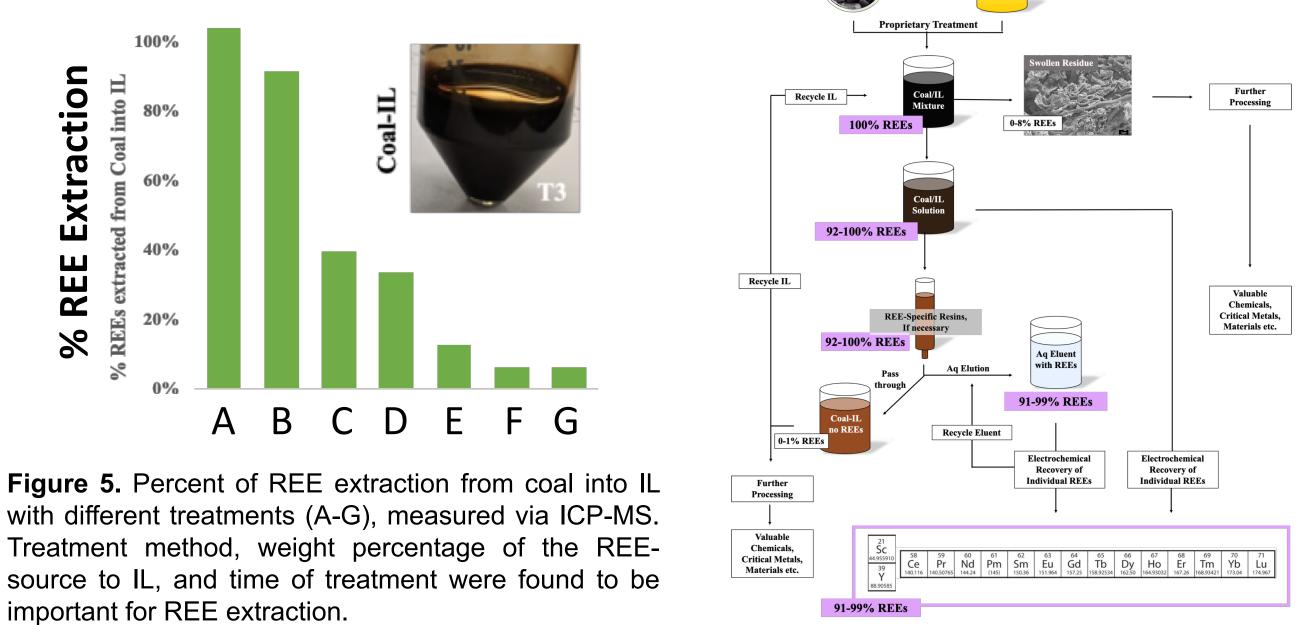
lonic Liquids as Advanced Solvents for the Extraction of Rare Earth Elements from Coal Products Kristin R. Di Bona¹, Caleb M. Hill^{1,2}, Gabriela Gurau¹, Robin D. Rogers¹ ¹Wyonics LLC, Laramie WY, ²University of Wyoming, Laramie, WY

Introduction

Coal and coal by-products are known to contain a significant amount of rare earth elements (REEs), which are vital to modern technologies and national security. However, the recovery of these materials is challenging, with current REE separations from ore requiring energy intensive processes using acids and other solvents. Ionic liquids (ILs) are low melting salts (< 100 °C), which can be nonvolatile, nonflammable, and be tuned to specific applications. Wyonics has developed and demonstrated an energetically and environmentally sustainable process for the extraction and recovery of REEs and other valuable materials directly from coal and coal by-products using IL technologies. This process will generate a U.S. supply of REEs and other valuable carbonbased materials and metals using coal as a feedstock.

Rare Earth Element Extraction into Ionic Liquid(s)

Treatment/process variables were systematically tested to determine important factors for REE extraction. <u>92-100% of REEs were extracted</u> from coal into IL in 2 minutes of treatment



Wyonics' Strategy

Phase I Goal: Design and demonstrate the feasibility of an IL process to directly extract REEs from dissolved and/or swollen coal or coal byproducts, demonstrate REE recoverability, and begin process development. Tasks: REEs

- 1. Demonstrate dissolution/swelling of coal and REEs extraction with *specifically designed ILs*,
- 2. Isolate/Concentrate REEs (if necessary),

3. Recover REEs

Ionic Liquid Design

Figure 1. Wyonics' Strategy.

Coal/IL Solution

Coal/Ash

ILs exhibit tunability based on the properties of the chosen ions (Fig. 2). Nine ILs were 1) expertly designed for the dissolution of coal or coal byproducts and extraction of REEs, 2) synthesized or purchased, and 3) systematically tested with coal and/or fly ash for suitability to REE extraction. One IL was down-selected due to excellent REE extraction.

The chosen IL is:

Non-volatile Non-flammable

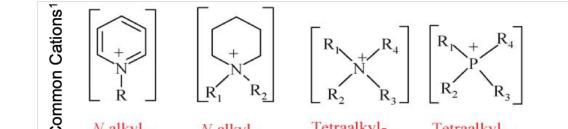


Figure 6. Schematic of Wyonics' Process.

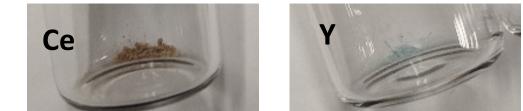
Isolation of REEs from REE/IL solutions

Sorbents were developed from the biopolymer chitin, and tested against commercial resins. Commercial resins work best at this time due to incompatibilities of the chitin with the best performing IL and the need for more development to improve the REE recovery for commercialization. The commercial resins isolated 99% of REEs from coal/IL or fly ash/IL solutions. The presence of IL does not interfere with resin selectivity.

Electrochemical Recovery of REEs

Proof-of-concept experiments were performed developed for a electrochemical technique, demonstrating REE recovery from both:

1) Aqueous solutions (i.e., after resin isolation) or 2) IL-containing solutions (such as the coal/IL solutions)





- Non-toxic
- Liquid at 25 °C
- Recyclable
- Scalable

Ö	N-alkyl- pyridinium	<i>N</i> -alkyl- <i>N</i> -methyl-	ammonium	phosphonium
	water-immiscibl	e	>	water-miscible
Anions ¹	[PF ₆]-	[B	F ₄]-	[CH ₃ CO ₂] ⁻
oin	$[NTf_2]$	[f ₂] ⁻ [OTf] ⁻		[CF ₃ CO ₂] ⁻ , [NO ₃] ⁻
<	$[BR_1R_2R_3R_4]^{-1}$	[N	$(CN)_2$]-	Br-, Cl-, I-
				$[Al_2Cl_7]$, $[AlCl_4]$ (decomp.)

Figure 2. Choice of anion can tune the hydrophilicity/hydrophobicity of the resulting IL.¹

Coal and Fly Ash Dissolution in Ionic Liquid

Dissolution of coal (Fig. 3) and fly ash (Fig. 4) was observed and found to be dependent on treatment conditions and source material.

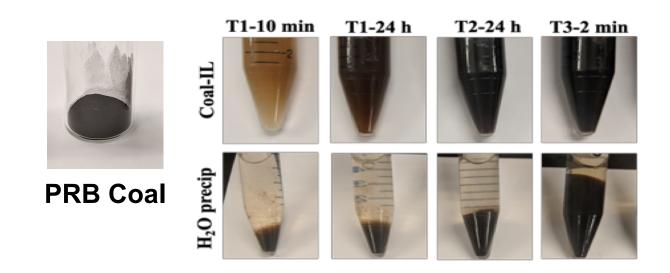


Figure 3. Dissolution of coal varied by treatment. Coal/IL solutions after residue removal (top). Precipitation of dissolved solids is observed with H_2O addition (bottom).



PRB Fly Ash



Figure 4. Dissolution of fly ash into IL varied by treatment conditions. Fly Ash/IL solutions.



Figure 7. Recovered REEs from IL-containing solutions via developed electrochemical methods (left). Model solutions were doped with REE salts for proof-of-concept experiments. Electrochemical apparatus (right).

Summary & Future Work

Wyonics developed and demonstrated a sustainable IL process for the direct extraction of REEs from coal and fly ash and recovery from coal/IL solution, without the addition of acid:

- Feasibility of this approach was demonstrated on both coal and ash with 92-100% extraction of REEs from coal into ILs in 2 minutes
- 99% of extracted REEs were isolated via commercially available resins
- REE solids were recovered via developed electrochemical methods ullet
- Essential chemistry and engineering knowledge was determined for process design and scale-up to a pilot prototype system in Phase II

The work proposed in Phase II will give necessary engineering and processing parameters and economic assessment for a commercial facility. Wyonics is developing additional processes to generate valuable co-products from this system, including carbon materials and recovery of high-value metals (Li, V) to make the process economically sustainable.





SUSTAINABL	LITY BY 1	JESIGN	

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