



# Application of supported liquid membranes for extraction of rare earth elements from acidic coal mine drainage

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## Extended Abstract

Waste streams such as acidic mine drainage can be enriched in rare earth elements (REE) and have been proposed as a low grade resource of critical minerals (Cravotta and Brady 2015; Cravotta III 2008; Hedin et al. 2019; Hedin et al. 2020; Stewart et al. 2017; Vass et al. 2019). These feedstocks are an attractive source of REE because of environmental benefits gained in converting wastes into valuable materials. However, major challenges exist in valorizing such wastes, including that drainage sites tend to be geographically dispersed and contain a variety of impurities that are a challenge for efficient extraction and purification of the REE (Ayora et al. 2016; Middleton et al. 2024; Mwewa et al. 2022; Park et al. 2020).

This presentation reports our previous study (Middleton et al. 2024) of supported liquid membrane (SLM) technologies for concentrating REE from acid mine drainage (AMD) of coal mine sites. As described in our prior publications (Middleton et al. 2024; Smith et al. 2019), the SLM approach is similar to solvent exchange processes except that the REE-chelating organic phase is embedded in a hydrophobic membrane (Fig. 1). The feed and the acid strippant solutions are placed on opposite sides of the membrane, and the concentration gradients drive metal ion transfer from the feed to the product side of the membrane. This configuration aims to maximize the area of the liquid-liquid interface to enable increased rates of mass transfer (Chen et al. 2018). A potential advantage of the SLM process over conventional solvent extraction methods is that SLM requires much less volume of hazardous organic solvents and could be implemented in a modular system.

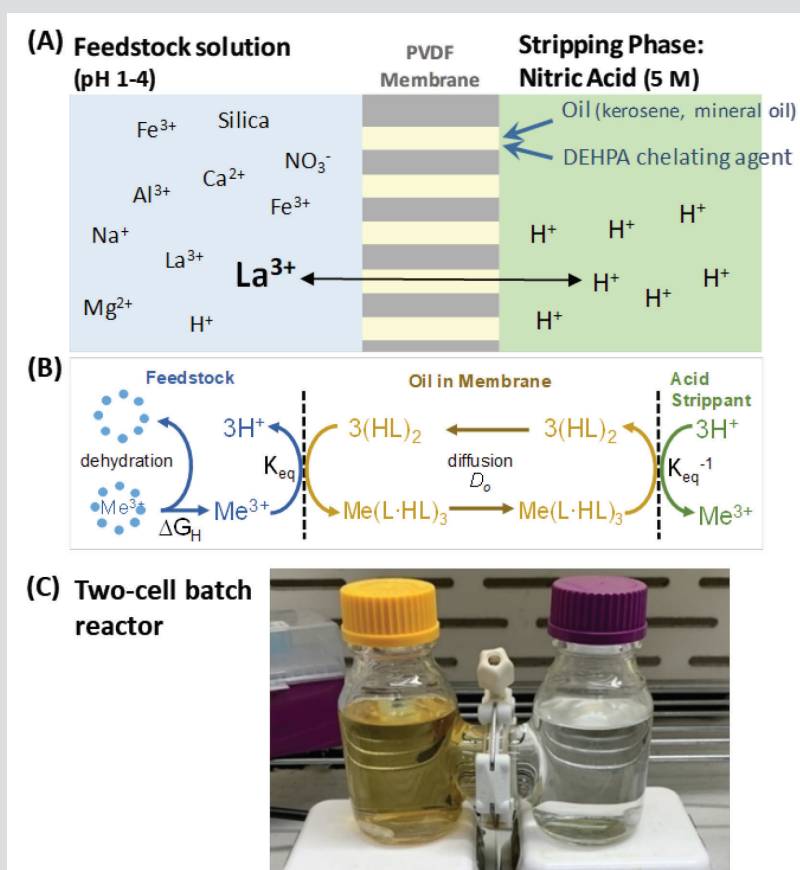
The objective of this study was to test the efficacy of SLM-based separations for the extraction of AMD fluids for the REE (herein defined as the 14 stable lanthanides, yttrium and scandium). We focused on the effect of AMD fluid composition for controlling SLM performance for REE extraction. Our overarching hypothesis is that REE flux during the SLM separation is dependent on a specific set of AMD feedstock variables such as pH, REE speciation, and major ion (e.g., Fe, Al, Mn, Ca) concentrations.

SLM-based separations were performed on AMD fluid samples collected at 7 different sites in western Pennsylvania (USA). These sites were selected to represent the typical composition of REE-rich AMD sources and encompass a range of concentration values for Fe, Al, Mn, and Ca. The efficacy of the extraction process was evaluated by measuring the permeability coefficients of REE ions (i.e., the extraction flux normalized to the initial feedstock concentration).

Permeability values for each REE were approximately 10-25 L m<sup>-2</sup> h<sup>-1</sup> and tended to be greater for the heavy REE compared to the light REE, similar to our prior work with coal ash leachates (Smith et al. 2019). Permeability of the REE during SLM

extraction also depended on the composition of the feedstock matrix. More specifically, permeability increased with increasing pH of the AMD feedstock and decreased with soluble iron and aluminum concentrations. For AMD samples that were allowed to age in the ambient (oxygenated) environment prior to SLM separations, REE recovery rates were substantially decreased. This result is likely due to oxidation of ferrous iron Fe(II) in the AMD feedstock and the formation of Fe(III) as a major interfering ion for the extraction process, as we observed in other experiments with synthetic feedstock solutions (Middleton and Hsu-Kim 2023). Filtration of freshly collected AMD limited Fe(II) oxidation, enabling flexibility in feed stock storage time for the AMD fluid prior to extraction by the SLM.

Altogether, this work establishes a framework for applying SLM for REE recovery from AMD sources by establishing primary water quality parameters that influence separation flux and REE purity in the product. Such insights support a mechanistic understanding of critical metals separation by SLM and facilitate their application for complex and nontraditional feedstocks such as mine drainage fluids and other waste residuals.



**Figure 1** (A) Schematic of the supported liquid membrane separation process for selective recovery of trivalent metal ions from feedstocks (i.e., AMD fluids). The membrane comprises a polyvinylidene fluoride (PVDF) membrane saturated with a mixture of 10% v/v di(2-ethylhexyl)phosphoric acid (DEHPA) in 90% kerosene; (B) Mechanism of ion exchange at the feedstock-membrane-stripping interface. (C) Two-cell batch reactor configuration employed for this study

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