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Lessons Learned From Ionic Clay Testwork

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

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Introduction

Ionic Clays

- The global demand for rare earth elements is on the rise due to the increasing adoption of modern and environmentally sustainable technologies, including wind turbines, electric vehicles, fuel cells, and advanced materials.
- REE-bearing ores are typically found in the form of carbonates or phosphates.
- Extraction from these ores involves processing with concentrated sulfuric acid, hydrochloric acid, or sodium hydroxide at elevated temperatures.
- Ionic clays, found in areas like southern China, represent a unique class of REE-ores.
- These clays are formed through the chemical weathering of REE-containing parent rocks, resulting in the mobilization and enrichment of REE ions onto the clay surface through ion adsorption.

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Introduction

- No clay REE deposit exists purely as ‘ionic’. They are formed as nature and time weather a REE-rich hard rock source, like granite, into three distinct phases.
- The adsorbed (ionic) phase is easily, quickly and cheaply desorbed with a salt solution at pH4, for instance.
- Then you have a secondary mineral phase. Here, as the minerals release the rare earths as they break down, which then form a secondary mineralisation.
- These rare earths can be extracted with a modest pH solution, which is more expensive, but possible.
- Finally, there is a resistive phase. That’s the mineral containing rare earths which hasn’t been broken down. This stuff is uneconomic to extract at the low-grade characteristic of IAC deposits.

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Ionic Clays

- Ionic clays are a special type of clay formed through the chemical weathering of rocks containing rare earth elements (REEs).
- REEs, such as lanthanum, cerium, and neodymium, are mobilized and adsorbed onto the surface of the resulting clay particles.
- Chemical breakdown of parent rocks containing these rare earth elements.
- The ions of rare earth elements are mobilized and adsorbed onto the surface of the resulting clays.
- Ionic adsorption is a phenomenon where ions adhere to the surface of a solid, in this case, clay particles.

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Ionic Clays

- A distinctive feature of Ionic Clays is that rare earth elements are primarily found on the surface of clay particles, rather than being encapsulated within larger mineral phases. This makes rare earth elements more accessible and, consequently, easier to extract compared to other types of rare earth minerals.

- Ionic Clays, especially those found in subtropical regions like southern China, often allow for the leaching of rare earth elements under relatively mild conditions. This can be achieved through heap leaching or in-situ leaching with mild leaching solutions, resulting in the collection of a stream rich in rare earth elements.

- These resources have become of significant interest in the pursuit of more sustainable and economically viable alternatives for the production of rare earth elements.

- Driven by the growing global demand and the challenges associated with conventional production methods.

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Properties and Characteristics of Ionic Clays

Surface Adsorption	• One of the key features is the surface adsorption of rare earth elements (REEs) onto clay particles. • REE ions are concentrated on the surface, making them more accessible for extraction.
Accessibility of REEs	• Unlike some rare earth minerals encapsulated within larger mineral phases, REEs in Ionic Clays are predominantly found on the clay surface. • This surface location enhances the ease of extraction, contributing to the economic viability of these clays.
Ionic Adsorption Phenomenon	• The adsorption of REE ions onto clay particles is an ionic adsorption phenomenon. • This phenomenon involves the adherence of ions to the surface of the solid clay particles.
High Cation Exchange Capacity	• Ionic Clays exhibit a high cation exchange capacity, allowing them to readily absorb and release ions. • This property contributes to their versatility and applicability in various industries.
Formation Flexibility	• The formation of Ionic Clays occurs through the chemical weathering of rocks containing rare earth elements. • This natural process allows for the formation of clays in diverse environments, contributing to their global distribution.

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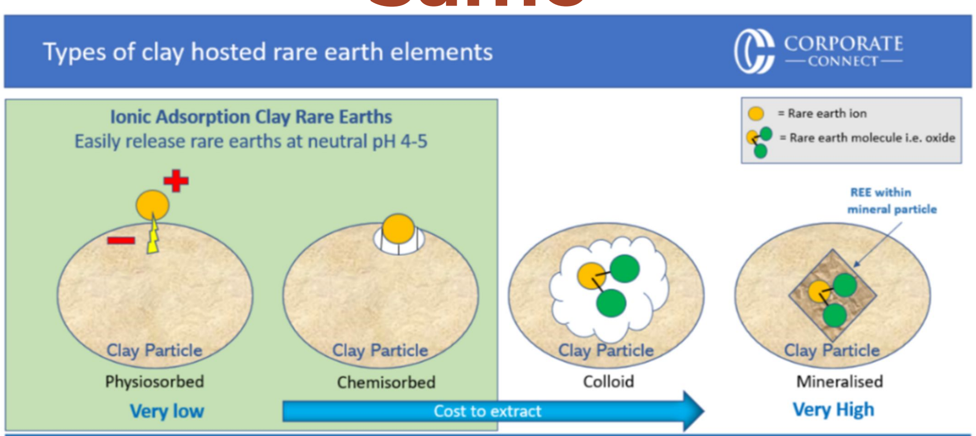
Not All Ionic Clays Are The Same



Extraction method and acid consumption costs NB: Acid (Sulphuric) costs approximately US$150/kg			
No acid	< 30 kg/tonne acid < US$4.50 tonne of ore	100kg/tonne acid ~US$15.00 per tonne of ore	> 500kg/tonne acid > US$75.00 tonne of ore
Desorbed with simple monovalent salt solution	Desorbed with simple monovalent salt solution & weakly acidic conditions	Acid Leach	Aggressive alkaline bake or acid leach

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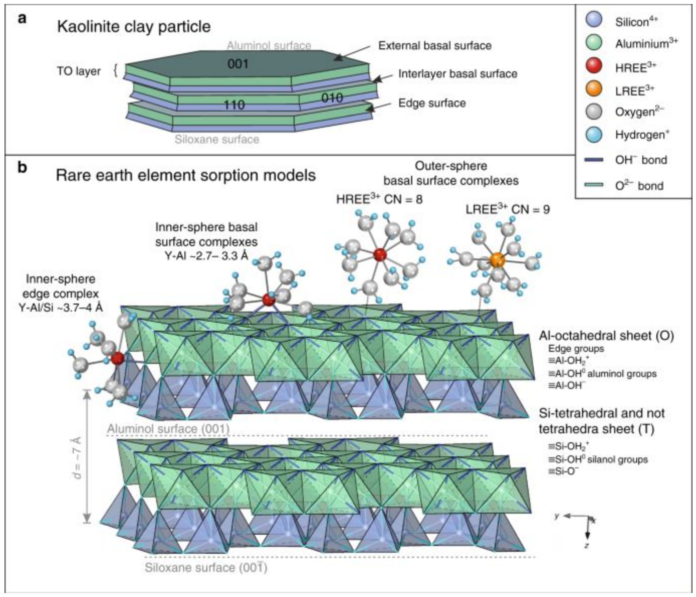
Occurrence characteristics of rare earth elements on the surface of kaolinite



Extraction techniques

- Chemical leaching plays a crucial role in the extraction of Rare Earth Elements (REEs) from regolith-hosted deposits.

- This process involves using a leaching solution, or lixiviant, to initiating an ion-exchange reaction with clay minerals of the ore. As the lixiviant interacts with the REE-adhered clay minerals, displacement occurs, causing the REEs to dissolve into the leaching solution.

- An illustrative example involves the use of a metal sulphate lixiviant, where the ion-exchange reaction transforms REEs adhered to clay minerals into dissolved REEs in the leaching solution.

- This chemical leaching method serves as a key mechanism for liberating and recovering REEs from their mineral matrix in host deposits.

$$2\,\mathrm{Clay{-}REE} + 3\,\mathrm{M_2SO_4} \longrightarrow 2\,\mathrm{Clay{-}M_3} + \mathrm{REE_2(SO_4)_3}$$

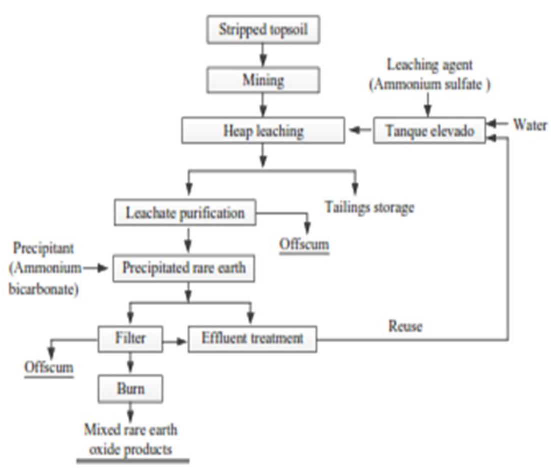
Overview of Leaching Technologies for Ion-Adsorption Clays

- Ion-adsorption clays are characterized by containing 0.05 to 0.3 wt.% rare earth elements (REE)
- With over 60% typically existing as physically adsorbed species recoverable through simple ion-exchange leaching. The leaching process involves the use of concentrated inorganic salt solutions with monovalent cations.
- During leaching, physically adsorbed REE are easily and selectively desorbed, substituting on the substrate with monovalent ions and transferring into solution as soluble sulfates or chlorides, following a theoretical 3:1 stoichiometry.
- However, the actual lixiviant usage often exceeds stoichiometric requirements due to competing desorption of other cations (e.g., Al) also adsorbed on clays.

Variety of Leaching Methods

Leaching methods for extracting REEs from IACs include:

- **Heap leaching**: Excavating minerals, placing them in a mound, and spraying with solutions.
- **Tank/VAT leaching**: Placing minerals into a tank/VAT and immersing them with solutions.
- **In-situ leaching/ recovery (ISL/ISR):** Dominating technology due to less topsoil removal, on-site processing, and reduced environmental impacts.



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Lixiviants

Ammonium Sulphate $(NH_4)_2SO_4$

- A traditional lixiviant used for REE extraction, particularly from ionic adsorption clays.
- Weakly acidic ammonium sulfate is often used to leach REEs from the ore matrix.

Hydrochloric Acid HCl

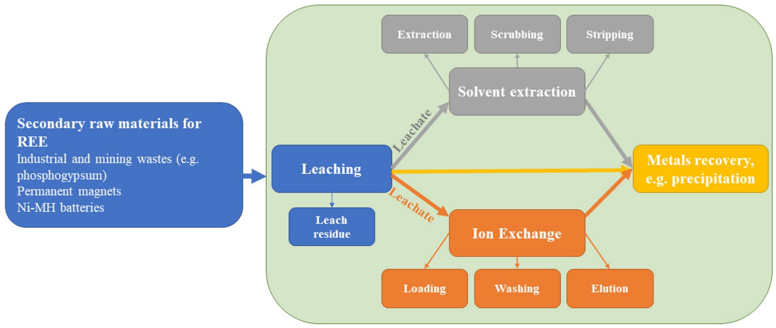
- A strong acid commonly employed in laboratory and industrial settings for REE extraction.
- Hydrochloric acid, particularly at pH<5 and elevated temperatures (e.g. 80°C), has shown effectiveness in dissolving REEs.

Sulphuric Acid H_2SO_4

- A strong acid commonly employed in industrial settings for REE extraction at elevated temperatures commonly seen in the sulfuric acid baking process.
- Has shown effectiveness in dissolving REEs.

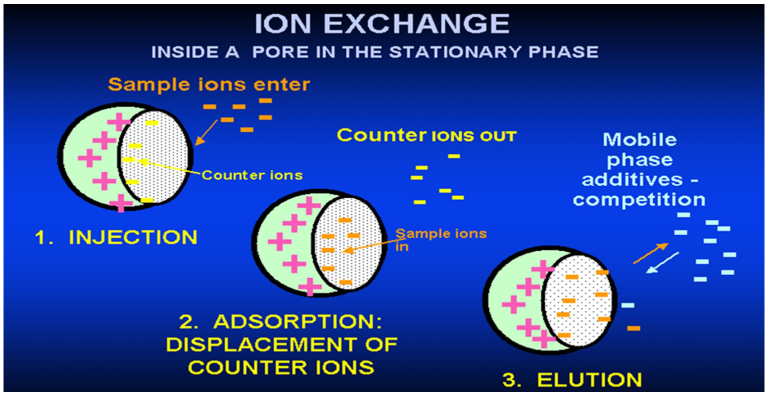
Recovery Techniques-Adsorption

- Adsorption techniques play a crucial role in the recovery and concentration of Rare Earth Elements (REEs) from leach solutions.
- These techniques involve the selective adherence of REEs to certain surfaces or materials, facilitating their separation from the solution.
- Selection of specific adsorption agents or ion exchange resins to selectively capture and concentrate the dissolved REEs from the leach solution.



Ion exchange

- Ion exchange (IX) is the separation of ions from a solution using solid inorganic oxides or organic ion exchange resins with negative or positive charges.
- Ion exchange resins can selectively capture and concentrate specific REEs from a leach solution.



Adsorption techniques

Chelating Agents:

- Chelating agents are organic compounds that form stable complexes with metal ions. In the context of REE extraction, chelating agents can surround and capture individual REEs, forming soluble complexes.

Clays and Minerals:

- Clays and minerals have high surface areas and specific chemical properties that enable adsorption through surface interactions. The minerals' surfaces attract and bind with REEs present in the solution.
- Some clay minerals can act as natural adsorbents for REEs, and the selection of the appropriate clay or mineral depends on the specific characteristics of the ore and solution.

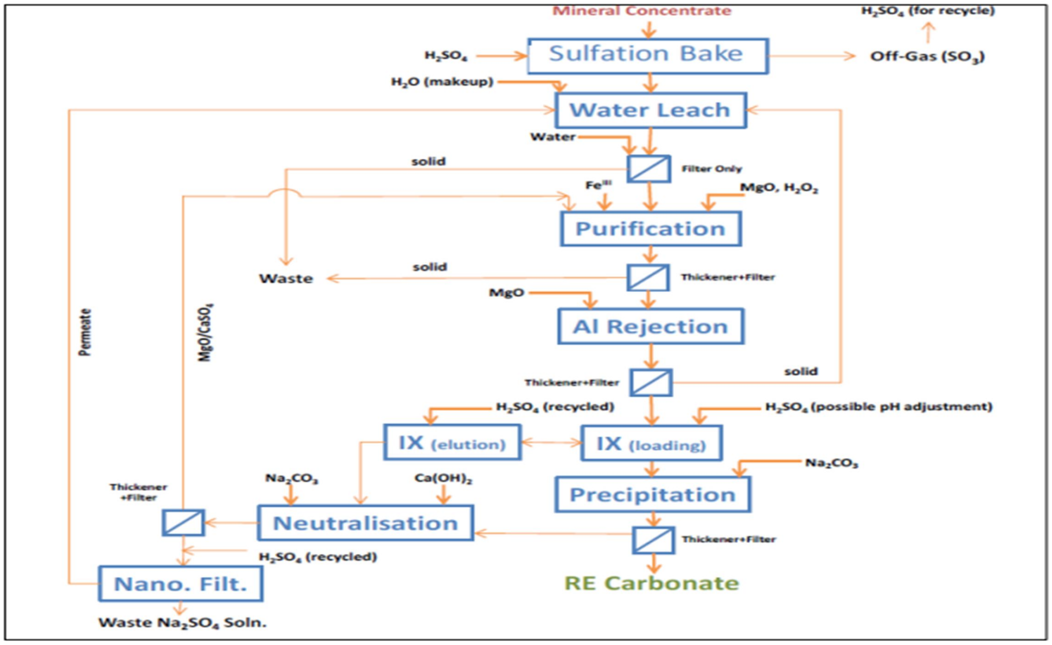
Activated Carbon:

- Activated carbon has a highly porous structure with a large surface area. It adsorbs substances through physical interactions, such as van der Waals forces and pi-pi interactions.
- In REE extraction, activated carbon can be employed as an adsorbent to capture REEs from solution, offering versatility in different extraction processes.

Silica Gel:

- Silica gel, composed of porous silicon dioxide, can adsorb substances through physical adsorption and capillary condensation within its pores.
- Silica gel can be utilized as an adsorbent for REEs under specific conditions, providing a selective capture method.

Plant Flowsheet



Current and Future Demand

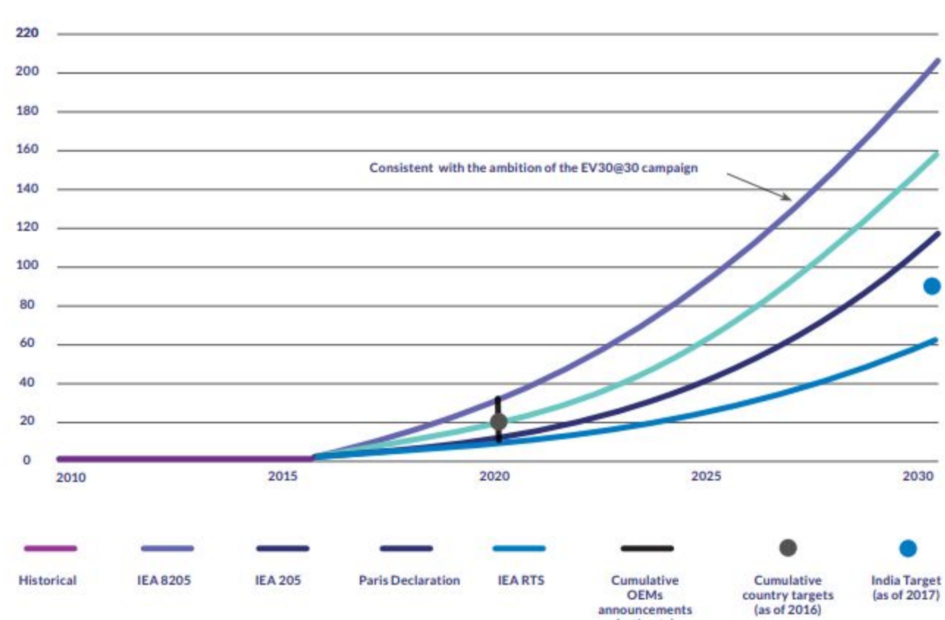
- Rare earths play a key role in modern society featuring use in a variety of applications.
- Many current applications include being used for catalytic converters in cars and are used as magnetics for components in wind turbines.
- They are also used in the production of smart phones where they are used for producing the colours of a phone display.
- In the future demand is expected to continue due to the growing industry for electric vehicles (EVs)where they are required for rechargeable batteries and traction motors.

General Uses of Rare Earths

- Globally, most REEs are used for catalysts and magnets
- In USA, more than half of REEs are used for catalysts, ceramics, glass and polishing
- Other important uses of REEs include the production of high performance alloys, glasses, and electronics
- REE has also been used in agriculture as REE-enriched fertilizers

Electric Vehicles

Figure 12-2 Deployment scenarios for the stock of electric cars to 2030



Ionic Adsorbent Clay (IAC) Testwork

- Testwork approach in ionic adsorbent clay (IAC) need to be a systematic and technical examination conducted in a laboratory setting to understand and optimize the process of extracting rare earth elements (REE) from these clay deposits.

- This intricate process involves conducting experiments using various methodologies and leaching agents to assess the feasibility and efficiency of liberating and adsorbing REE from IAC.

- Key objectives include identifying effective leaching agents, maximizing REE recovery, overcoming initial challenges observed in the results, and continually optimizing the process to achieve economic and sustainable performance.

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Ionic Adsorbent Clay (IAC) Testwork

- Collaboration with metallurgical experts to ensure a comprehensive understanding of the material's behavior. This technical approach plays a pivotal role in enhancing operational efficiency and reducing costs, while potentially yielding valuable by-products such as kaolin.

- By providing a solid foundation, the insights gained from testwork contribute to informed decision-making for the scale-up implementation of REE extraction processes from IAC. This technical focus sets the groundwork for potential expansions and future research in this specialized field.

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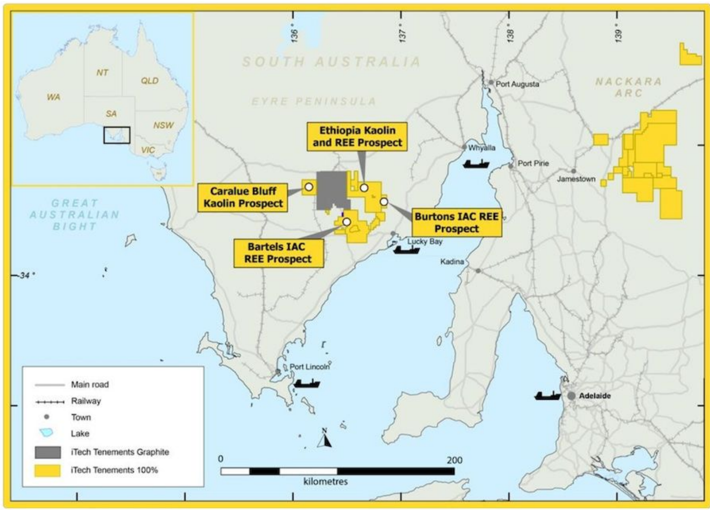
Study Cases - Caralue Bluff, Australia

1. **Discovery:**
   - Originally identified as a high-purity kaolin prospect.
   - 2022 drilling by iTech revealed significant REEs in kaolin-rich intervals.
2. **Exploration Target:**
   - Caralue Bluff Prospect's exploration target: 110-220 Mt @ 635-832 ppm TREO, 19-22% Al_2O_3.
   - Based on 80 drill holes from a total program of 260 holes across a 12km x 12km area.
3. **Mineralization Characteristics:**
   - REE mineralization rich in key magnet REEs (Nd-Pr-Dy-Tb), averaging 25% of the REE basket.



iTech Minerals Testwork

The Situation

- iTech Minerals' initial testwork at a commercial lab.
- Initial testwork failure achieved near zero recovery.

The Challenge

- The challenge was to identify the cause of the zero recovery.
- Overcome the difficulties in extracting REEs from the iTech sample.

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Methodology

Metallurgical Testwork Program

1. **Leaching Testwork:**
   - iTech Minerals sought assistance from METS.
   - A metallurgical testwork program was developed and executed.
   - Improved leaching recovery of REEs.
2. **Lixiviants Investigation:**
   - Various lixiviants, including ammonium sulfate and hydrochloric acid, were tested.
   - Laboratory results favored hydrochloric acid at pH<5 and 80°C for >87% REE extraction.
3. **Beneficiation Testing:**
   - Beneficiation through screening doubled the REE grade for processing.
   - Process optimization led to reduced OPEX and CAPEX.
5. **Variability in IAC Deposits:**
   - Tests on an Australian IAC revealed differences in deposits.

Leaching Testwork

Recoveries:
- 86% TREO achieved in leaching tests.
- 88% MREOs (Nd, Pr, Dy, Tb) recovered.

High Chloride Environment:
- Hydrochloric acid was used to create a high chloride environment.
- High chloride environment is required to liberate REEs from the clay solution.

IAC Characterisation:
- Bulk of the REEs not bound to within the lattice structure of the clay particles or in resistive minerals such as zircon or monazite.

REE Extractions (%)			
	Test 1 (10% HCl)	Test 2 (20% HCl)	Test 3 (32% HCl)
La	70.66%	84.22%	82.50%
Ce	73.36%	85.32%	81.68%
Pr	78.21%	87.60%	84.44%
Nd	81.84%	90.22%	85.78%
Sm	83.23%	91.60%	85.78%
Eu	74.40%	88.37%	79.56%
Gd	83.36%	88.32%	88.28%
Tb	80.96%	92.41%	86.64%
Dy	76.14%	82.06%	77.58%
Ho	68.06%	82.01%	72.17%
Er	70.01%	75.20%	75.98%
Tm	0.00%	0.00%	0.00%
Yb	56.05%	54.91%	50.97%
Lu	0.00%	0.00%	0.00%
Y	73.21%	81.10%	77.82%
Total	**75.34%**	**86.31%**	**82.95%**

Beneficiation Testwork

Concentration of REEs:

- Through simple screening at 20 µm.
- Concentration in the -20 µm fraction of just over half sample mass (51%).

Recoveries:

- 74.5% total REEs deport to fine fraction.
- >75% Magnet REEs (Nd + Pr).

Reduction Leach Feed Volume:

- Lower acid consumption.
- Smaller clay volumes to leaching.
- OPEX and CAPEX reductions

Valuable By Product:

- This fraction contains the potentially valuable kaolin by-product.

Size (µm)	TREE+ Y Mass (mg)	TREE+Y Dist. (%)	Nd Dist. (%)	Pr Dist. (%)
+150	57.08	10.13	9.46	9.32
+106	15.63	2.77	2.74	2.70
+75	15.39	2.73	2.64	2.58
+45	23.65	4.20	3.96	4.00
+38	4.10	0.73	0.68	0.69
+20	27.99	4.97	4.96	4.87
-20	419.78	74.48	75.57	75.84
Head Assay	563.62	100	100	100

Notes:

TREE: Total Rare Earth Elements

HREE: Heavy Rare Earth Elements

LREE: Light Rare Earth Elements

Testwork Outcomes

Initial Testwork Challenges:

- iTech Minerals faced zero recovery in initial commercial lab testwork.

METS Collaboration:

- Collaboration with METS led to an 87% leaching recovery of REEs.
- Process optimization to reduced operational and capital expenditures.
- Simultaneously produced a kaolin product as a by-product during the process.

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Conclusion

- The existence of ionic clays highlights the diverse nature of rare earth ores, particularly in subtropical regions like southern China, expanding the scope for resource exploration.
- The success of the Caralue Bluff Prospect's drilling program suggests significant potential for rare earth extraction, with an open-ended exploration target and rich magnet REE mineralization.
- iTech Minerals' metallurgical achievements, including an 86% leaching recovery and process optimization, not only enhance resource extraction efficiency but also yield a valuable kaolin by-product, demonstrating sustainable resource utilization.

Conclusion

- iTech Minerals' collaboration with METS showcased resilience in overcoming challenges, transforming zero recovery in initial testwork to an impressive 87% leaching recovery for REEs through process optimization.
- The success in China using weakly acidic ammonium sulphate underlines the economic efficiency of processing IAC, aligning with very low overall costs.
- Varied outcomes in Australian IAC testwork emphasize the need for tailored beneficiation strategies, with screening doubling REE grades, showcasing the diversity within IAC deposits.

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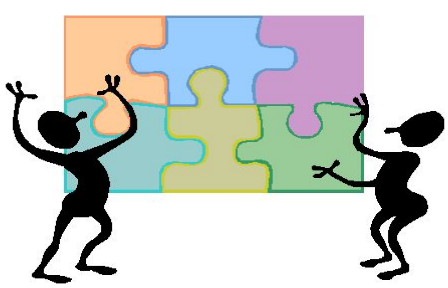
Attendee Outcomes

What did you get out of this presentation?
Please share your thoughts in an informal discussion



Any Questions?

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