Integrating critical minerals recovery and CO_2 mineralization using mine tailings for net-zero sustainable mining

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The mining of critical minerals (CMs), such as e.g. lithium (Li), cobalt (Co), nickel (Ni), and rare Earth elements (REEs), is paramount for the development of advanced renewable energy generation and storage systems. CMs are usually found in ores located only in a few areas around the world and extracted through inefficient and environmentally unsustainable processes [1]. Moreover, Europe is massively dependent on imports from third countries for CMs and their current supply will not be able to meet future demand. Therefore, CMs mining with innovative and green solutions from alternative and more widespread resources is envisaged.
Potential alternative resources are mining waste such as mine tailings and gangue minerals [2]. Mining waste holds a legacy of earlier mining activities with recognized negative impact on the environment and at the same time they are naturally enriched in CMs. They provide geographically distributed potential resources for CMs within Italy and worldwide creating a unique opportunity to combine CMs' recovery with CO_2 removal through carbon mineralization, making mining a sustainable and carbon neutral operation.

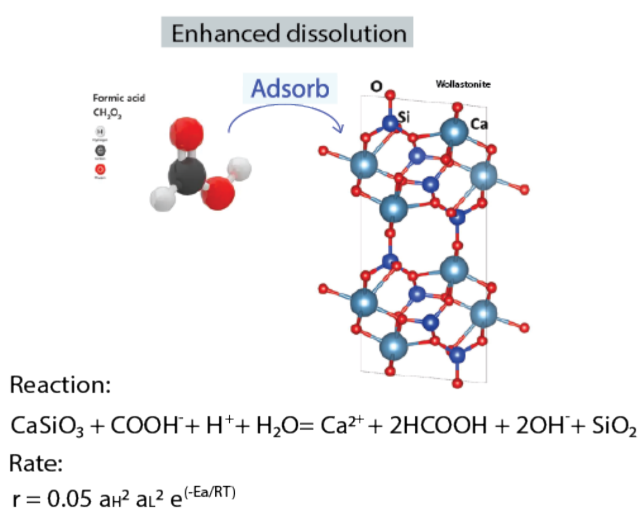

Figure 1. Schematic of the enhanced dissolution process of wollastonite using formic acid [10]. Structures modified after [11].

In the proposed project, we aim at developing a framework for a process that integrates CMs recovery with CO_2 mineralization using mining waste. The materials will be provided by the mining companies in Italy and United States with whom the PIs have established collaborations. The integrated process will comprise enhanced mineral dissolution/leaching followed by a CMs selective separation unit based on either electro-membrane separation, ion-sieves, or even a combination of them, and carbonate precipitation for CO_2 removal and residues stabilization. Organic acids (e.g., citric acid, oxalic acid, acetic acid, and formic acid) will be used to enhance dissolution/leaching at circumneutral pH and low temperature [3,4]. Upon characterization of the waste, the composition of the solution for enhanced mineral dissolution/leaching will be designed through density function theory (DFT) calculations which will allow us to customize the process to the mineral phases in the waste and the elements to recover [5,6]. A kinetic model will be developed and validated with the experiments performed in the labs of the PIs using a set-up fully monitored with inline and online sensors.
In the three-year research period, the specific tasks to be addressed include:
1) **Task 1:** Characterization of the material (1st-3rd month). An extensive characterization of the received mine tailing will be carried out for the determination of the mineral composition and CMs content.

2) **Task 2:** DFT calculations (4th-14th month). DFT calculations will be carried out in the PI group [7–9] to select the optimal solution composition for enhanced dissolution/leaching for CMs extraction and the functionalization of the ion-sieve for recovery.
3) **Task 3:** Laboratory experiments of extraction and recovery (13th-30th month). Tests of dissolution/leaching and precipitation (University of Padua), and recovery (Clarkson University) will be carried out. The PIs' laboratories are equipped with the set-ups and tools for the proposed tests.
4) **Task 4:** Kinetic model (29th-36th month). The data obtained in Task 3 will be used to derive kinetic laws for the selected enhanced dissolution/leaching and recovery processes.
Cross-fertilizing the expertise from two PIs across geosciences and chemical engineering and leveraging the comprehensive knowledge built through recent collaborations, the proposed project will create a framework for material characterization and process design. The approach will help to valorize waste by mitigating emissions of CO_2 and other contaminants in the environment and helping to implement sustainable mining practices.

Expected Impact

This research will result in a framework that provides an approach for custom design of the extraction and the separation of CMs and alkaline Earth elements using organic acids and functionalized surfaces aided by computational chemistry to avoid massive experimentation.
The PhD student will have the opportunity to spend time within the 13^{th} and the 30^{th} months of the research period at Clarkson University in the laboratory of the co-PI Liguori. There, the student will run experiments on electro-membrane separation and/or ion-sieves and will gain the experience to work in an international laboratory in the United States.

Funding

Carbon Dioxide Initiative (CDI) and currently under review projects of the PIs on similar topics.

Reference

[1] European Commission, *Critical Raw Materials*, url: https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en#fifth-list-2023-of-critical-raw-materials-for-the-eu.

[2] X. Zhao, F. Khelifi, M. Casale, A. Cavallo, E. Padoan, K. Yang, and G. A. Dino, Critical Raw Materials Supply: Challenges and Potentialities to Exploit Rare Earth Elements from Siliceous Stones and Extractive Waste, Resources **13**, (2024).

[3] J. Wang, A. Nurdiana, Y. Sato, N. Watanabe, and N. Tsuchiya, Characteristics of congruent dissolution of silicate minerals enhanced by chelating ligand under ambient conditions, American Mineralogist **109**, 1096 (2024).

[4] J. F. Song, J. X. Ru, X. P. Liu, and X. Y. Cui, Oxalic Acid and Succinic Acid Mediate the Weathering Process of Granite in the Cold-Temperate Forest Regions of Northeast China, Eurasian Soil Science **52**, 903 (2019).

[5] C. Sun, Z. Yao, Q. Wang, L. Guo, and X. Shen, Theoretical study on the organic acid promoted dissolution mechanism of forsterite mineral, Appl Surf Sci **614**, 156063 (2023).

[6] M. Gao, J. Guo, S. Liu, C. Chang, and Z. Xie, Promoting effect of organic acids on dissolution of anorthite: DFT calculations and experiments, Surfaces and Interfaces **58**, 105829 (2025).

[7] Q. Shi, X. Meng, and V. Prigiobbe, Mechanistic Study of Radium Adsorption onto Goethite, The Journal of Physical Chemistry C **124**, 805 (2019).

[8] V. Prigiobbe, A. S. Negreira, and J. Wilcox, Interaction between Olivine and Water Based on Density Functional Theory Calculations, JOURNAL OF PHYSICAL CHEMISTRY C **117**, 21203 (2013).

[9] Q. Shi, G. E. Sterbinsky, V. Prigiobbe, and X. Meng, Mechanistic Study of Lead Adsorption on Activated Carbon, Langmuir **34**, 13565 (2018).

[10] Valentina Prigiobbe, Valentina Brombin, Omid Jazari, and Simona Liguori, Extraction of critical minerals from mine tailings through enhanced dissolution, In Preparation (2025).

[11] N.-H. Hoang, D. T. Ha, and T. T. Trinh, A first-principles insight into thermodynamic and mechanical properties of Xonotlite and Wollastonite phases of high temperature geothermal well cement, Results in Materials **20**, 100454 (2023).