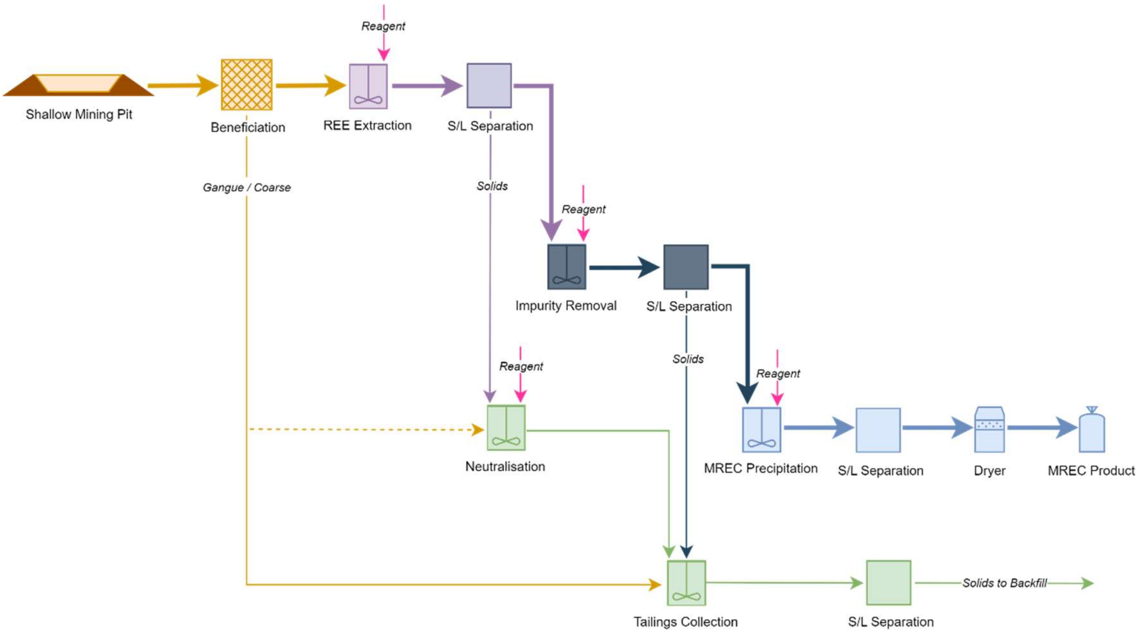

Figure 3: Proposed MREC production flowsheet for the Koppamurra deposit (simplified).

Beneficiation

Several beneficiation methods have been evaluated for the Koppamurra ore, encompassing size classification, attrition, flotation and wet high-intensity magnetic separation (WHIMS). The viability of these methods to upgrade the ore was appraised on a two-fold basis:

- Reducing gangue minerals - to reduce reagent consumption and reduce impurities in the final REE product; and
- Reducing the overall feed mass - to reduce the size of the processing plant.

Size Classification

The most recent assay by size analysis was undertaken by ANSTO, on a composite sample generated from spatially diverse drill cores across the deposit. The analysis showed a promising reduction in both gangue minerals and overall feed mass in the <75 µm fraction.

Accordingly, to determine the proportion of extractable REE at given leach conditions, wet screening and subsequent diagnostic leaches was undertaken by ANSTO on ±38 µm and ±75 µm size fractions. Whilst further optimisation test work is required, initial results showed promising extractions of the four valuable magnet REE at a 75 µm size split, for a pH 1 leach at ambient conditions. Such findings warranted an assessment of size classification technologies, with bench-scale sighter test work currently underway using the FLSmidth REFLUX classifier. Insights from this test work will feed into the assessment of the benefits of these single-unit and high-capacity classifiers against other conventional technologies such as a hydrocyclone cluster.

Attrition

The Koppamurra Trial Pit revealed a small proportion of excavated ore presenting as large compact clay agglomerates, necessitating further investigation into attritioning technologies such as log washers or low-powered tumble mills. Accordingly, ISO tumble mill sighter tests were undertaken without media on a 35 kg ore charge, whereby extended tumbling motion appeared to have no/limited attritioning behaviour on the clay agglomerates, which remained competent throughout the test. Concurrently, simple in-field dispersion tests involving placement of the clay agglomerates in tap water without agitation were undertaken. These tests revealed a natural dispersion of the agglomerates over time without any form of attrition. As such, further investigation into standalone attritioning technologies was suspended, with future assessments to be undertaken to assess the inherent attritioning and dispersion that will occur during mining and front-end processing units.

Flotation

A total of 19 bench-scale rougher flotation tests were undertaken between KYSPYMet and SGS Lakefield, whereby a range of test parameters such as particle size, reagent type (depressant, surfactant, frother, etc) and addition rates and temperature were assessed. Further investigation into flotation viability was suspended as no economic improvement to the grade or mass were established.

Wet High-Intensity Magnetic Separation

WHIMS sighter tests were undertaken by SGS Lakefield on a 250 g ore sample, screened at 300 µm. Three passes of the magnet at increasing magnetic strengths, using steel wool as the mattress pad, found there to be no economic improvement to the grade or mass and as such further investigation into WHIMS viability was suspended.

REE Extraction

The characterisation and extraction potential of the Koppamurra deposit has involved the analysis of more than 200 leach samples by ANSTO and The University of Toronto, encompassing a broad range of leach parameters, as presented below. These leach results represent a significant advancement in the understanding of the Koppamurra deposit and can serve as a valuable resource for further development of the proposed processing flowsheet and further optimisation test work programs.

Table 1: Range of leach parameters tested by ANSTO and The University of Toronto.

Parameter	*Minimum*	*Maximum*
Temperature (°C)	Ambient	125
Slurry Density (wt%)	2	35
pH	1	5
Duration (h)	0.5	24

In addition to the range of leach parameters analysed, an exhaustive analysis of the following nine leach lixiviants has been carried out:

- CH_3COONH_4
- H_2SO_4
- HCl
- NaCl
- $MgCl_2$
- $MgSO_4$
- NaOH
- NH_4Cl
- $(NH_4)_2SO_4$

These lixiviants have been studied both individually and in various combinations, at different molar concentrations, to gain a comprehensive understanding of their leaching potential. Leach programs additionally analysed re-leaching and post-leach washing stages to optimise the recovery of the REE. Parameters tested include the number of washes/re-leaches, ratio of lixiviant to wash water, type of lixiviant, temperature, pH, and more.

Characterisation and extraction potential test work to date has revealed that the Koppamurra deposit is composed of ion-adsorbed and strongly ionically bonded phases of REE. The prevalence of these phases was established through enhanced leach performance at pH 1, in comparison to pH 4, as presented in Figure 4. Further, a third REE mineral phase has been identified, albeit of a limited proportion, through caustic leaches at temperature undertaken by The University of Toronto.

Accordingly, further optimisation test work is being undertaken by ANSTO, to maximise the REE recovery of both the ion-adsorbed and strongly ionically bonded REE, under economically viable test parameters. Recent test work focused on the pH range 1.5 to 2.0, under ambient conditions, yielded a 50% reduction in acid consumption and gangue dissolution, particularly iron and aluminium. Notably, this reduction was achieved whilst maintaining average recoveries of 65% and up to 77% for the four valuable magnet REE, as presented in Figure 4.

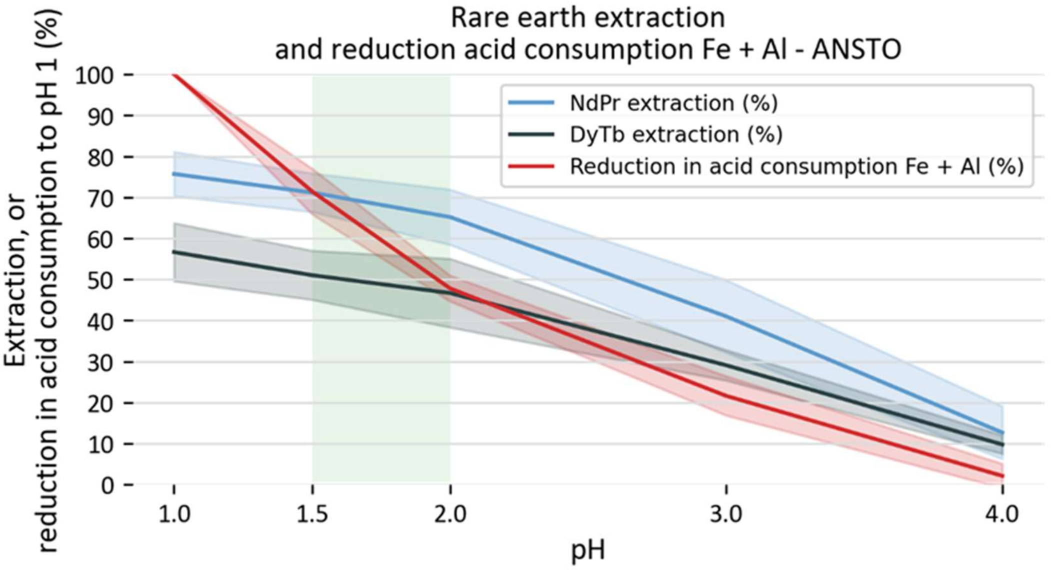

Figure 4: REE extraction at different pH diagnostic leach tests for samples KM0-241_4 and KM0-234_3.

Consistent REE extraction results were shown for the spatially diverse samples, CP001 to CP010, across the deposit, as presented in Figure 5. The results highlighted the uniformity of recoveries across the resource composition variation, thereby confirming the proportionate presence of both ion-adsorbed and strongly ionically adsorbed REE phases. These findings have significant implications for the development of a reliable REE recovery method, that is suitable for the whole Koppamurra deposit without the requirement for significant blending of feed ore.

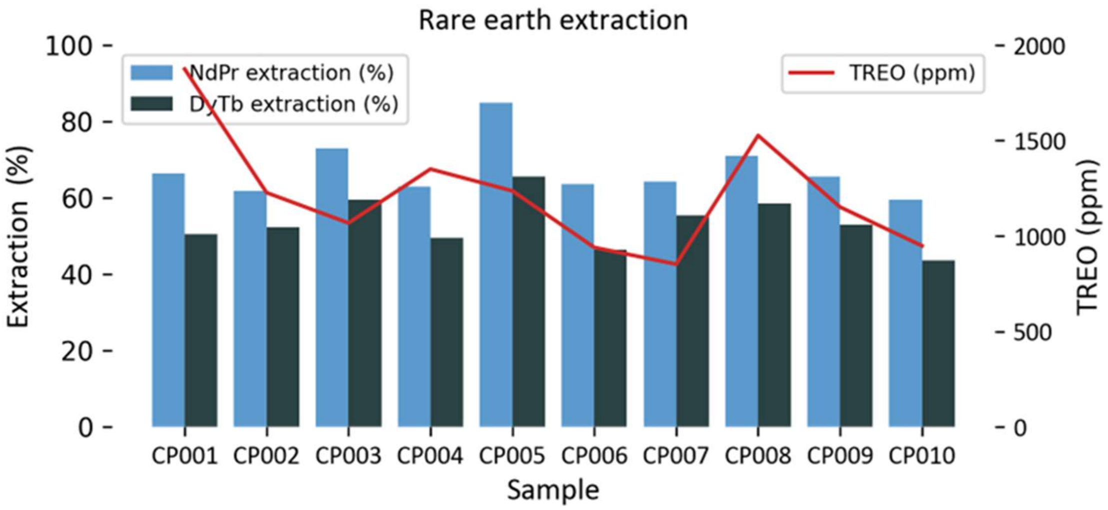

Figure 5: Valuable magnet REE extraction for the spatially diverse Koppamurra deposit composite samples CP001 to CP010 at pH 1, 6 hours.

Solid-Liquid Separation

Post leach completion, the REE that are entrained in the liquor, are separated from the waste clay host. The solid-liquid separation technologies, that have been assessed to-date, either as a sole technology or in combination with another technology (i.e., thickener followed by a filter press) are presented in Table 2.

Table 2: Leach residue solid-liquid separation technologies assessed to-date.

Technology	***Vendor***	***Assessment Type***	***Sample***
Thickener	Metso Outotec & GBL Process	Bench-scale test	Leach slurry
Plate & Frame Filter	Metso Outotec & GBL Process	Bench-scale test	Leach slurry
Belt Filter Press	Phoenix	Bench-scale test	Un-treated ore
Screw Press	IFS	Desktop assessment	-
Centrifuge	Alfa Laval & GEA	Bench-scale test	Un-treated ore

Although ongoing testing is still being conducted, thus far, centrifuge and screw press technologies have emerged as the most feasible solution based on all relevant factors, with a particular emphasis on product moisture, capital and operational expenditures, and land rehabilitation potential. As shown in Figure 6, the bench-scale centrifuge tests conducted by Alfa Laval, using an un-treated ore sample, produced a firm and spadable cake, suitable for trucking / conveying, with no free draining water and did not present as ‘sticky’. Ongoing centrifuge test work will assess a range of parameters, including use of an optimal flocculant and a leach residue sample.

Figure 6: (left to right) Re-slurried composite sample CP008. Re-slurried sample flocculated with Magnafloc 1101. Resultant centrifuge Centrate. Resultant centrifuge cake.

Concurrently with bench-scale solid-liquid separation test work, a flocculant screening program was undertaken by flocculant supplier, BASF, using leach residue samples from the pilot-scale MREC production tests. The program initially screened nine conventional non-ionic flocculant products, as well as two anionic flocculants from the Rheomax DR range:

- Non-ionic: Magnafloc 10, 333, 338, 351, 155, 1011, 5250, 156, 336
- Anionic: Rheomax 1030, 1050

In general the samples displayed easy flocculation behaviour at a 1:5 volume dilution ratio using pH adjusted tap water, enriched with Magnesium. Among the tested products, the conventional non-ionic agents, Magnafloc 333 and Magnafloc 351, demonstrated a favourable combination of superior supernatant clarity and acceptable settling rates. In contrast, the anionic product, Rheomax 1030, exhibited significantly faster settling rates at higher feed solids and markedly reduced dosage rates, which were approximately half of those required by the conventional agents, as presented in Figure 7. Although the clarity of the supernatant attained using Rheomax 1030 was not proportionate with that achieved by the conventional products, in most scenarios, it would be deemed suitable for the intended application. The optimal utilisation of this flocculant in forthcoming solid-liquid separation assessments is expected to enhance the overall product moisture.

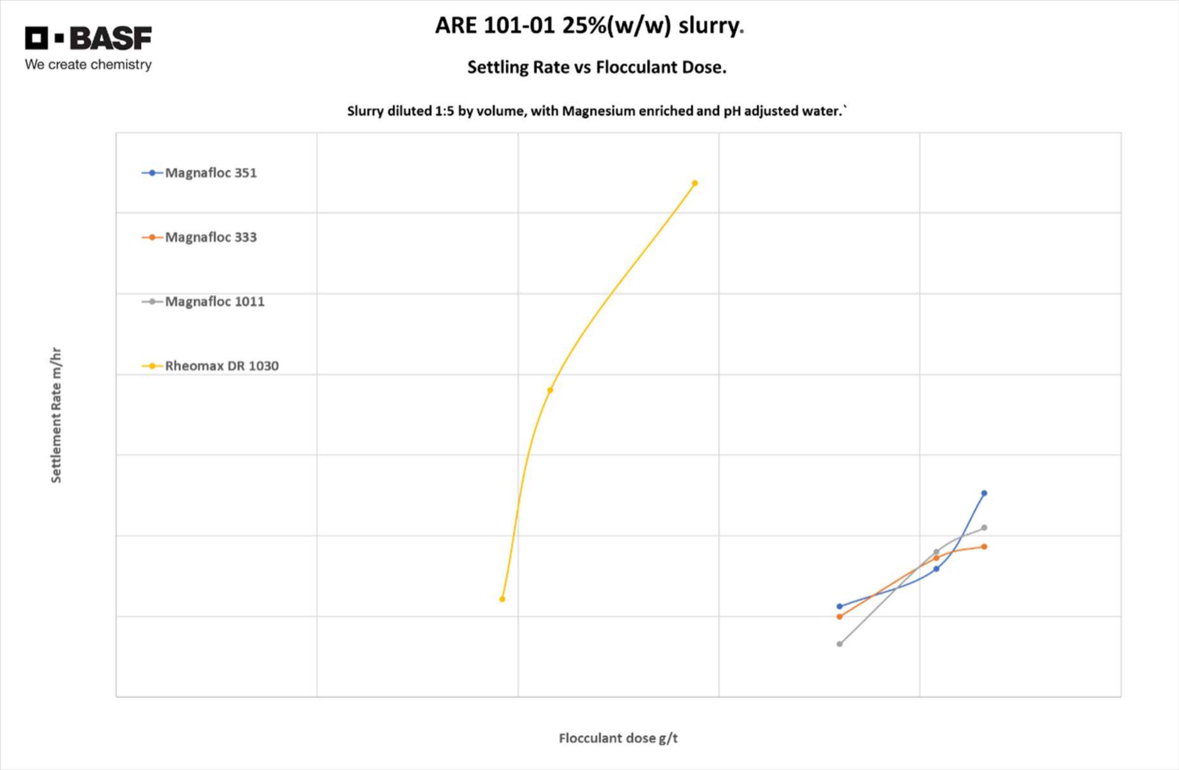

Figure 7: Settling rate versus flocculant dose for three best performing conventional non-ionic flocculants and one best performing anionic flocculant

Impurity Removal

The impurity removal (IR) stage aims to separate the REE entrained in the liquor as solids, from gangue minerals that that ultimately manifest as impurities in the final MREC product. Although several REE processing facilities employ costly and intricate separation techniques such as ion-exchange and solvent extraction, the Koppamurra flowsheet proposes a more economical and straightforward alternative. Specifically, the Koppamurra process entails selective precipitation in conventional tanks at ambient conditions utilising the precipitant ammonium bicarbonate, which elicits an increase in pH. In addition to facilitating impurity precipitation, ammonium bicarbonate also acts as a source of CO_3^{2-} that complexes with REE for the later precipitation of the REE as a carbonate(4).

In December 2022, a pilot-scale production program from Koppamurra ore was conducted, involving three IR batch tests, utilising leach liquor volumes ranging from 660-902 L. For two of these batches, a two-stage pH adjustment was employed, whilst a third batch employed a single-stage pH adjustment.

Mixed Rare Earth Carbonate Precipitation

The MREC stage aims to precipitate the REE as solids, for subsequent solid-liquid separation, drying and packaging for shipment to downstream processors., the MREC stage entails selective precipitation of the REE-laden IR filtrate, which is complexed with CO_3^{2-}. This precipitation is carried out in conventional tanks at ambient conditions utilising the precipitant ammonium bicarbonate to elicit an increase in pH.

The December 2022 pilot-scale production program, consisted of three IR filtrate batches with volumes ranging from 620-900 L. Each batch employed a single-stage pH adjustment. The following high-level MREC precipitation results were observed:

- Precipitation, reported as total rare earth elements plus Yttrium (TREY), ranged between 98-99.5% across the three batches.
- Individual REE precipitation for two of the batches, was typically over 98%, with slightly less precipitation observed for all individual REE in one of the three batches.

The positive results obtained from the first production of a mixed rare earth carbonate (MREC) from an Australian ionic clay hosted REE resource have provided valuable insights and avenues for further optimisation test work. In collaboration with Neo Performance Materials (NEO), a renowned producer of high-value rare earth products, AR3 is providing the MREC solids to NEO for product quality assessment. This collaborative effort aims to enhance the efficiency and purity of the Koppamurra REE production process and to further develop the commercial viability of this valuable resource.

Tailings Management

The proposed Koppamurra flowsheet consolidates tailings material from three process stages:

- Beneficiation - coarse/gangue material as a slurry
- REE Extraction - neutralised leach residue as a slurry
- Impurity Removal - precipitated impurities as a solid

The consolidated tailings will undergo solid-liquid separation, followed by transport back to the mined pit where it will be backfilled into the pit.

In consultation with specialist environmental consultancy, Landloch, leading-practice land management, rehabilitation, and landform design techniques are being assessed for the neutralisation and management of tailings material. Landloch are currently undertaking geochemical and geotechnical assessment of topsoil, overburden clay, un-treated mineralised clay, processed mineralised clay (from the December 2022 pilot-scale production program) and limestone basement samples.

CONCLUSIONS

The Koppamurra REE deposit has undergone thorough mineralogical assessment and minerals processing test work, leading to the successful production of a mixed rare earth carbonate (MREC) at pilot scale. This remarkable achievement has provided invaluable insights for the design and operational criteria required for larger scale testing of a 500-tonne bulk sample. In addition, pipeline bench-scale test work is currently underway to further optimise particle size separation, solid-liquid separation, impurity removal, and carbonate precipitation. These efforts will contribute to finalising the process flowsheet and provide key inputs for the mining lease application and a scoping study. With the support of a team of expert advisors, AR3 is well-positioned to develop an environmentally sustainable and commercially viable process pathway for economic production of a high-quality specification REE product.

ACKNOWLEDGEMENTS

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ECONOMIC AND TECHNICAL CHALLENGES OF NON-CHINESE CLAY HOSTED RARE EARTH DEPOSITS

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ABSTRACT

The primary source for the world's heavy rare earth elements (HREE) are exploited from the ionic adsorption deposits (IADs) in Southern China. These regolith hosted IADs are also often referred to as ion-adsorption clays due to the fact that the REs can be displaced from the clay minerals using solutions of a high ionic strength salt (predominantly ammonium sulphate). Typically, the method of mining and extraction used is in-situ leaching, hydraulic sluicing or heap leaching with the key requirement that the clays give up their weakly bound rare earths via a cationic exchange mechanism. Although these deposits are low grade compared to hard rock or alluvial deposits, the high proportion of valuable HREEs and the low mining and extraction costs is perceived to offer economic advantages over other deposit types.

In recent years, many low-grade clay hosted rare earth deposits have been reported outside of China. Very few of these have proven to date to be truly IAD in nature. Many companies have announced to have a significant weak acid extractable (WAE) rare earth content, however this is only part of the equation and introduces other challenges such as additional chemical costs required for purification, increased water requirements for residue washing and costly wastewater treatment/disposal requirements. Lastly, the assumed revenue from products is often simplistically and erroneously overstated by applying separated rare earth basket prices (perhaps with a discount factor) for the assumed saleable product.

A top-down analysis is presented discussing macroeconomic variables in context with the idiosyncrasies of treating both IAD and WAE rare earth feed types.

Keywords: clay hosted rare earths, ionic clay, rare earth elements, HREE

Mineralogy - IADs

- Ionic Adsorption Deposits (IAD) operating in China, Myanmar and Vietnam are characterised by clay minerals (kaolinite and halloysite)
- Rare earths (REs) are weakly adsorbed onto the surface structures, contained in hydration layers or substituted with exchangeable cations
- REs can be released (via desorption) into solution via cationic exchange – typically using ammonium sulphate solution
- Desorption efficiency and kinetics can be enhanced in slightly acidic conditions – typically ~ pH 2 to 4
- Typical RE content is 500 to 2000 ppm TREO with a higher distribution of the HREs (Sm to Lu + Y) than the hard rock and mineral sands deposits
- Currently accounts for ~70 to 80% of the world's HRE production

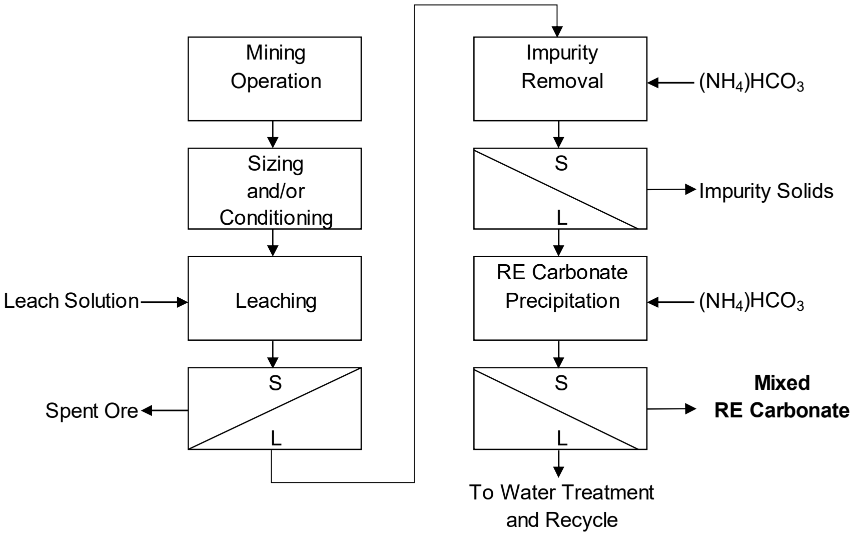
Mineralogy - WAE

- Weak Acid Extractable (WAE) clays are characterised by minimal RE extraction with straight cation exchange
- Require acidic solution to release the REs
- Typically some RE extraction are seen at moderate pH values (pH 4), however low pH values down to pH 1 are generally required
- Most likely a combination of strongly bound ionic adsorption clays and of acid soluble minerals (bastnaesite, apatite etc) present
- Some historical evidence of this processing in China, but now uncommon due mainly to environmental constraints
- Significant impurities (Fe, Al, Si etc) will also be solubilised

Mineralogy - Other

- Low concentration of RE host minerals such as:
  - Refractory phosphates (monazite/xenotime)
  - Refractory silicates (allanite/euxenite)
  - Acid soluble phosphates (apatite)
  - Acid soluble fluorcarbonates (bastnasite/synchesite)
- Ionic desorption via ammonium sulphate is not effective
- High acid consumptions expected for acid soluble minerals with gangue minerals being the major consumer
- Refractory RE minerals only minimally solubilised ever at strong acid strengths

General Flowsheet



Mining Operation

Sizing and/or Conditioning

Leach Solution → Leaching

S/L → Spent Ore

Impurity Removal ← $(NH_4)HCO_3$

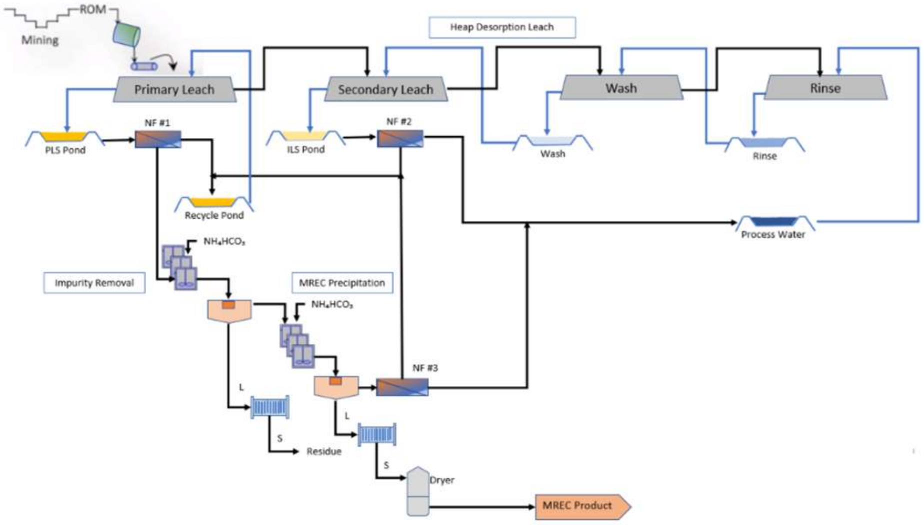
S/L → Impurity Solids

RE Carbonate Precipitation ← $(NH_4)HCO_3$

S/L → **Mixed RE Carbonate**

To Water Treatment and Recycle

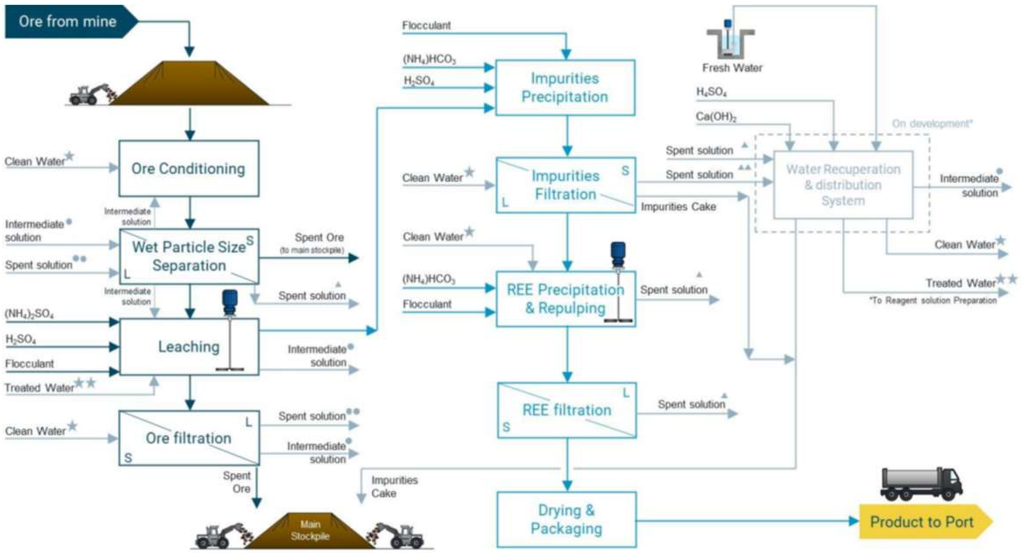
Heap Leach Flowsheet



Makuutu Rare Earths Project Stage 1 DFS Process Flowsheet

Ionic Rare Earths ASX Release 20 March 2023

Stirred Leach Tank Flowsheet



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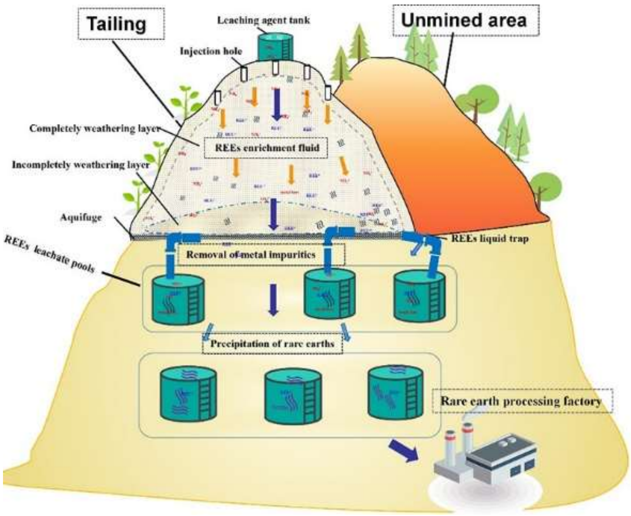
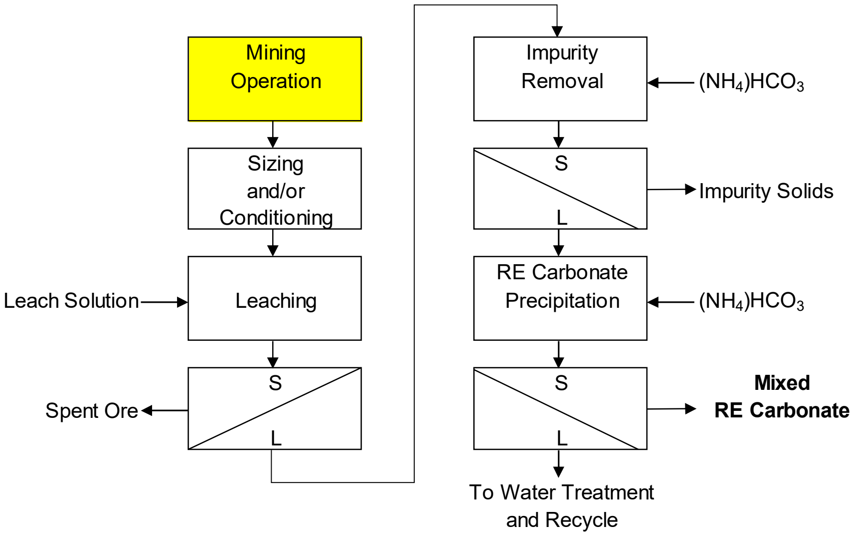
In-situ Leach Example



Example of In-situ Leaching

Mining



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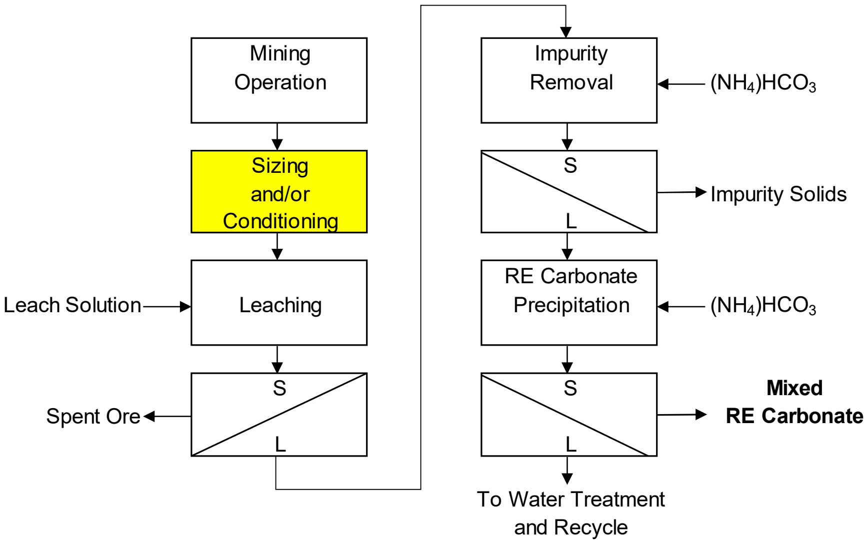
To Water Treatment and Recycle

Hydraulic Mining Example

Former rare earth mining site in Jiangxi province, China
Photo: Michael Standaert – Yale 360

Ore Preparation



Mining Operation

Sizing and/or Conditioning

Leach Solution

Leaching

S

L

Spent Ore

Impurity Removal

$(NH_4)HCO_3$

S

L

Impurity Solids

RE Carbonate Precipitation

$(NH_4)HCO_3$

S

L

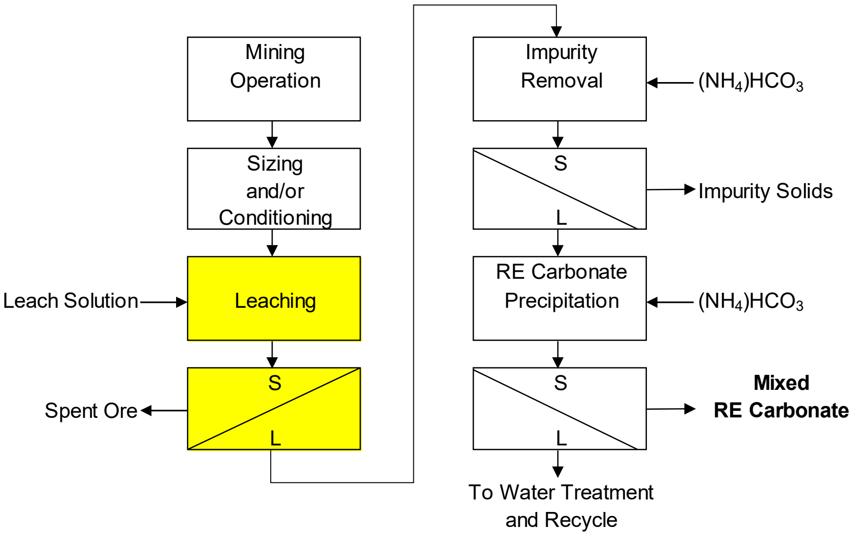
Mixed RE Carbonate

To Water Treatment and Recycle

Ore Preparation

- In-situ leaching
  - Requires appropriate aquifer and solution monitoring preparatory work along with injection and recovery holes
  - Questions of soluble sulphate and ammonia remaining in-situ?
- Heap leach
  - Screening, agglomeration, and careful stacking
  - Clays are prone to swelling and structural challenges in heaps
  - Percolation and channelling considerations
- Stirred leach tanks
  - Scrubbing and desliming – can use leach or spent solution
- Significantly more costly than Chinese practices!

Leaching



Mining Operation

Sizing and/or Conditioning

Leach Solution

Leaching

S

L

Spent Ore

Impurity Removal

$(NH_4)HCO_3$

S

L

Impurity Solids

RE Carbonate Precipitation

$(NH_4)HCO_3$

S

L

Mixed RE Carbonate

To Water Treatment and Recycle

Leaching

- Leach conditions typically:
  - ~20 g/L ammonium sulphate
  - pH 2 to 4 adjusted with sulphuric acid for IAD mineralogy
  - pH 1 or lower for WAE with acid consumptions 50 to 100 kg/t
  - Fast desorption or REs – typically <15 minutes
- RE extraction is usually "modest" at between 30 to 50%
- Heap leach requires agglomeration for stability and percolation
- Tank leaching will require:
  - Classification (screening and/or cycloning)
  - Filtration is challenging in these clays
  - Spent ore must be well washed of sulphates and ammonia for pit/unlined disposal

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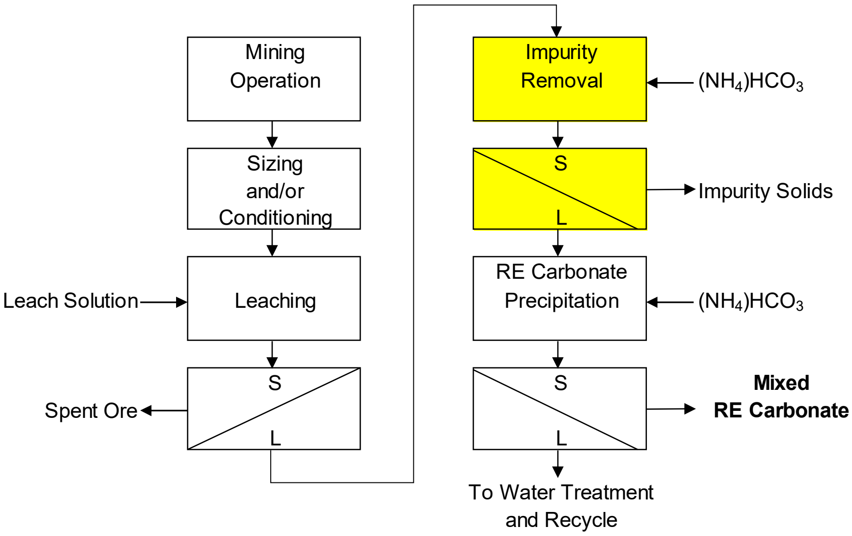
Impurity Removal



Mining Operation

Sizing and/or Conditioning

Leach Solution

Leaching

S

L

Spent Ore

Impurity Removal

$(NH_4)HCO_3$

S

L

Impurity Solids

RE Carbonate Precipitation

$(NH_4)HCO_3$

S

L

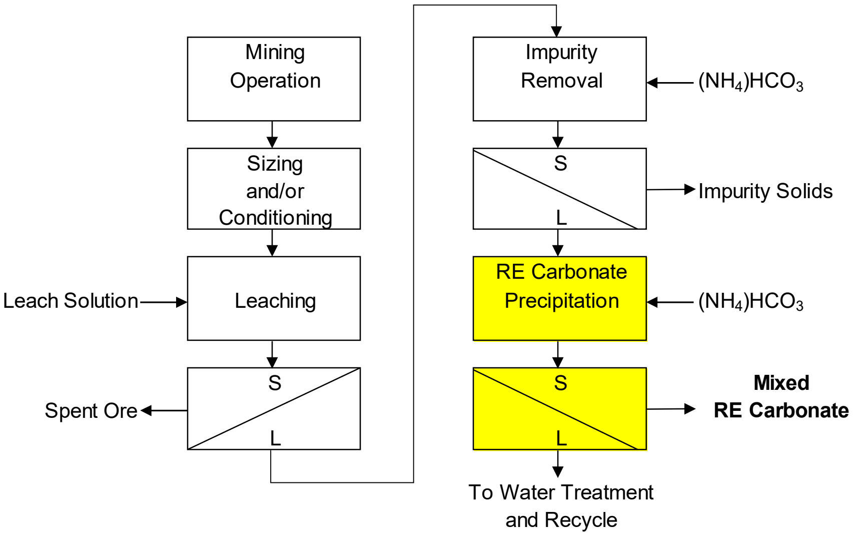
Mixed RE Carbonate

To Water Treatment and Recycle

Impurity Removal

- Raw leach solution has a very high impurity:RE ratio compared to RE mineral concentrate refineries - **an order of magnitude higher**
- RE losses invariably are high during solution purification
- Ammonium bicarbonate commonly used – expensive
  - Caustic soda and lime can't be used due to co-precipitation of REs
- Removes Fe, Al, Si and Th as hydroxides
- Aluminium and silicon can often make gels which can "rob" dissolved REs
- High addition rates of flocculent required

Mixed RE Carbonate Product


Mining Operation

Sizing and/or Conditioning

Leach Solution

Leaching

S

L

Spent Ore

Impurity Removal

$(NH_4)HCO_3$

S

L

Impurity Solids

RE Carbonate Precipitation

$(NH_4)HCO_3$

S

L

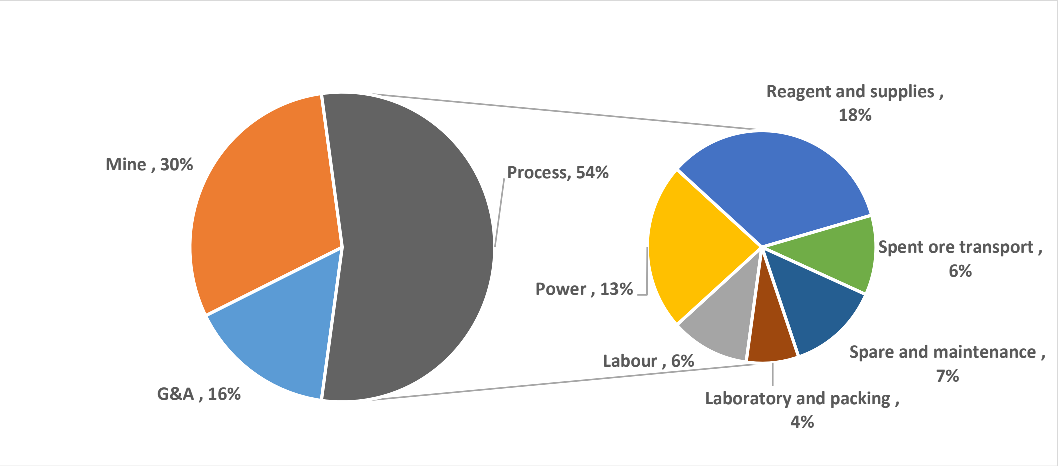
Mixed RE Carbonate

To Water Treatment and Recycle

Mixed RE Carbonate Product

- MREC is generally precipitated using ammonium bicarbonate
- Low Al_2O_3 (0.1%) is required for Chinese spec MREC. Even lower for Europe.
- Purity often difficult to meet unless RE recovery compromised or MREC refined
- Usually radionuclides (Th and U) within spec, but watch the decay daughters
- Final product is dried and bagged for export

Example of OPEX Cost Breakdown



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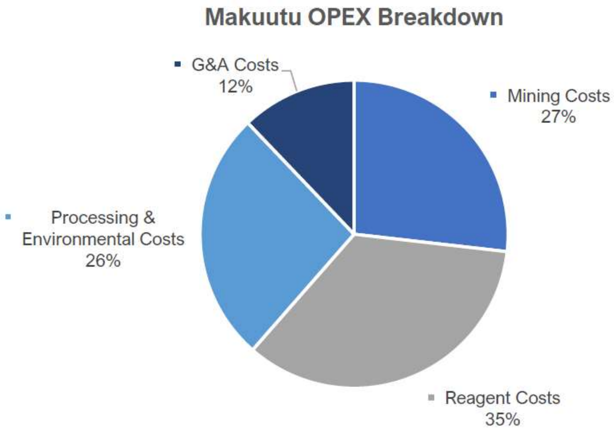
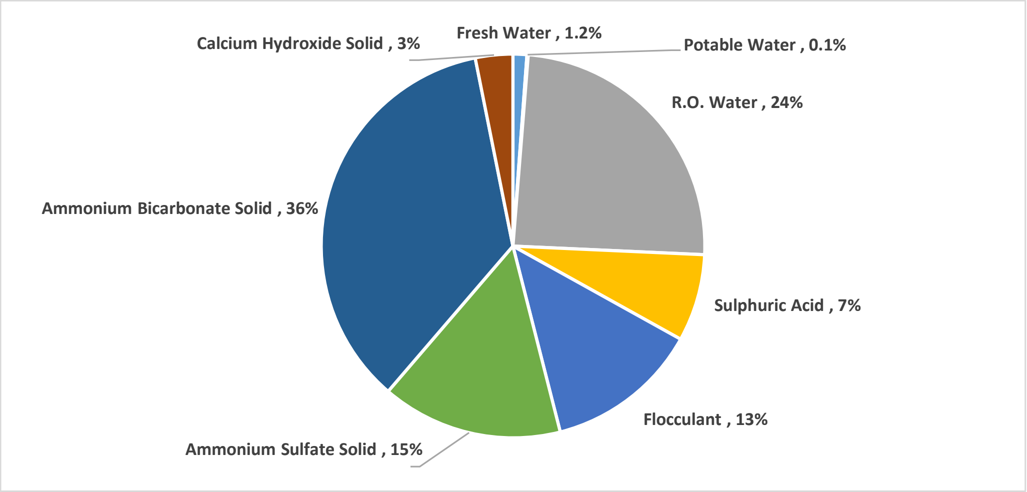
Example of OPEX Cost Breakdown



Makuutu Rare Earths Project Stage 1 DFS Process Flowsheet

Ionic Rare Earths ASX Release 20 March 2023

Example of Reagent Cost Breakdown
% of Total Reagent Only



NI 43-101 Technical Report PEA for Penco Module Project

Aclara SEDAR 15 September 2021

OPEX Commentary

- Reagent costs represent between 10 to 35% of total OPEX
- Ammonium carbonate reagent is the largest reagent expense – especially if leach liquor contains excess free acid
- Due to the high volumes of clays, flocculent costs are significant.
- The process requires a LOT of water to both extract REs and to remove soluble sulphates and ammonia from spent ore prior to rehabilitation
- Water treatment costs for recycle (nanofiltration) and/or discharge should not be underestimated

CAPEX Commentary

- Stirred tank reactor design:
  - Large tanks required, but offset by very fast desorption kinetics
  - <u>Very</u> large plate and frame filters
- Heap leach:
  - Potential for significantly reduced plant costs
  - But – increased risk of poor percolation
  - Agglomerator and stackers required

Assumed Revenue from RE Carbonate

- Off-take contract terms are now becoming more widely known
- Typically only 6 REs are paid for:
  - La, Ce, Pr, Nd, Tb and Dy
- Terms may be “simple”, eg
  - Very small % of La/Ce and high % of Pr, Nd, Tb and Dy of separated oxide pricing paid outright
- Or “complex”, eg
  - Above 6 RE separated oxide pricing less: refining charges, losses, admin charges
- Assigning a blanket discount value to fully separated basket pricing as oxide equivalents will overstate likely true sales revenues!

Take Home Thoughts

- Simple laboratory desorption tests provide a “go-no-go” assessment as to RE desorption mechanisms at play
- How much reagent are you using? If the combined cost of the H_2SO_4 and $(NH_4)_2SO4$ if more than >10% of the “basket price” of Nd, Pr, Tb + Dy then you will be up for a challenge
- Don’t forget radionuclides – these may be low in the ore but will concentrate with the REs into the RE carbonate (hint – Ac^{227})
- Last thought – are the Chinese/Myanmar operations actually “profitable” in a Western business model?

DRY, EFFLUENT-FREE, FLUORINATION OF RARE EARTH CARBONATES AND OXALATES

By

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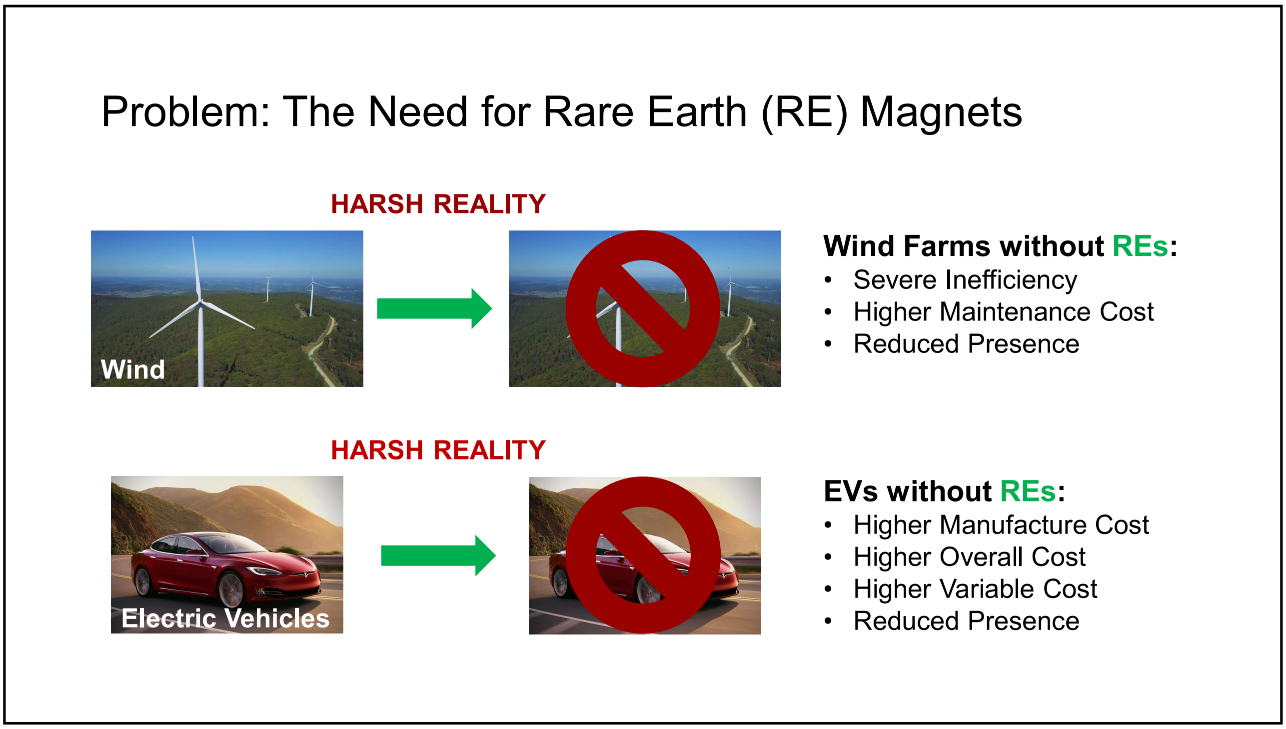
ABSTRACT

A dry fluorination process was developed for the production of rare earth fluorides using a novel and environmentally friendly process. The process produces rare earth fluorides in a batch process by reacting rare earth carbonates or oxalates with anhydrous hydrogen fluoride (AHF) at 125 °C and atmospheric pressure. The waste produced is water vapour and carbon dioxide. Any excess hydrogen fluoride may be reacted to extinction or scrubbed using wet or dry abatement systems.

The technology has been demonstrated on a semi-commercial scale, in a facility that produces 80 tpa rare earth fluorides. Piloting work was undertaken using neodymium carbonate as a feedstock. The kinetic studies undertaken show that the formation of NdF_3 *via* dry fluorination favours the use of $Nd_2(CO_3)_3 \cdot H_2O$ as a feedstock as opposed to Nd_2O_3. $Nd_2(CO_3)_3 \cdot H_2O$ is a less expensive raw material than Nd_2O_3 due to the calcination step required to go from the carbonate to the oxide. The kinetic study also indicated that the fluorination of $Nd_2(CO_3)_3 \cdot H_2O$ by AHF is not a strong function of temperature enabling a relatively low reaction temperature, 125 °C. Lower temperature operation allows the use of less exotic materials of construction and limits energy input requirements resulting in optimised CAPEX and OPEX.

Results from kinetic studies undertaken during the piloting phase of the work will be presented, highlighting the economic benefit of fluorinating the carbonate as opposed to the oxide. Lessons learned from the operation of the semi-commercial plant will be discussed along with recent campaigns completed using mixed oxalates as feed material. Finally, the applicability of dry fluorination technology in other critical materials will be discussed.

Keywords: Fluorination, carbonate, neodymium, rare earth



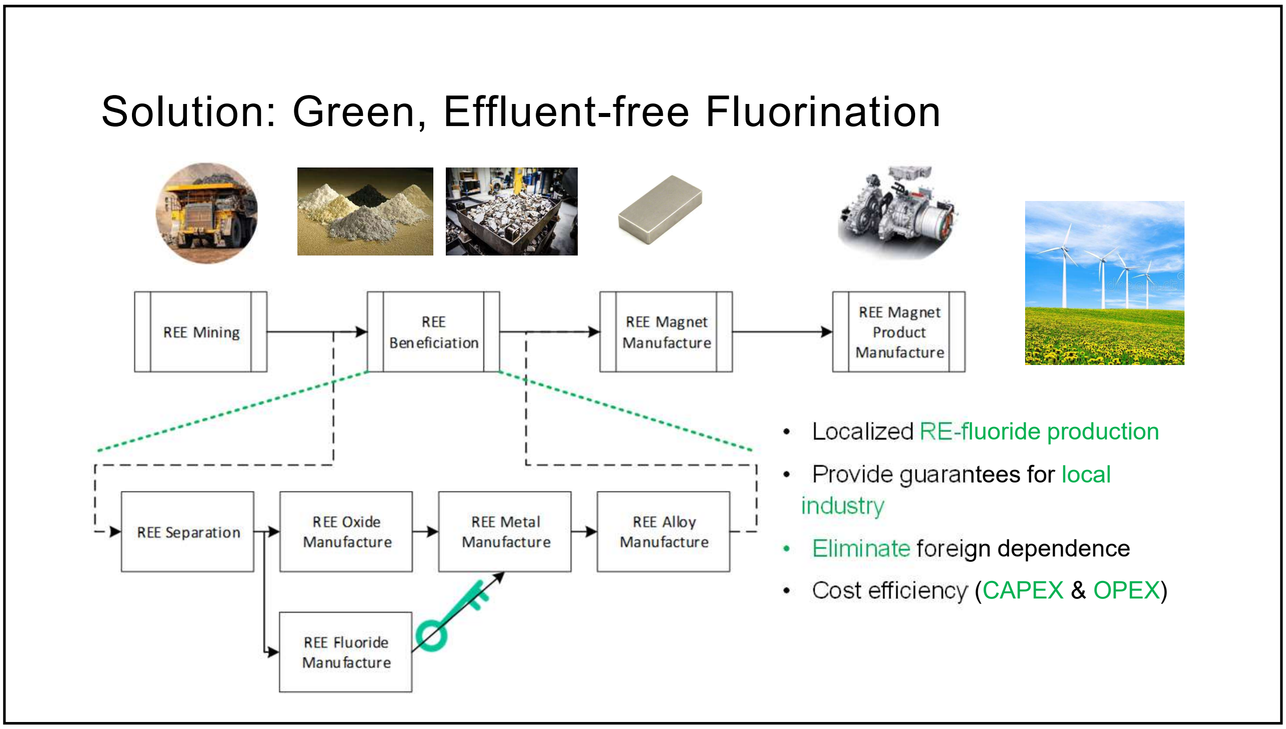
Problem: The Need for Rare Earth (RE) Magnets

HARSH REALITY

Wind Farms without REs:
- Severe Inefficiency
- Higher Maintenance Cost
- Reduced Presence

HARSH REALITY

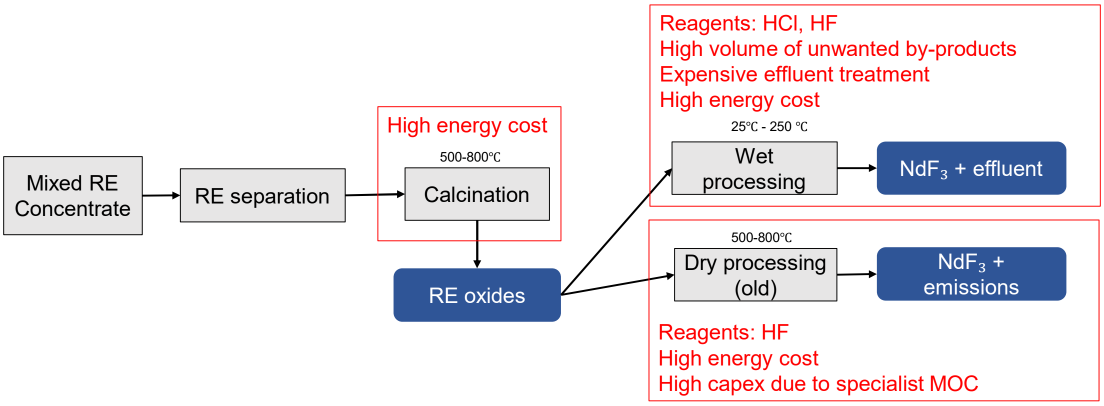
EVs without REs:
- Higher Manufacture Cost
- Higher Overall Cost
- Higher Variable Cost
- Reduced Presence



Solution: Green, Effluent-free Fluorination

- Localized RE-fluoride production
- Provide guarantees for local industry
- Eliminate foreign dependence
- Cost efficiency (CAPEX & OPEX)

Industrial Process Options



Mixed RE Concentrate

RE separation

High energy cost

500-800℃

Calcination

RE oxides

Reagents: HCl, HF
High volume of unwanted by-products
Expensive effluent treatment
High energy cost

25℃ - 250 ℃

Wet processing

NdF_3 + effluent

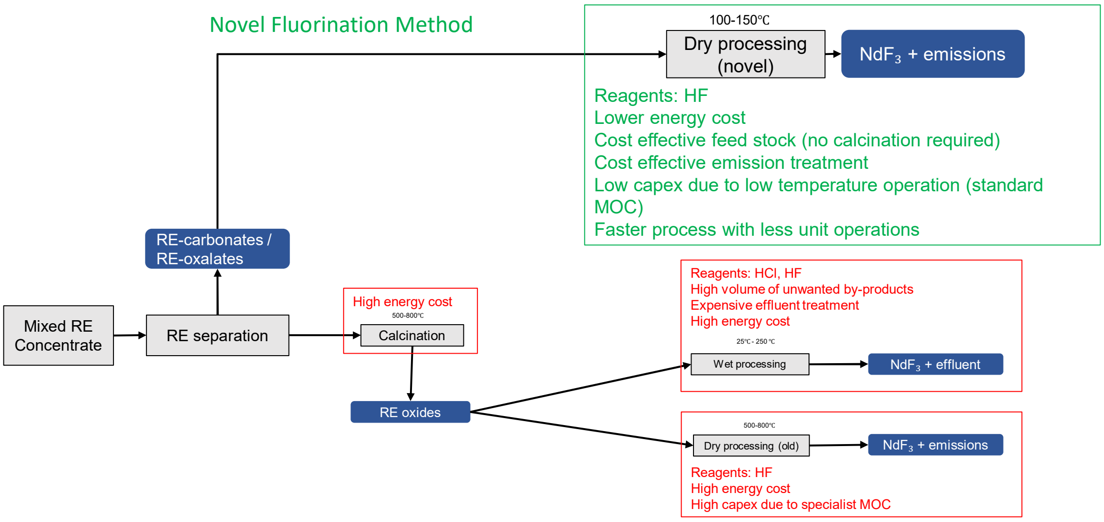
500-800℃

Dry processing (old)

NdF_3 + emissions

Reagents: HF
High energy cost
High capex due to specialist MOC

Industrial Process Options



Novel Fluorination Method

100-150℃

Dry processing (novel)

NdF_3 + emissions

Reagents: HF
Lower energy cost
Cost effective feed stock (no calcination required)
Cost effective emission treatment
Low capex due to low temperature operation (standard MOC)
Faster process with less unit operations

RE-carbonates / RE-oxalates

Mixed RE Concentrate

RE separation

High energy cost

500-800℃

Calcination

RE oxides

Reagents: HCl, HF
High volume of unwanted by-products
Expensive effluent treatment
High energy cost

25℃ - 250 ℃

Wet processing

NdF_3 + effluent

500-800℃

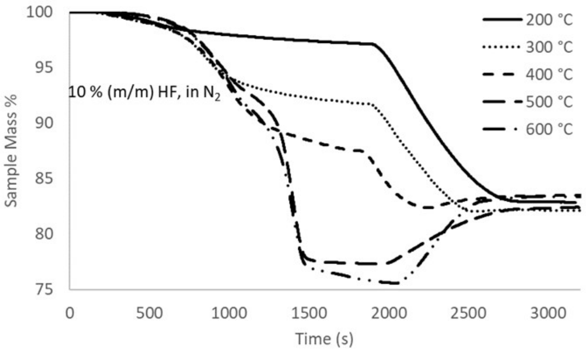
Dry processing (old)

NdF_3 + emissions

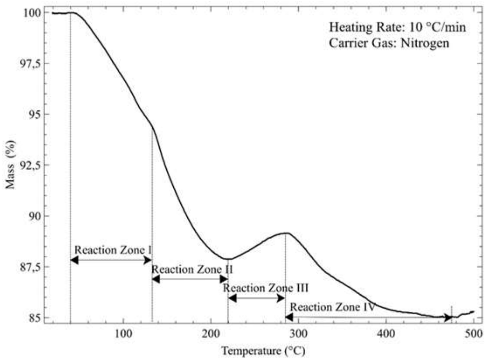
Reagents: HF
High energy cost
High capex due to specialist MOC

Fundamental Reaction Investigation

$$Nd_2(CO_3)_3 \cdot 8H_2O(s) + 6HF(g) \rightarrow 2NdF_3(s) + 11H_2O(g) + 3CO_2(g)$$

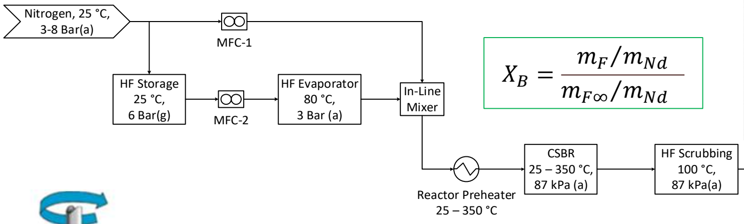


Isothermal thermogram of $Nd_2(CO_3)_3 \cdot H_2O$ during isothermal reaction with AHF at various temperatures.



Dynamic thermogram of $Nd_2(CO_3)_3 \cdot H_2O$ in a 10 % (m/m) HF atmosphere.

Pilot Operation and Reaction Kinetic Determination



Nitrogen, 25 °C, 3-8 Bar(a)

MFC-1

HF Storage 25 °C, 6 Bar(g)

MFC-2

HF Evaporator 80 °C, 3 Bar (a)

In-Line Mixer

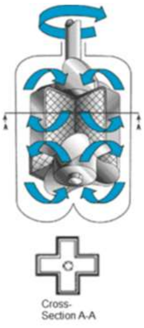
Reactor Preheater 25 – 350 °C

CSBR 25 – 350 °C, 87 kPa (a)

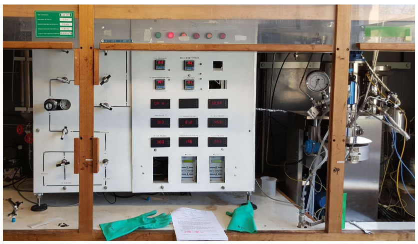
HF Scrubbing 100 °C, 87 kPa(a)

To Vent

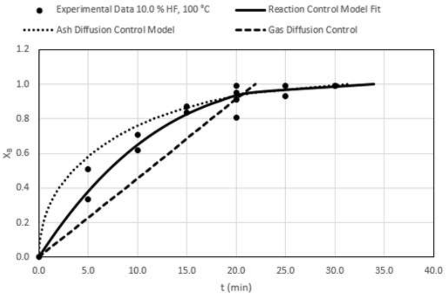
$$X_B = \frac{m_F / m_{Nd}}{m_{F\infty} / m_{Nd}}$$

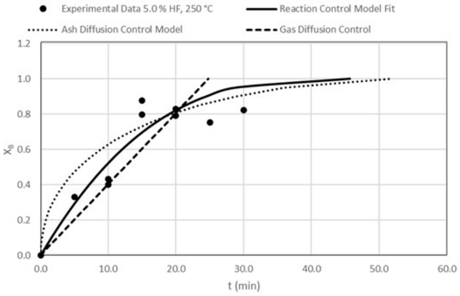


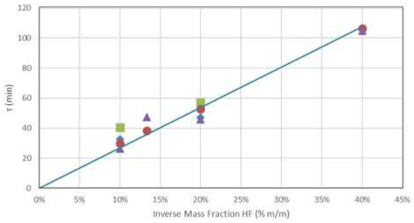
HF Concentration (m/m %)	Experimental Temperature (°C) 100	150	200	250
2.5		X		X
5.0	X	X	X	X
7.5		X		X
10.0	X	X	X	X



Experimental, Results and Kinetics







$$\tau = \frac{1}{\alpha^n k_0 e^{-E_a/RT}}$$

$$\boxed{\tau = \frac{2.6}{\alpha} \pm 10\%}$$

"Fluorination of neodymium carbonate monohydrate with anhydrous hydrogen fluoride in a Carberry spinning basket reactor" – Royal Society of Chemistry: Reaction Chemistry & Engineering

"Preparation Process for Rare Earth Metal Fluorides" - WO 2018/142337-PCT/IB2018050665

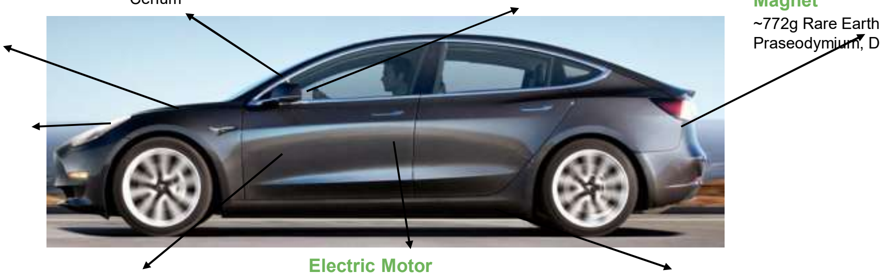
Demonstration Plant

- Enclosed system containing three heated Monel tube reactors, anhydrous hydrogen fluoride (AHF) storage and evaporation as well as a wet and dry scrubbers.
- Raw materials processed: $Nd_2(CO_3)\cdot xH_2O$, $(Nd_2,Pr_2)(C_2O_4)_3\cdot xH_2O$.
- Samples produced to client specifications (complete conversion): NdF_3, $(Nd,Pr)F_3$.
- Plant Capacity: 200 kg of RE-fluoride per batch.
- Confirmation of kinetic parameters.
- Plant OPEX and CAPEX.

Conclusions

- We developed a chemical reaction from a line on a piece of paper, through a bench scale concept, to a commercially capable technology product.
- Our process produces rare earth fluorides with a simple one-step chemical reaction in an effluent-free, cost effective manner.
- Samples were produced to client requirements.
- Our process is a more sustainable alternative to traditional processes.
- We offer significant advantages to other methods of fluorination both in terms of capital, operating and maintenance costs.
- Designs are finalised for modularly expandable plant solutions and can now be offered to clients for in-house licensed manufacture.

Rare Earths Every Day



Component Sensors
Yttrium

UV Cut Glass
Cerium

LCD Screen
Europium, Yttrium, Cerium

Electric Motor Permanent Magnet
~772g Rare Earths[1]: Neodymium, Praseodymium, Dysprosium, Terbium

Headlight Glass
Neodymium

Speaker Magnets
Neodymium

Electric Motor Magnets – HVAC, windows, seats
Neodymium

High Performance Batteries
Cerium
Lanthanum

[*] Advanced Research Projects Agency, "REACT Program Overview," Arpa, Washington, 2015.