

Separation of rare-earth elements by non-aqueous solvent extraction

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Solvometallurgy

Introduction: Solvometallurgy

Research plan and goals

Testing of PMOS

Correlation to solvent properties

Conclusions

Non-aqueous solvent extraction (NASX)

- Distribution of a solute between two immiscible organic phases
- Expands scope of conventional SX
- Can offer enhanced selectivity and treat water-sensitive compounds

Requirements

- Low mutual solubility of two phases
- Fast phase separation
- Extractant is soluble in less polar (LP) phase, not in more polar (MP) phase
- Starting metal compound is soluble in the MP phase
- Metal compounds should not react with the organic solvents



Binnemans and Jones, **2017**, J. Sustain. Met. 3, 570–600

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Non-aqueous solvent extraction for REE separation

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Group separation and purification of individual REE

- Conventional process: 1000s of stages comprising numerous extraction-scrubbing-stripping cycles
- Non-aqueous SX: higher separation factors \rightarrow more efficient separation process

Examples:

- Eu/Y separation from ethylene glycol
- 3 extraction and 2 scrubbing stages
- Precipitation stripping (oxalic acid)
- 99.92% pure Y₂O₃

Nd/Dy separation from poly(ethylene) glycol

- Bridging the gap with hydrometallurgy: 30 vol% water
- 2 extraction and 1 scrubbing stages
- Precipitation stripping (oxalic acid)

REE group separation from ethylene glycol

- Y, Dy, Ho // Er // Tm, Yb, Lu
- Based on industrial hydroxide concentrate
- Impurity removal and separation < 30 stages
- Precipitation stripping (oxalic acid)



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SOLVOMET GROUP Sep. Purif. Technol. 2020, 235, 116193

ACS Sustainable Chem. Eng. 2020, 8, 19032-19039

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- Valorization of low-grade sulphide mining waste: 600 Mtonne/yr + historic stockpile 28,000 Mtonne in Europe
- 15 partners across Europe, 3 case studies, 4 pilots
- REE recovery: study of solvometallurgical routes



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Research questions and hypotheses

1. Why are some polar solvents better in separation of REE than others?

2. How do solvent properties correlate with SX results?

Metal-ion complexation strongly depends on the solvent:

- Metal-ion solvent interaction
- Metal-ion counterion interaction (ion pair formation, dielectric cte.)
- Counterion solvent interaction
- Solvent solvent interaction (bulk structure, protic/aprotic)



Experimental setup

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Less polar (LP) phase: Cyanex 923, 10 vol% 1-decanol, n-dodecane

More polar (MP) phase:

O = F

- La, Nd, Eu, Dy, Yb (0.01 mol L⁻¹ each)
- LiCl: 0 4 mol L⁻¹
- Different polar molecular organic solvents (PMOS):
 - methanol, ethanol
 - ethylene glycol, 1,2-propanediol, 1,3-propanediol
 - diethylene glycol, triethylene glycol
 - methoxyethanol, ethanolamine
 - mono-, di-, triglyme
 - DMSO, acetonitrile, formamide, DMF, DMA

 $Ln^{3+} + 3Cl^{-} + \overline{nC923} \leftrightarrows \overline{LnCl_3 \cdot nC923}$

Water vs. Methanol vs. Ethylene glycol



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Water:

- negligible extraction at low [LiCl]: strong hydration of lanthanide ions
- limited separation

MeOH:

- At low [LiCl]: mutual solubility issues causing lower %E
- Complete extraction without separation at high [LiCl]: solvation strength lower, lower ε Ethylene glycol:
- Enhanced separation REE, especially HREE
- Bidentate binding

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Enhanced separation by DMSO and ethylene glycol

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- DMSO shows enhanced separation of the MREEs
- DMSO is a highly structured solvent, strong solvation of REE ions $\leftarrow \rightarrow$ weaker solvation of anions
- Dielectric constant DMSO = 47 similar to that of EG (41, both at 293 K)



Glycol structure effects



- Extraction efficiency: ethylene glycol < 1,2-propanediol < 1,3-propanediol
- Dielectric constants: 1,2-propanediol ~ 1,3-propanediol < ethylene glycol
- Solvent structure, solvent-solvent interactions will play an important role
- Steric effects of the extra methyl group or lengthening carbon chain: bidentate vs. monodentate

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UV-Vis: bathochromic shift indicates contact ion pair formation

Effect on REE-ion – chloride ion pairing?

- ${}^{4}G_{5/2} \leftarrow {}^{4}I_{9/2}$ hypersensitive transition
- Crystal-field splitting or presence different species
 → challenging!
- Nephelauxetic effect: redshift H₂O < EG; 1,2-PD < 1,3-PD
- Glycols: redshift of peak position with increasing
 [LiCl] → increased RECl₃ formation
- Water: no such shift observed



Conditions: 0.1 mol L⁻¹ NdCl₃ and 0 – 3 M LiCl Legend: EG = ethylene glycol; 1,2- and 1,3-PD = 1,2- and 1,3-propanediol

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Conclusion: contact ion pair formation increased in glycols

Preferential solvation

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• Can be an indication of solvation strength of the REE ion

- No change in preferential solvation
- Order of preferential solvation:

Ethylene glycol > 1,2-propanediol > water > 1,3-propanediol

- \rightarrow Resembles extraction results
- → Water: stronger affinity for the chloride counterions, effect not included in the order of preferential solvation

Conclusion: solvation strength of glycols follows the order of extraction



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Main research conclusions

- Extraction of REE is strongly influenced by the polar organic solvent
- Extraction of REE from a series of glycols: extraction partly to be explained by solvent structure, contact ion pair formation and solvation strength
- Correlation dielectric constant extraction results
- Combination of large number of factors impedes prediction of extraction results based on solvent properties
- Effects of solvent bulk structure should be investigated in more detail



https://solvomet.eu https://kuleuven.sim2.be/ https://h2020-nemo.eu/

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