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Hydrometallurgical processes for the recovery of critical raw materials from coal mining waste

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Why Coal Waste?

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- **Resource Rich:** Coal combustion wastes (ash) and mining tailings can concentrate valuable elements, including REEs, Gallium, Germanium, and others, often from natural enrichment during coal formation.

- **Sustainability:** Offers a circular economy approach, turning environmental liabilities (waste heaps) into economic assets, reducing virgin mining, and lowering energy/waste

Key Targets in Coal Waste

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- **Rare Earth Elements (REEs):** Critical for green technologies (magnets, batteries).
- **Gallium (Ga), Germanium (Ge):** Important for electronics and high-tech applications.
- **Titanium (Ti):** Recoverable from some slags, useful as a raw material.

Minerals	Formula	Reference
Allanite	$(Y, La, Ca)_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$	Dushyantha et al. (2020)
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Challenges & Future

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- **Low Concentrations:** CRMs often occur at low levels, requiring efficient separation.
- **Process Integration:** Developing cost-effective, integrated flowsheets with high recovery and purity.
- **Policy Support:** Need for regulations and R&D to scale these promising technologies

Core Hydrometallurgical Steps

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Leaching (Dissolution):

- Uses acids (like sulfuric or hydrochloric acid) or biological agents (bioleaching) to dissolve targeted metals from the solid coal waste into a liquid solution.
- Pre-treatment (like roasting) might be needed for refractory metals.

Solution Concentration & Purification (Separation):

- Solvent Extraction (SX): A key method for separating REEs and other metals using organic solvents that selectively bind to the desired ions.
- Ion Exchange (IX): Uses resins to capture and release metal ions from the solution.
- Selective Precipitation: Chemicals are added to cause specific metals to form solid precipitates, leaving others in solution.
- Membrane Separation: Using semi-permeable membranes to filter and concentrate metals.

Metal Recovery:

- Electrowinning: Applying an electric current to deposit pure metals onto cathodes (common for copper, zinc).
- Precipitation: Forming pure metal salts or compounds (e.g., REE carbonates) from the purified solution.

Mineral Processing Pathways

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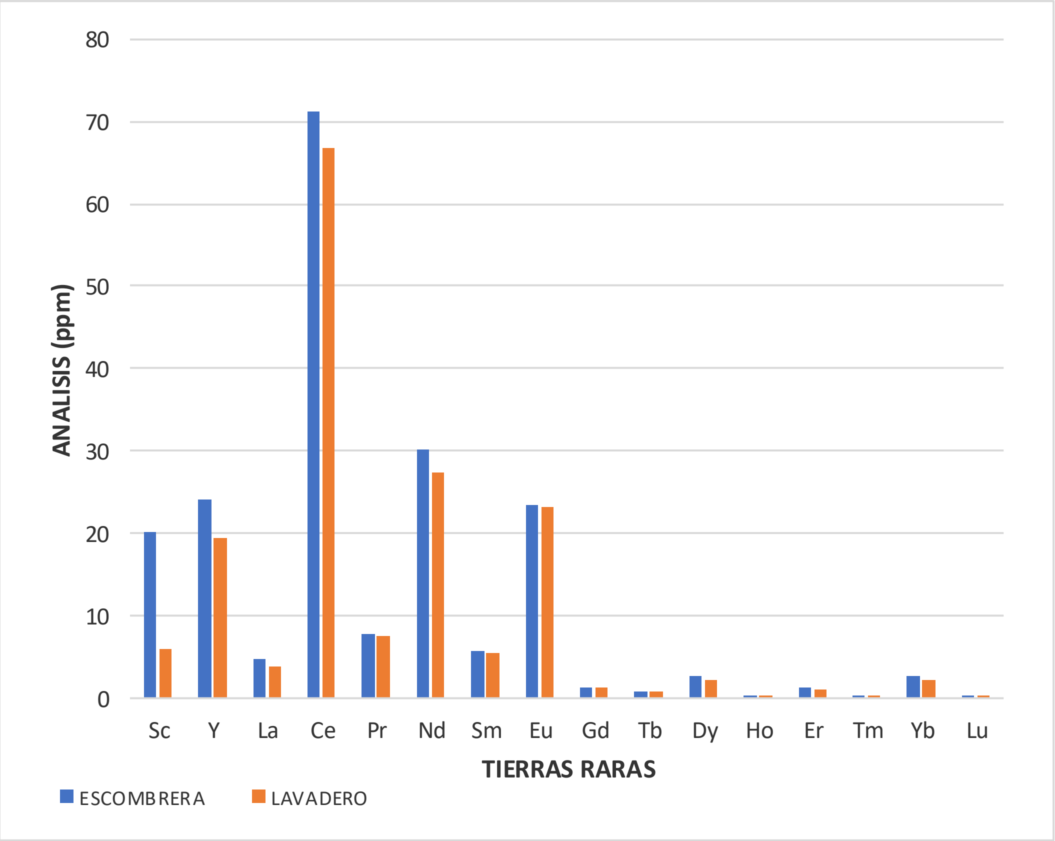
- Gravity concentration exploits density contrasts to isolate heavy mineral phases that may host critical metals.
- Magnetic separation targets Fe-bearing or paramagnetic phases, allowing early removal of gangue and concentration of value-host minerals.
- Froth flotation enables selective upgrading of mineral fractions based on surface chemistry, improving grades before leaching.
- Mineral liberation and particle size control are essential: insufficient liberation leads to poor flotation and magnetics performance.



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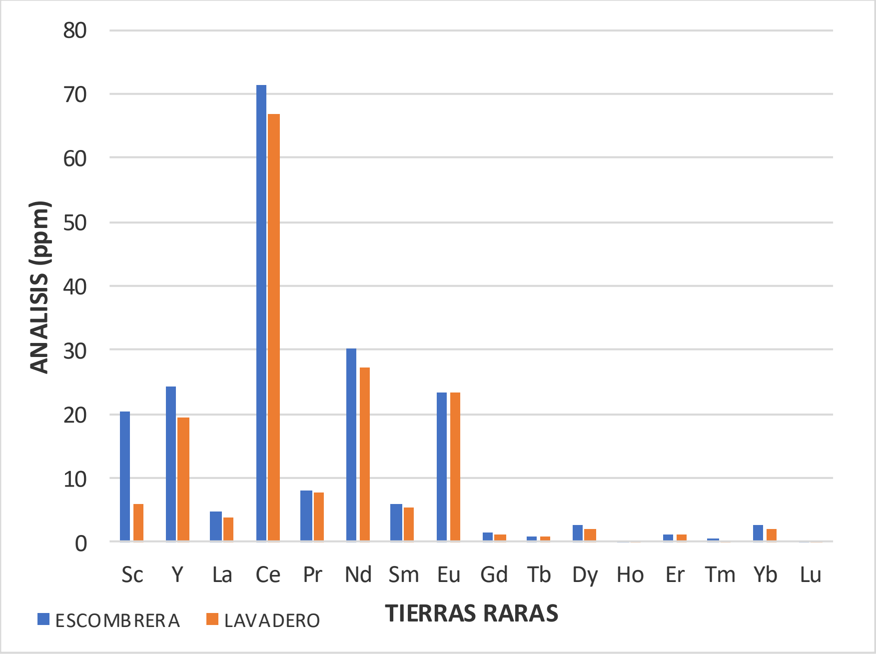

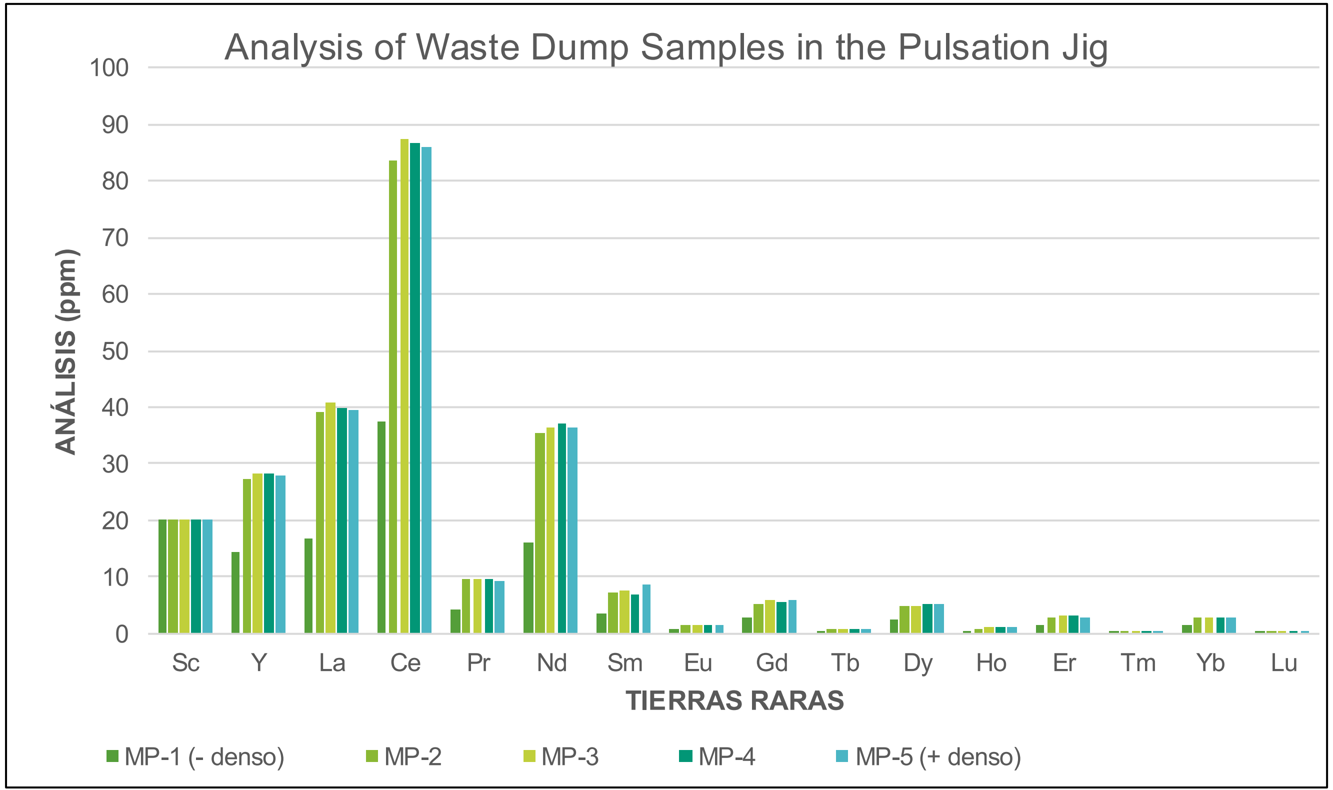

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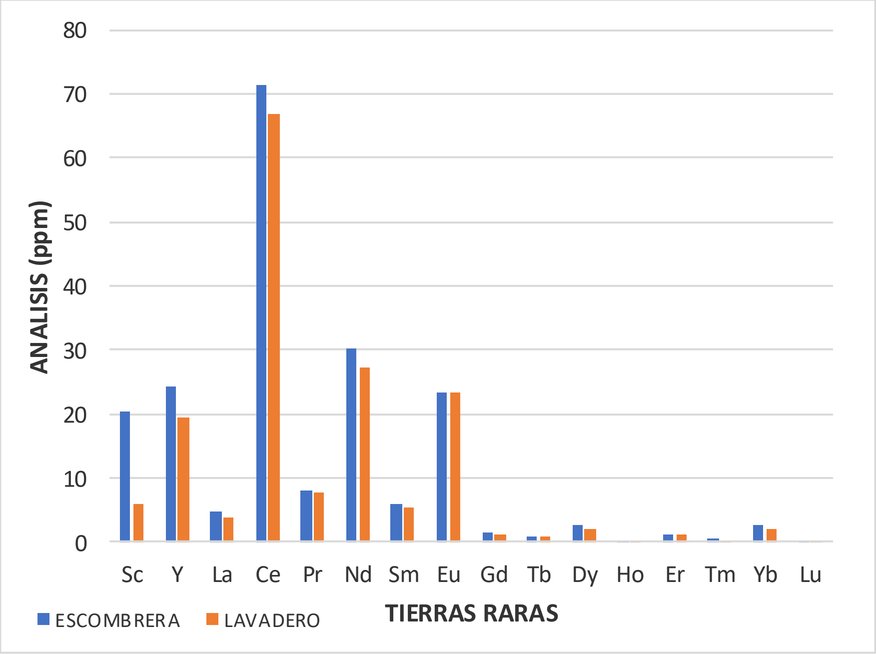

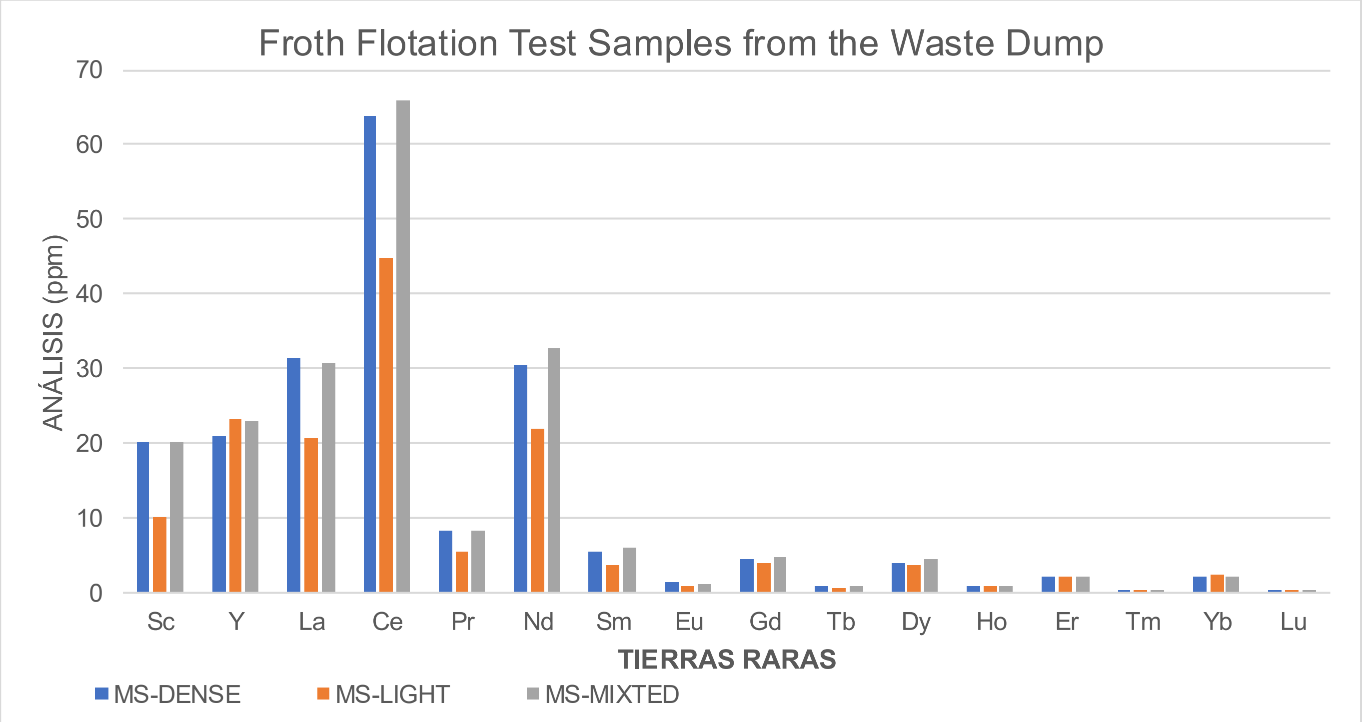

Geometallurgical Characterization Through Backscattered Electron SEM.

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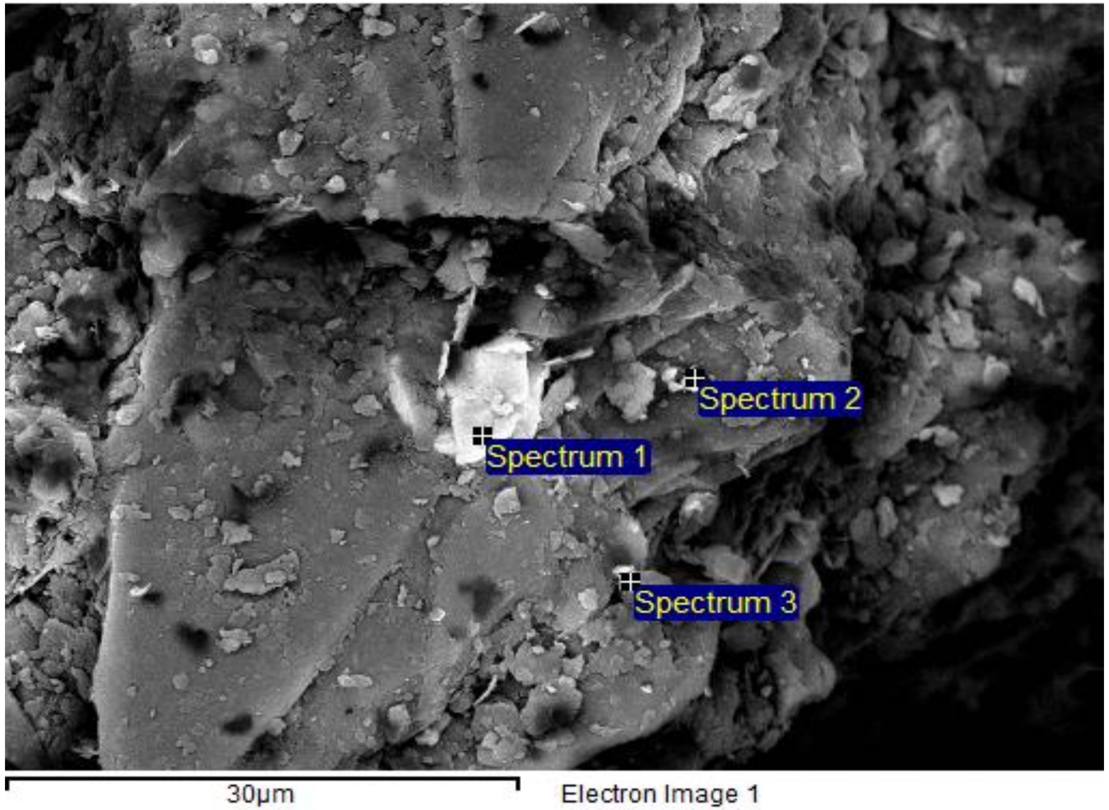
- Backscattered electron (BSE) image showing clear contrast between heavy-element phases and the silicate matrix.
- Bright domains (Spectrum 1–3) indicate minerals enriched in higher-Z elements, potentially hosting critical metals/REEs.
- Fine-grained particles and irregular microtextures suggest limited liberation and complex mineral associations.
- EDS analysis at Spectra 1–3 targets zones with distinct compositions to identify mineral hosts and extraction-relevant phases.
- Microstructural heterogeneity highlights the need for geometallurgical modeling to predict leaching behavior and recovery efficiency.



Backscattered Electron SEM Showing Mineral Phases and Elemental Hotspots (Spectra 1–3)

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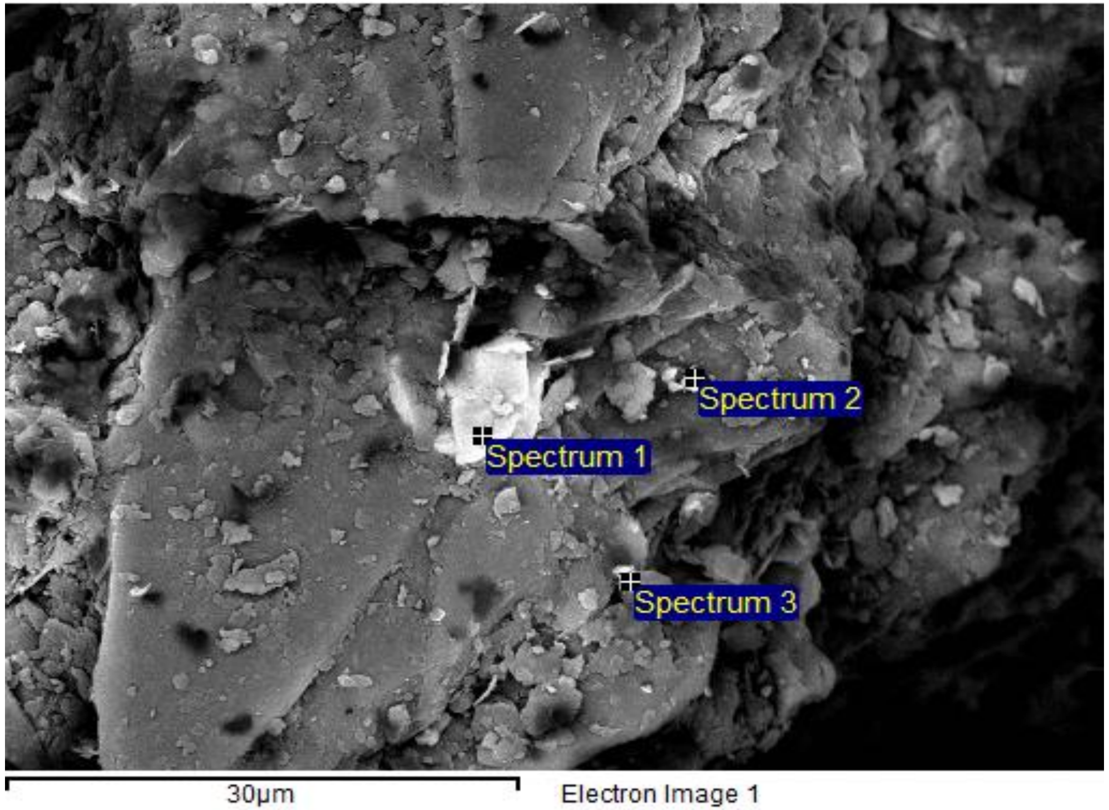

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Spectrum	In stats.	C	O	F	Mg	Al	Si	P	S	K	Ti	Fe	La	Ce	Nd	Total
Spectrum 1	Yes	18.34	37.39	-0.32		0.78	0.94	10.38				0.47	8.27	17.93	5.82	100.00
Spectrum 2	Yes	17.50	23.61		0.63	2.19	2.99		24.08	0.57	0.56	27.87				100.00
Spectrum 3	Yes	18.95	55.52			9.43	10.61			0.91	0.46	4.12				100.00
Max.		18.95	55.52	-0.32	0.63	9.43	10.61	10.38	24.08	0.91	0.56	27.87	8.27	17.93	5.82	
Min.		17.50	23.61	-0.32	0.63	0.78	0.94	10.38	24.08	0.57	0.46	0.47	8.27	17.93	5.82	

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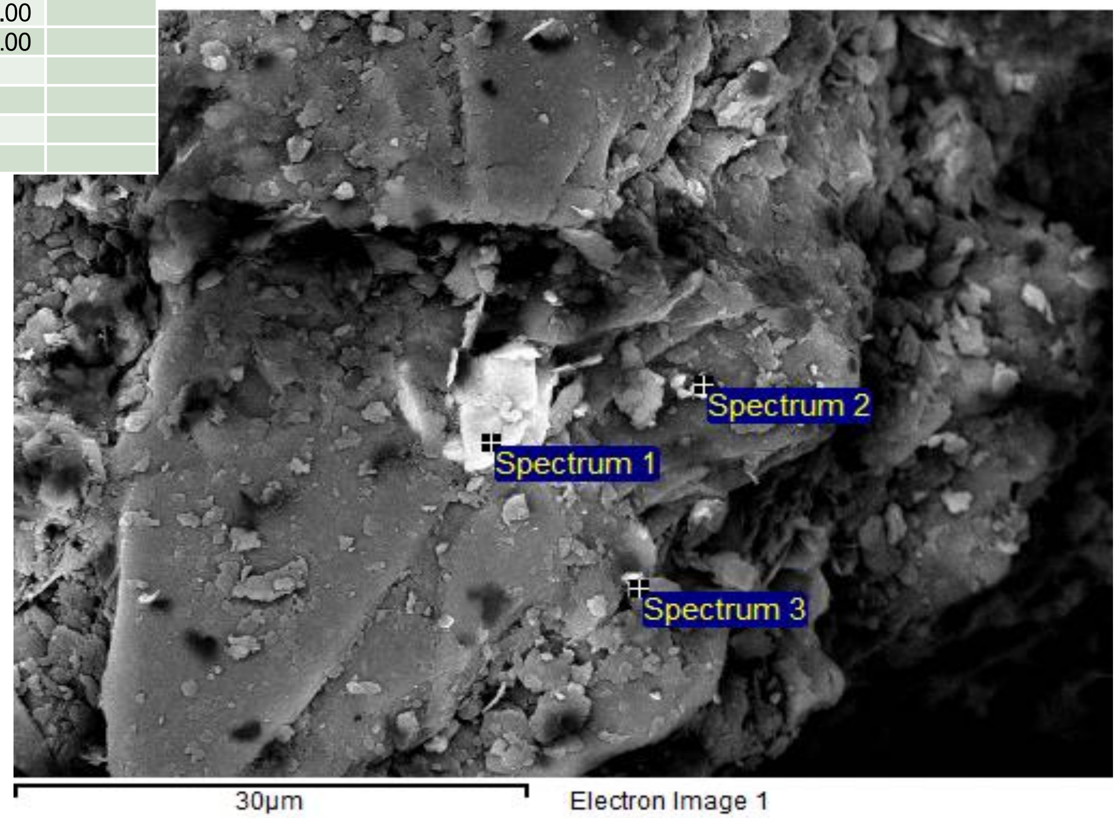

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Mineral Processing Pathways Prior to Hydrometallurgical Extraction

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- Pre-concentration improves downstream leach kinetics by increasing exposure of reactive phases and reducing inert material.
- Beneficiation responses are strongly linked to mineralogical variability—core to geometallurgical modeling and domain definition.
- Physical beneficiation reduces mass to be processed hydrometallurgically, lowering reagent consumption and operational costs.

Hydrometallurgy Applied to Coal-Derived Residues: General Framework

A hydrometallurgical flowsheet begins with a detailed mineralogical and chemical characterization, supported by SEM-EDS, XRD and sequential extractions:

- **amorphous aluminosilicate glass,**
- **phosphate minerals (monazite–xenotime series),**
- **Fe–Al oxides,**
- **organically coated or ion-exchange sites.**

This heterogeneity controls acid consumption, leaching efficiency, and speciation of dissolved metals. Geometallurgy therefore ensures that process parameters reflect real mineral associations.

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Hydrometallurgy Applied to Coal-Derived Residues: General Framework

Since CRMs may be locked within refractory phases, the literature highlights several pre-conditioning routes:

- **Thermal activation to disrupt glassy matrices and enhance REE solubility.**
- **Alkaline treatments (e.g., NaOH roasting) to dissolve silicates or remove Al, reducing gel formation during acid leaching.**
- **Microwave irradiation to induce microcracking and increase reactive surface area.**

These pre-treatments aim to **increase extraction kinetics** while reducing co-dissolution of impurities such as Fe, Si, and Al.

Hydrometallurgy Applied to Coal-Derived Residues: General Framework

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Leaching is the central step of hydrometallurgical extraction:

- Acid Leaching
- Mineral acids (HCl, H_2SO_4, HNO_3) effectively dissolve REEs, Sc, Ga, and transition metals.
- HCl tends to improve REE dissolution and mitigate formation of insoluble double sulfates.
- H_2SO_4 is widely used but risks co-dissolution of Fe and formation of silica gels.

Process variables—temperature, pH, pulp density, and time—strongly influence yields due to diffusion-controlled dissolution and mineral matrix resistance.

Leaching via Ion-Exchange Mechanisms

Similar to ion-adsorbed clays, some REEs in coal residues can be mobilized using mild salts (e.g., ammonium sulfate), promoting selective desorption rather than total matrix dissolution.

Bioleaching

Microbial systems (e.g., Acidithiobacillus spp.) produce acidic environments and oxidizing agents capable of mobilizing Fe, Mn, and some REEs from residues. Although slower, bioleaching offers a low-energy and environmentally benign pathway.

Hydrometallurgy Applied to Coal-Derived Residues: General Framework

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The pregnant leach solution (PLS) typically contains a complex mixture of REEs and base metals:

- **Solvent extraction (SX)** with extractants such as D2EHPA, PC88A, TBP, or Cyanex 272 provides selective separation of REE groups or individual elements.
- **Ion exchange (IX)** resins can further purify REEs and separate them from Fe, Al, Ca, and other interfering ions.
- **Selective precipitation** (e.g., oxalate precipitation) generates REE oxalates, which can be calcined to REO products.

The overall challenge lies in achieving high selectivity while reducing reagent consumption and minimizing secondary waste streams.

Hydrometallurgy Applied to Coal-Derived Residues: General Framework

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The final steps include:

- **Crystallization or precipitation** of purified metals or salts,
- **Calcination** to produce rare earth oxides (REOs),
- **Electrowinning** for transition metals like Co or Mn in relevant systems.

These operations transform low-grade coal residues into valuable **marketable CRM products**.

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Acid Leaching Experiments: Overview

Two acid leachants were tested: hydrochloric acid (HCl) and acetic acid.

Three experimental series were performed for each acid system.

Leaching tests were conducted at **four temperatures:**

•Room temperature

•**30 °C**, **60 °C**, **90 °C**

Each temperature condition was evaluated at **five leaching times:**

•**1 h**, **3 h**, **6 h**, **12 h**, **24 h**

This design enables assessment of:

•**Dissolution kinetics**, temperature effects, and CRM mobilization

•**Comparative performance** between strong acid (HCl) and weak acid (acetic acid)

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Acid Leaching Experiments: Overview

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Alkaline Pretreatment: NaOH Roasting

- A **NaOH alkaline roasting step** was conducted as an additional pretreatment.
- The objective was to **break down aluminosilicate matrices** and enhance metal liberation.
- This step helps reduce issues observed in acid leaching, such as:
    - **Silica gel formation**
    - **Low reactivity of glassy phases**
    - **Poor accessibility to REE- or CRM-bearing mineral phases**
- Alkaline roasting is expected to **increase leaching efficiency** in subsequent acid dissolution tests.

Key Leaching Results

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Hydrochloric acid (HCl) demonstrated significantly higher leaching efficiency compared with acetic acid under equivalent experimental conditions.

The stronger acidity and higher dissolution power of HCl led to **greater mobilization of CRM-bearing phases**, particularly those hosted in aluminosilicate and oxide matrices.

Acetic acid showed limited extraction, consistent with its weaker acid strength and lower ability to break down resistant mineral phases.

The application of an **alkaline roasting pretreatment using NaOH** prior to acid leaching resulted in a **43% increase in overall leaching efficiency**.

NaOH roasting promoted **chemical breakdown of aluminosilicate glass and improved liberation of encapsulated REEs/CRMs**, thus enhancing subsequent acid dissolution.

These results collectively indicate that **process optimization must consider both acid selection and pretreatment strategy** to maximize CRM recovery from coal-derived residues.

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Future Work

We are now progressing to the **selective precipitation stage** to separate REEs from the leach solutions obtained in the previous experiments.

The current focus is on optimizing **oxalate and carbonate precipitation routes**, aiming to selectively recover REE fractions while minimizing co-precipitation of major elements such as Fe, Al, and Ca.

Parallel to precipitation studies, we will begin **solvent extraction (SX) experiments using Cyanex reagents**, especially *Cyanex 272* and *Cyanex 572*, which are widely used for REE separation.

These trials will evaluate:

- Extraction selectivity for light vs. heavy REEs
- pH control and phase separation behavior
- Loading, stripping, and reagent recycling performance

The combined approach of selective precipitation + solvent extraction aims to develop a more efficient and scalable purification flowsheet for REE recovery from coal-derived residues.

Future optimization will integrate these steps into a complete hydrometallurgical pathway, enabling high-purity REE products and supporting the development of a geometallurgical model for CRM recovery.

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Limitations of the Study

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- The research timeline was significantly affected by the **relocation of the laboratory facilities**, which required a complete shutdown of experimental activities.
- This transition caused an estimated **six-month delay** in the progression of the project.
- During the relocation, access to essential equipment, analytical instruments, and sample preparation infrastructure was temporarily suspended.
- As a result, several experimental stages—particularly leaching optimization, selective precipitation, and solvent extraction trials—could not be executed according to the original schedule.
- Despite these constraints, the core experimental program has resumed, and the project is now back on track with updated timelines.

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