PROCESS SELECTION CONSIDERATIONS FOR RECOVERY OF RARE EARTHS FROM MINERAL SANDS CONCENTRATES

Gavin Beer

Met-Chem Consulting Pty Ltd

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Caveats and Context

Public Domain Information:
The content presented is based on publicly available information. For further details, refer to original sources where applicable.

Estimates and Guides:
All values provided are approximate and should be used as general guides only. Values presented are project and location specific and have been prepared by third parties based on specific flowsheets and required outcomes.

Personal Opinion:
The insights and interpretations shared are based on the author's personal perspective. It is advised to consider multiple viewpoints and expert sources for a particular application.

No Professional Advice:
The information provided does not constitute professional advice. For expert advice, consult relevant professionals or authoritative sources.

Dynamic Field:
The field is continuously evolving; newer findings and data may supersede the information presented.

Rare Earth Sources

The world production of rare earths are derived from 3 deposits styles:

- Hard rock - 85 to 90% of world supply:
  - Mainly from China and Australia.
  - Bastnaesite and monazite are the main host minerals.

- Ionic clays – 5 to 10% of world supply:
  - Mainly Southern China and Myanmar.
  - This is the main contributor to the “heavy rare earths” (HRE) Sm to Lu.
  - See my paper from ALTA 2023.

- Mineral sands – 3 to 5% of world supply:
  - Mined in Australia, South Africa, China and India.
  - Main host minerals are monazite and (to a lesser extent) xenotime.

Mineral Sands Processing

Minerals sands have seen an increased focus as a viable and sustainable source of rare earths (REs).

- Economic deposits typically contain up to ~5% by weight of saleable products comprising of:
  - Titanium minerals (rutile, leucoxene, ilmenite).
  - Zirconium minerals (zircon).
  - RE minerals (monazite and xenotime).

- As the minerals are already liberated, comminution (crushing and grinding) isn’t required. Flowsheets typically include gravity (spirals), magnetic, electrostatic and flotation separation processes.

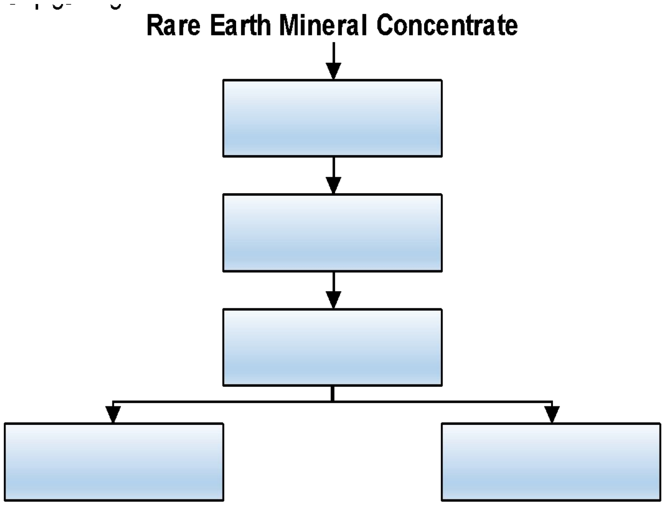
- RE mineral concentrates can contain grades up to 60% rare earth oxide (REO) depending on the mineralogy.

Mineral Sands Rare Earth Mineral Concentrates

- The most common RE mineral found in these deposits is monazite (Ce, La, Th, Nd, Y)PO4.
  - Main source of praseodymium (Pr) and neodymium (Nd) essential to RE magnets in EV drivetrains, wind turbines, micro motors etc.
  - Contains significant thorium (Th) – typically 5 to 12% by weight.
  - It is “refractory” and resistant to dissolution in most acids at ambient temperature.
- The mineral xenotime (HRE, Y)PO4 is often (but not always) present.
  - A significant source of high value terbium (Tb) and Dysprosium (Dy) after ionic clays. These elements when added to RE magnets provide high temperature stability.
  - This mineral is considered more refractory than monazite – particularly with respect to caustic cracking.

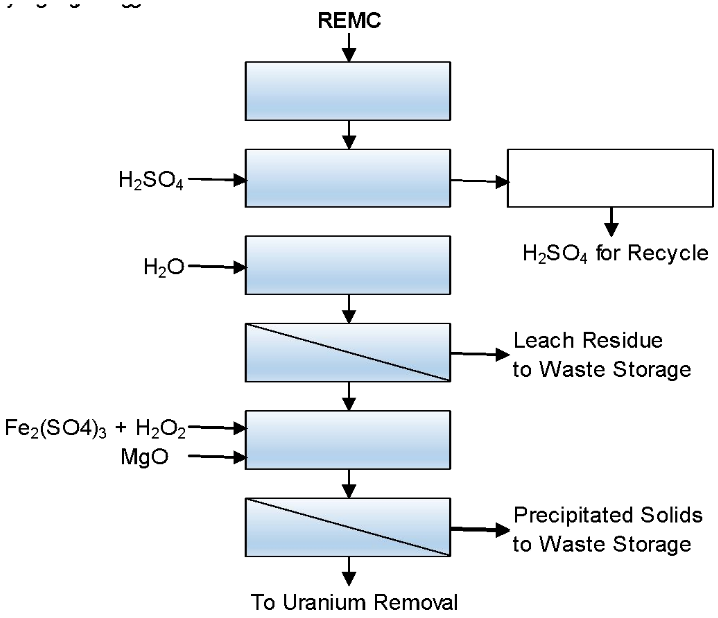
General Flowsheet

- RE mineral concentrates require “cracking”.
- Cracking is via concentrated acid or alkali conditions at elevated temperatures.
- Cracked solids are acid leached via added acid or residual acid from cracking.
- Impurities are removed from the solution.
- Purified solution is sent to separation or a mixed RE product is precipitated.



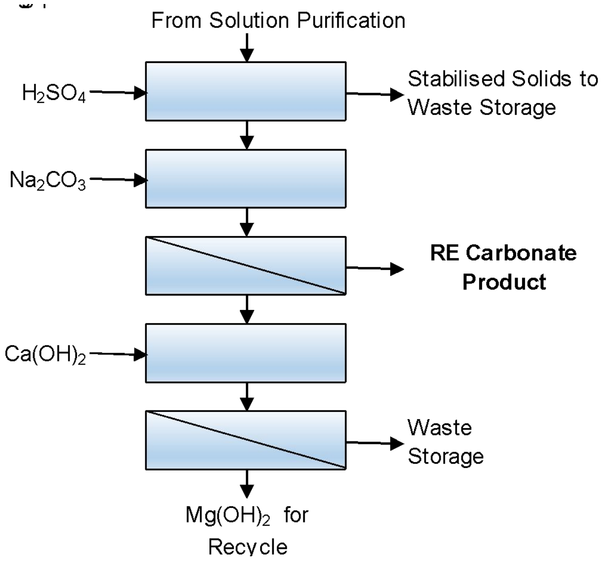
Acid Bake Flowsheet (1)

- Rare earth mineral concentrate (REMC) dried via rotary drier.
- Concentrated sulphuric acid mixed with dry REMC @ 1.2 to 1.5 tonnes per tonne of REMC.
- Acid baking undertaken in rotary kilns at 250°C to 350°C but may be as high as 700°C.
- Water leaching in rubber lined or fiberglass reinforced polymer (FRP) stirred tank reactors.



Acid Bake Flowsheet (2)

- Purified solution treated via ion exchange (IX) to remove uranium. Uranium is generally precipitated to form stable sodium diuranate.
- RE carbonate product is usually formed by adding soda ash.
- Alternatively, the RE sulphate solution can be sent directly to an onsite solvent extraction (SX).
- Magnesium hydroxide can be regenerated from the RE depleted solution using cheaper slaked lime.



Acid Bake Features (1)

- Very robust process and widely employed. Used in Australia, Malaysia and China.
- High extraction rates (~95% or better) of REs from monazite with similar extractions for xenotime.
- Risks are more around equipment selection, engineering and installation.
- The REMC must be dried before mixing with acid (i.e. CAPEX and energy cost considerations).
- Significant quantities of sulphuric acid required – more than the feed mass.
- Energy (generally natural gas) for acid bake kiln is considerable.
- Gas scrubbing circuit is substantial both in footprint and CAPEX.

Acid Bake Features (2)

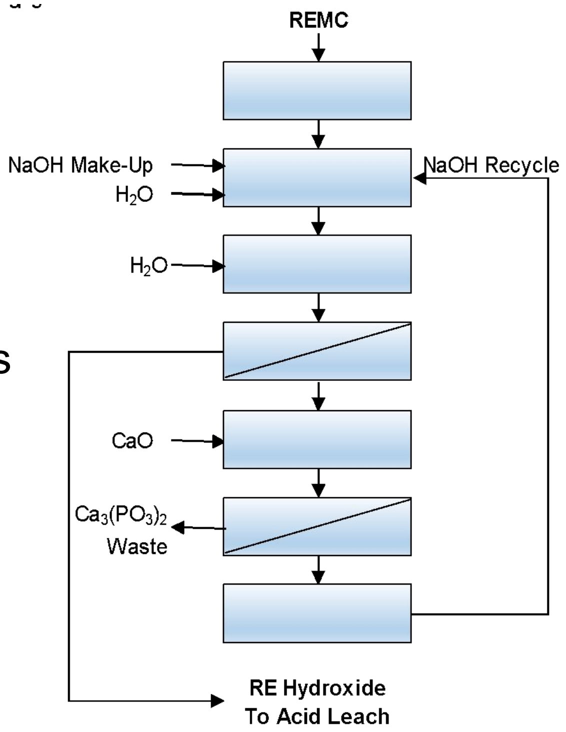
- Significant ferric sulphate (more than half the feed mass) may be required in purification at significant cost.
- Uranium can be easily recovered as a saleable minor by-product if required.
- ANSTO Minerals has developed and piloted the magnesia recycle process using cheap lime. This generates a significant (but not radioactive) waste stream of calcium sulphate.
- Large water requirement/disposal (>20 times dry feed mass) or significant additional CAPEX to recycle (i.e. nano filtration and evaporators).
- Large solid waste volumes (circa 4 times feed mass).

Acid Bake Features – Water, Waste and Radioactivity

- Large water requirement & disposal (>20 times dry feed mass) or significant additional CAPEX/OPEX to recycle (i.e. nano filtration and evaporators).
- Large solid waste volumes - circa 4 times feed mass.
- Radionuclides are spread across multiple waste streams:
  - Leach residue is often higher in radioactivity than the feed due to mass loss and un-leached thorium. This will be categorised as Dangerous Goods (Class 7).
  - Purification precipitate contains thorium but is diluted with (mainly) iron phosphate. Potentially can be combined with gypsum waste from magnesia regeneration.
  - Uranium recovered from IX can be stabilised during waste-water treatment stage where overall solids streams radioactivity will be low.
- Actinium (specifically Ac-227) follows the rare earths and reports to the RE carbonate rendering it radioactive (or even potentially DG Class 7). It can be removed during subsequent solvent extraction (SX).

Caustic Crack – Front End

- REMC generally needs grinding (~53um) but not drying.
- Cracking is done in high nickel reactors in concentrated caustic solution (>50% w/w) at elevated temperatures (>140°C).
- Phosphates from monazite/xenotime minerals are solubilised.
- Lime can be used to regenerate caustic soda and form calcium phosphate waste solids.
- REs converted to hydroxides and remain in solid phase. These go to acid leach.

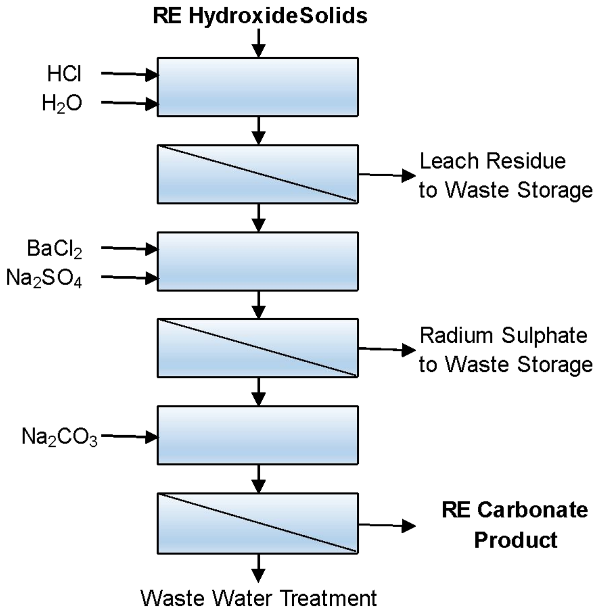


Caustic Crack Features

- REMC requires grinding to maximise the cracking process extractions.
- Undertaken on wet feed which reduces risk of radioactive dust exposure.
- The energy requirements for the heated reactors are lower than acid baking.
- High nickel content reactors are required due to very corrosive environment.
- Gas scrubbing is significantly smaller than acid bake process. Overall footprint also much smaller reducing civil/structural costs.
- RE conversion is generally very high (>95%) for monazite. Conversion of the heavy REs in xenotime can be significantly lower affecting Tb/Dy revenue.
- Thorium extractions similar to RE. U extractions typically 50 to 80%.
- Caustic soda recycle is very high (>90%) using cheap slaked lime.

Caustic Crack Chloride Route

- Selective leach using weak hydrochloric acid (pH 3 to 4) is undertaken in stirred reactors (rubber lined or FRP).
- As radium chloride is soluble, this radioactive element is removed by co-precipitating with barium as a sulphate.
- The purified RE solution from radium removal can be sent to an adjacent SX separation plant or precipitated as a RE carbonate as per the Acid Bake route.



RE HydroxideSolids

HCl

H_2O

Leach Residue to Waste Storage

$BaCl_2$

Na_2SO_4

Radium Sulphate to Waste Storage

Na_2CO_3

RE Carbonate Product

Waste Water Treatment

Chloride Route Features, Waste and Radiation (1)

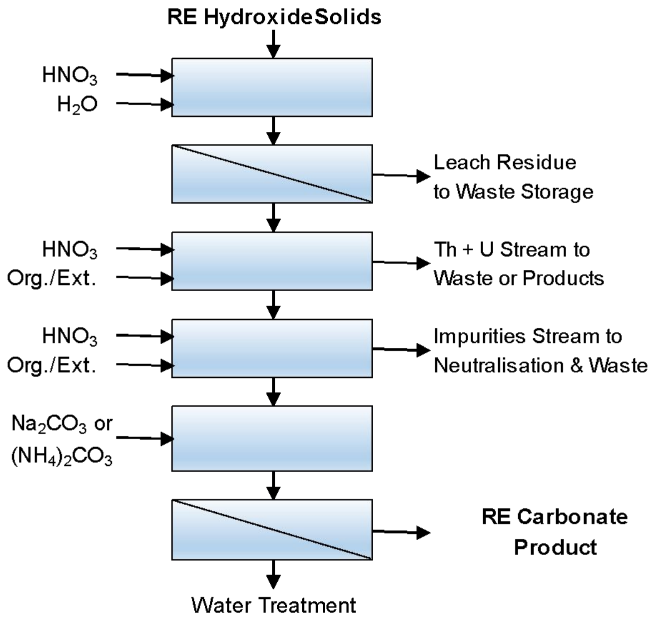
- No longer widely practiced but been well demonstrated commercially in India (IREL since 1950's). USA (Energy Fuels) and Canada (SRC) are constructing large scale demonstration plants.
- The selective leach is designed to target mainly RE dissolution but does result in a large volume radioactive waste stream.
- Cerium dissolution can be controlled by hot air drying the caustic cracked solids if required.
- HCl requirement is significant with slightly more than 1 tonne of 32% HCl required per tonne of REMC feed. Proximity to HCl supply is important.

Chloride Route Features, Waste and Radiation (2)

- Radium/barium sulphate precipitate waste stream is low volume but categorised as DG Class 7.
- Overall solid waste stream low mass – just over the REMC feed mass.
- Waste-water stream is ~ 75% of Acid Bake and is mainly dilute NaCl solution.
- Overall OPEX is ~20% less than Acid Bake depending on HCl cost.
- Overall CAPEX is expected to be higher than the Acid Bake mainly due to the NaOH recycle circuit which includes an evaporator.

Caustic Crack Nitrate Route

- “Hard” leach (1 to 5% nitric acid) typically in stainless steel stirred reactors.
- First SX stage targets Th and U which can be subsequently separated to product(s) or stabilised for waste disposal.
- Second SX loads all REs and rejects metal impurities including radium.
- Strip solution can go to adjacent SX plant or precipitate RE carbonate. Precipitant choice based on water disposal strategy and if SX separation plant is installed adjacent.



RE HydroxideSolids

HNO_3

H_2O

Leach Residue to Waste Storage

HNO_3

Org./Ext.

Th + U Stream to Waste or Products

HNO_3

Org./Ext.

Impurities Stream to Neutralisation & Waste

Na_2CO_3 or $(NH_4)_2CO_3$

RE Carbonate Product

Water Treatment

Nitrate Route Features, Waste and Radiation (1)

- Main commercial application was at La Rochelle in France (Rhodia 1950’s to 1990’s).
- The hard leach using nitric acid solubilises Th and U almost completely with increased solubilisation (compared to chloride route) of other impurities.
- HNO_3 requirement is similar to HCl (for the chloride route) by volume but at a higher strength (60%).
- SX uses commercially available extractant (TBP) which is widely employed for uranium processing. This is presently used for RE processing in Estonia (Silmet) and France (Solvay). Western Australia will also use TBP in nitric acid for separating REs at Iluka’s Eneabba facility which is under construction.

Nitrate Route Features, Waste and Radiation (2)

- SX uses diluted nitrate solution for stripping which is then concentrated using evaporators. This has a significant saving in reagent (OPEX) costs but at a positive CAPEX differential. Note power for evaporators will offset some savings.
- Radiation is concentrated into Th/U SX strip solution. This precipitated as a low volume (but high radioactivity) solids for disposal. It can also be further separated via SX into Th and U nitrate “products”.
- Radium in principle could be removed by barium sulphate co-precipitation, however SX with TBP is effective and very similar to the preceding Th/U SX.
- Overall solid waste stream volumes are the lowest of all three routes.
- Waste water stream volumes are low and can engineered to be net zero via nano filtration and evaporator use.

General Selection Matrix

METRIC	COMMENT	SULPHATION BAKE	CAUSTIC CONVERSION - CHLORIDE	CAUSTIC CONVERSION - NITRATE
CAPEX	Assumes caustic soda and magnesia recycle.	Lowest - however complex gas scrubbing with acid recycle may elevate costs.	Mid	Highest
OPEX	Highly dependent on reagent and power cost.	Highest	Mid	Lowest
LIGHT RE (Nd/Pr) RECOVERY	Recovery to RE carbonate.	High	High	High
HEAVY RE (Tb/Dy) RECOVERY	Recovery to RE carbonate.	High	Lower - especially if xenotime is present.	Lower - especially if xenotime is present.
FLOWSHEET OPERABILITY and TECHNOLOGY SUPPORT	How easy is the circuit to commission, operate and maintain.	Considered a "standard" process in China and Australia. Tolerent to multiple concentrate mineralogies.	Only commonly now used in India but plants under construction in USA and Canada. Chemistry and know how well known, however.	Previously practiced in France but ceased in 1993. Know how available via Carester. SX technology well known from uranium industry.
RADIONUCLIDE DEPORTMENT	With regards to operations and waste streams.	Dust inhalation (during drying, baking and gas scrubbing) most likely source for exposure. Leach residue & purification residue classified radioactive.	Selective leach results in large volume radioactive leach residue stream. Also radioactive radium/barium precipitate waste stream.	Th/U concentrated to a high purity small volume waste stream. Same for radium.
SOLID WASTE GENERATION	Focus on volume which requires onsite storage or 3rd party disposal.	Largest volume of waste solids.	Significantly lower voluime of waste solids volume.	Lowest volume of solid waste.
REAGENTS	Quantity and cost contribution of reagents to OPEX.	A lot of sulphuric acid ferric sulphate required. These reagents are a significant proportion of overall OPEX along with kiln fuel requirements.	Main reagent costs are hydrochloric acid and soda ash. Proximity to cheap acid is important.	Main reagent costs are nitric acid and soda ash. Proximity to cheap acid is important. No requirement for barium salt for radium removal.
WATER REQUIREMENTS	Water requirements dictate both cost of supply and cost of recycle or disposal.	Highest	Low	Lowest or net zero.

Note green shading indicates preferred route for the specific metric

Summary

Choice of flowsheet is quite a complex exercise and must be undertaken once the following metrics are locked down:

- Feed mineralogy and sources tested through the flowsheet options.
- Expected life of facility – i.e. long term lower OPEX versus higher CAPEX.
- Location:
  - Proximity to reagents and cost.
  - Power costs.
  - Water availability.
  - Waste disposal options for solids, solutions and radioactive streams.
  - Access to technical resources for construction, commissioning and operation.
- Whether a separation plant will be included at the same location.

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