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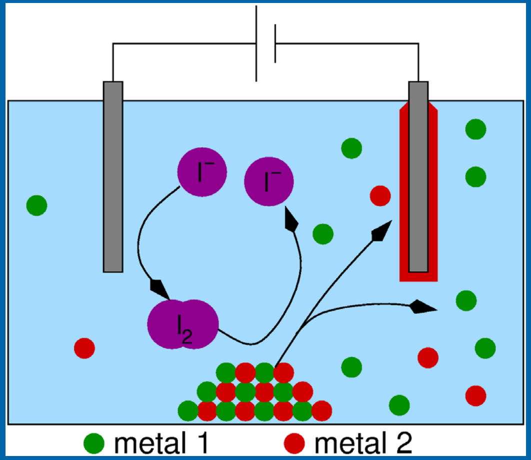
Salt & Mineral Chemistry

Chances and challenges of ionometallurgy

Why we (don't) use ILs and DESs in metal processing



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ION4RAW

J. Sustain. Metall. (2017) 3:570–600
DOI 10.1007/s40831-017-0128-2

CrossMark

REVIEW ARTICLE

Solvometallurgy: An Emerging Branch of Extractive Metallurgy

Koen Binnemans[1] · Peter Tom Jones[2]

2017: Let's save the world with ionic liquids!

Journal of Sustainable Metallurgy (2023) 9:423–438
https://doi.org/10.1007/s40831-023-00681-6

OPINION ARTICLE

Check for updates

Ionic Liquids and Deep-Eutectic Solvents in Extractive Metallurgy: Mismatch Between Academic Research and Industrial Applicability

Koen Binnemans[1] · Peter Tom Jones[2]

2023: We have not saved the world since 2017, so everyone should dump this and move on to our next hot topic!

Ionic liquids researcher's perspective on metallurgy

- no vapour pressure
- good conductivity
- low ecotoxicity
- miscible or immiscible with water
- high solubility for metal salts
- control of solubilities
- control of coordination/structure
- relatively cheap

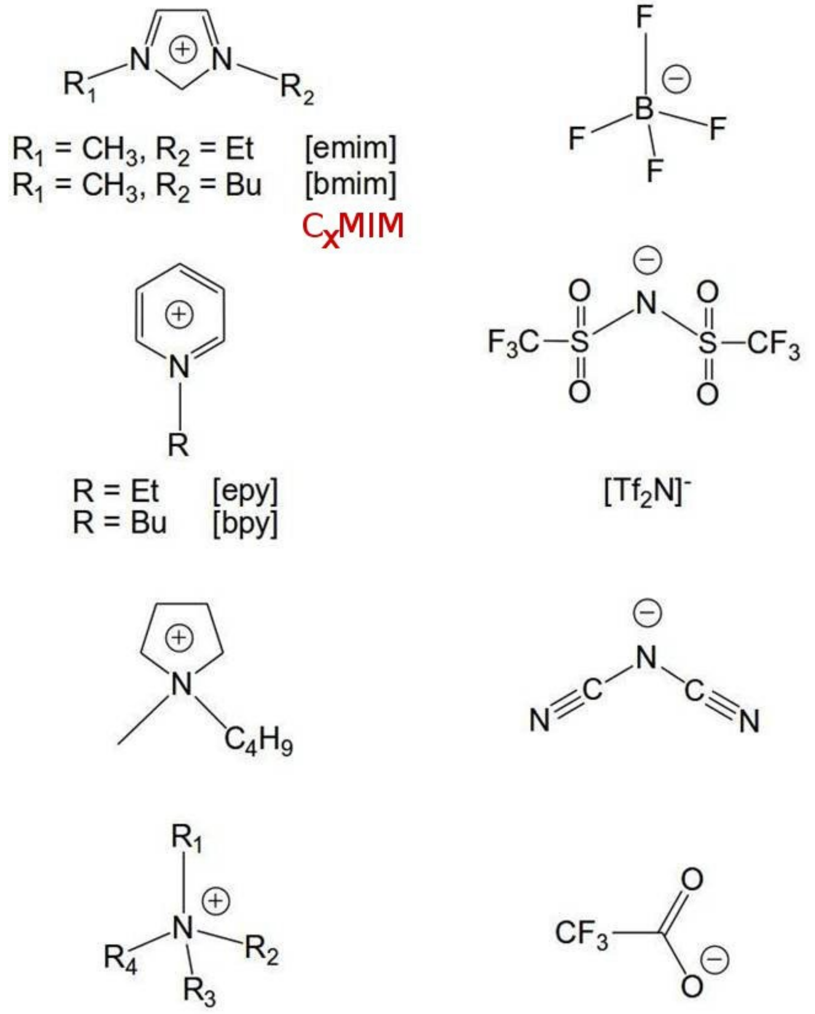
PTFE or glass!): high solu
volumes.
3. They exhibit Brønsted,
as well as superacidity.
4. They have no effective va
5. Their water sensitivity
trial applications.
6. They are thermally stable
7. They are relatively cheap,

Unlike water and other hy
dissolve a wide range of organic molecules to an appre-

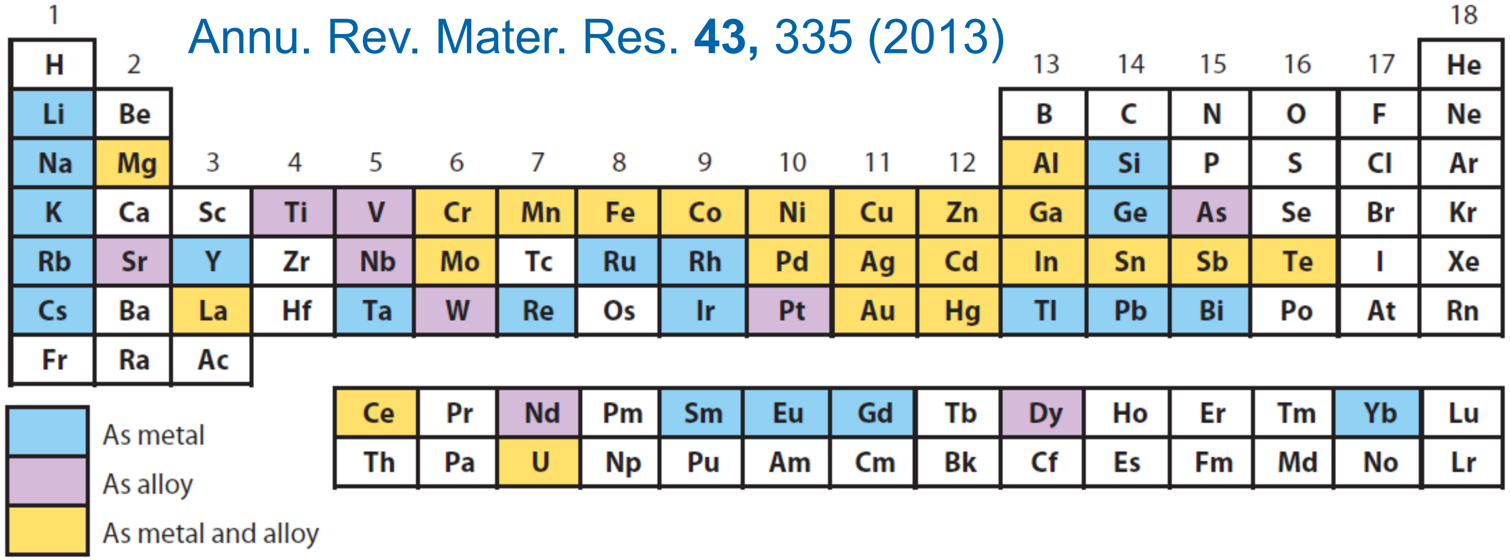
claim: great variety = tailored properties

„Designer Solvents“
„Green Metal Processing“
„Benign by Design“

low melting point
large potential window
no vapour pressure
~~good conductivity~~ high viscosity!
~~low ecotoxicity~~ it really depends!
miscible or immiscible with water
~~high solubility for metal salts~~
control of solubilities
control of coordination/structure
~~relatively cheap~~ mostly not!



Electroplating



Annu. Rev. Mater. Res. **43**, 335 (2013)

$ChCl + n\ CrCl_3 \cdot 6H_2O$

$CO(NH_2)_2 + n\ CrCl_3 \cdot 6H_2O$

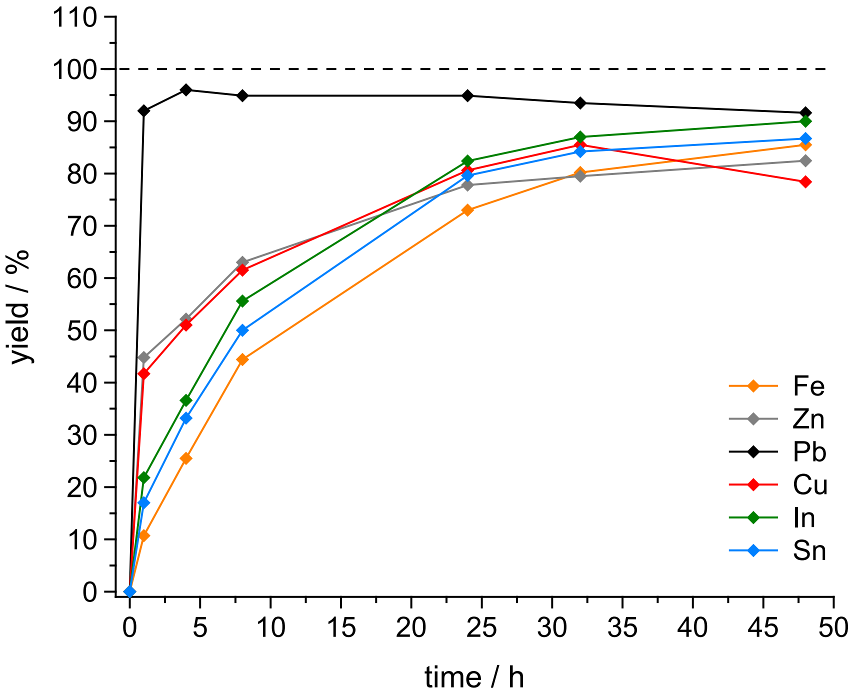
Phys. Chem. Chem. Phys. **16**, 9047 (2014)

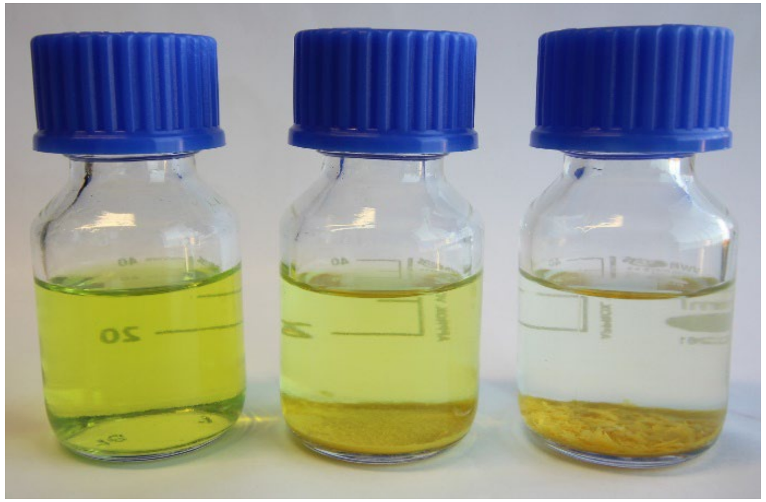
T.I.Met.Finish **82**, 14 (2004)

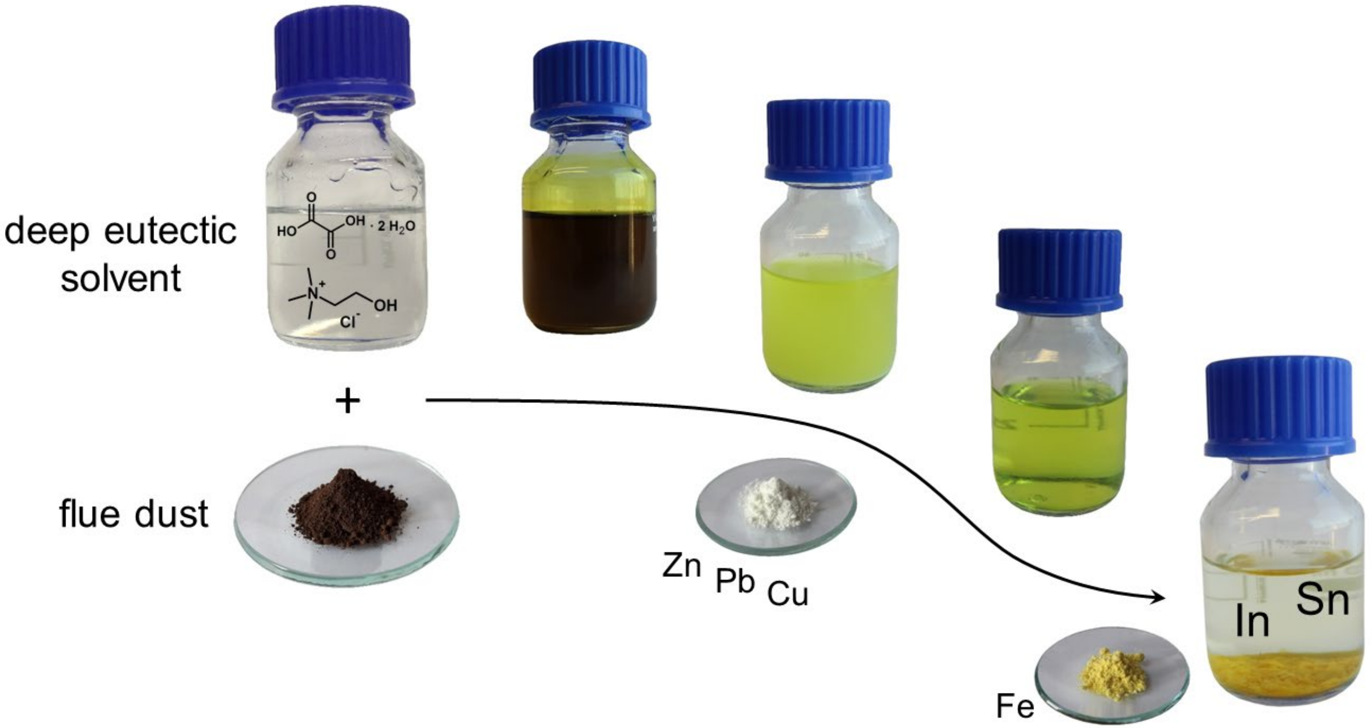
$C_4mimCl + n\ AlCl_3$

Abbott et.al., *Phys. Chem. Chem. Phys.* **12**, 1862 (2010)

Example application: flue dust leaching



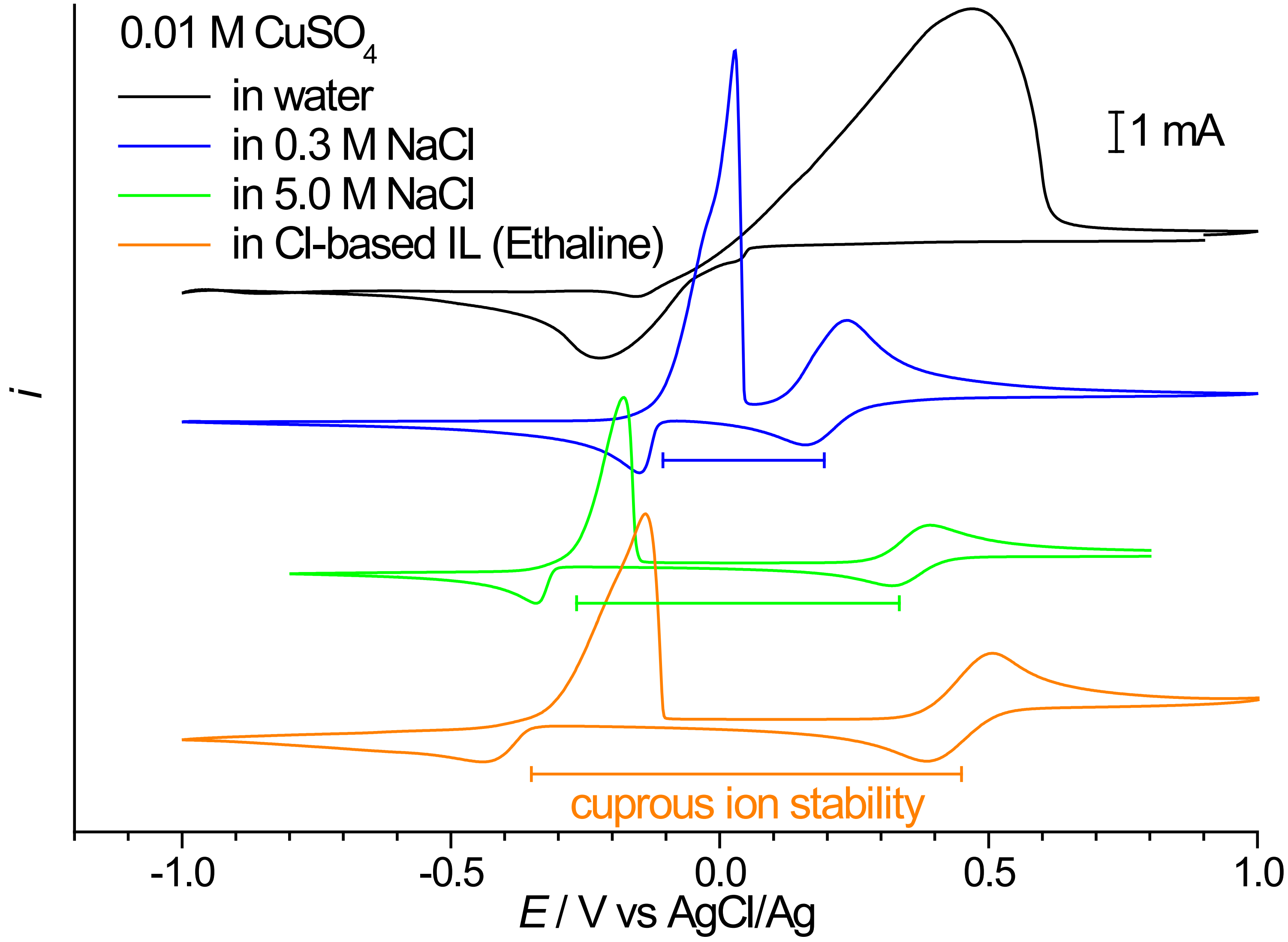




ACS sustainable chem. eng. **7**, 5300 (2019)

Patent DE102019101541B4

Key strength of IL/DES chemistry: speciation control and chemical behaviour



Chem. Commun. **47**, 10031 (2011)

Determining speciation

Inorganic Chemistry

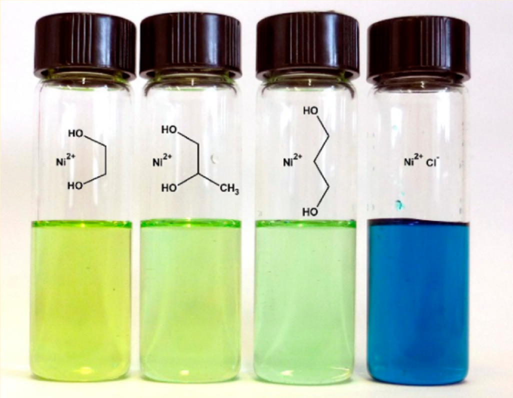
Article

pubs.acs.org/IC

EXAFS Study into the Speciation of Metal Salts Dissolved in Ionic Liquids and Deep Eutectic Solvents

Jennifer M. Hartley,[†] Chung-Man Ip,[‡] Gregory C. H. Forrest,[‡] Kuldip Singh,[‡] Stephen J. Gurman,[§] Karl S. Ryder,[‡] Andrew P. Abbott,[‡] and Gero Frisch*[,†]

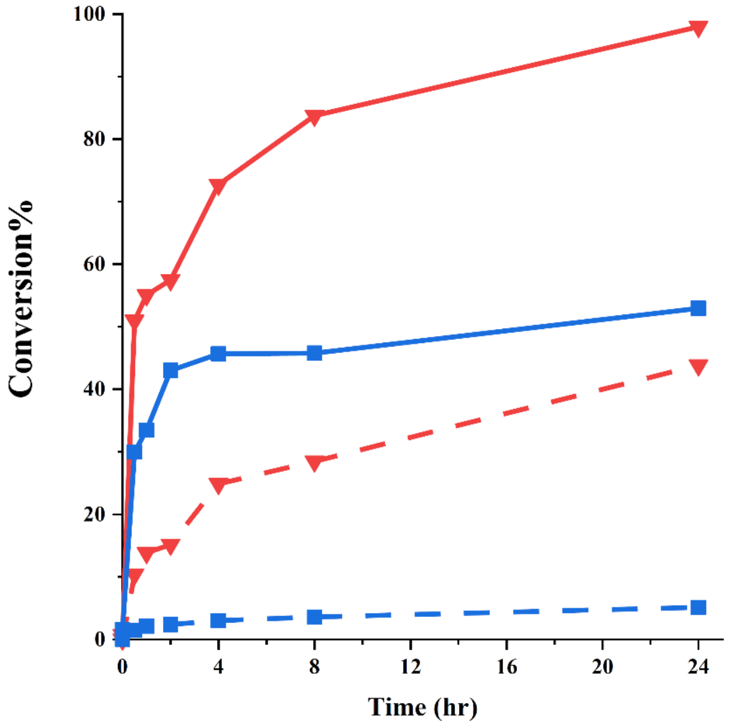
ABSTRACT: The speciation of metals in solution controls their reactivity, and this is extremely pertinent in the area of metal salts dissolved in ionic liquids. In the current study, the speciation of 25 metal salts is investigated in four deep eutectic solvents (DESs) and five imidazolium-based ionic liquids using extended X-ray absorption fine structure. It is shown that in diol-based DESs M^{I} ions form $[MCl_2]^-$ and $[MCl_3]^{2-}$ complexes, while all M^{II} ions form $[MCl_4]^{2-}$ complexes, with the exception of Ni^{II}, which exhibits a very unusual coordination by glycol molecules. This was also found in the X-ray crystal structure of the compound $[Ni(phen)_2(eg)]Cl_2{\cdot}2eg$ (eg = ethylene glycol). In a urea-based DES, either pure chloro or chloro–oxo coordination is observed. In $[C_6mim][Cl]$ pure chloro complexation is also observed, but coordination numbers are smaller (typically 3), which can be explained by the long alkyl chain of the cation. In $[C_2mim][SCN]$ metal ions are entirely coordinated by thiocyanate, either through the N or the S atom, depending on the hardness of the metal ion according to the hard-soft acid-base principle. With weaker coordinating anions, mixed coordination between solvent and solute anions is observed. The effect of hydrate or added water on speciation is insignificant for the diol-based DESs and small in other liquids with intermediate or strong ligands. One of the main findings of this study is that, with respect to metal speciation, there is no fundamental difference between deep eutectic solvents and classic ionic liquids.



Inorg. Chem. 2014, 53, 6280–6288

CuSO$_4$ in various ILs

Leaching kinetics: comparing like with like

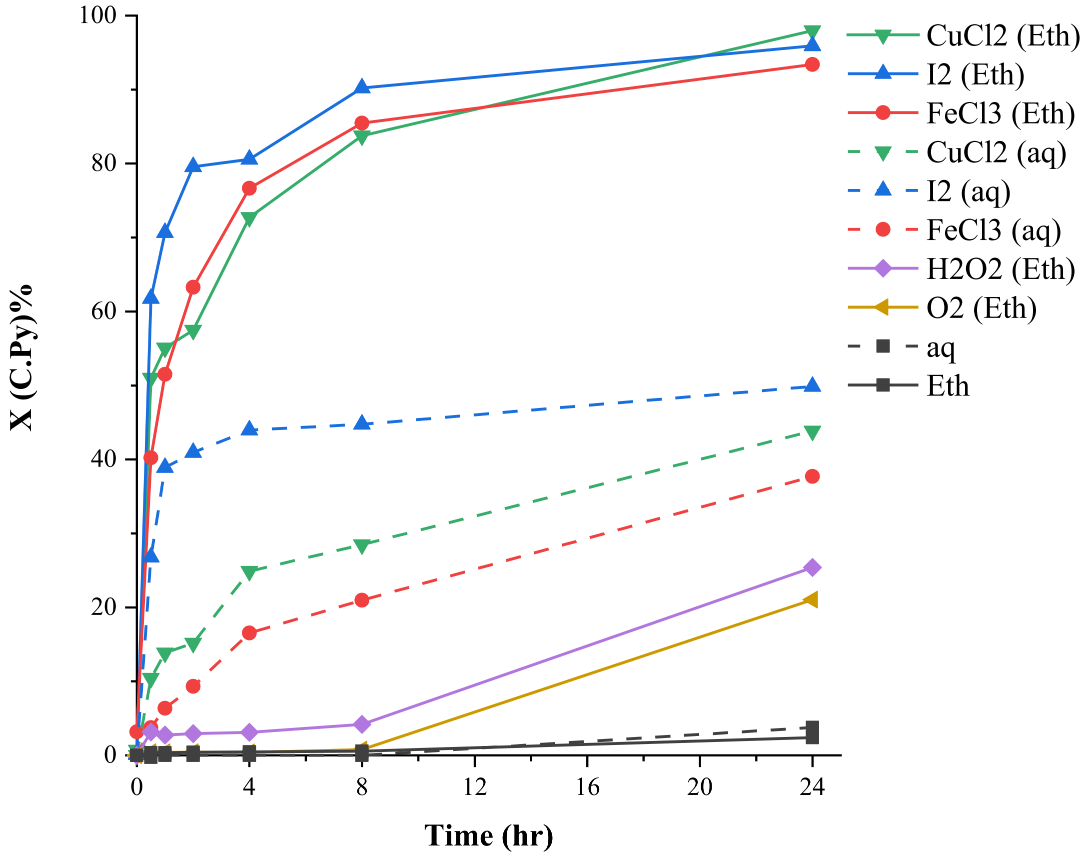


$$CuFeS_2 \xrightarrow{CuCl_2\ (Eth)} CuCl_2^-$$

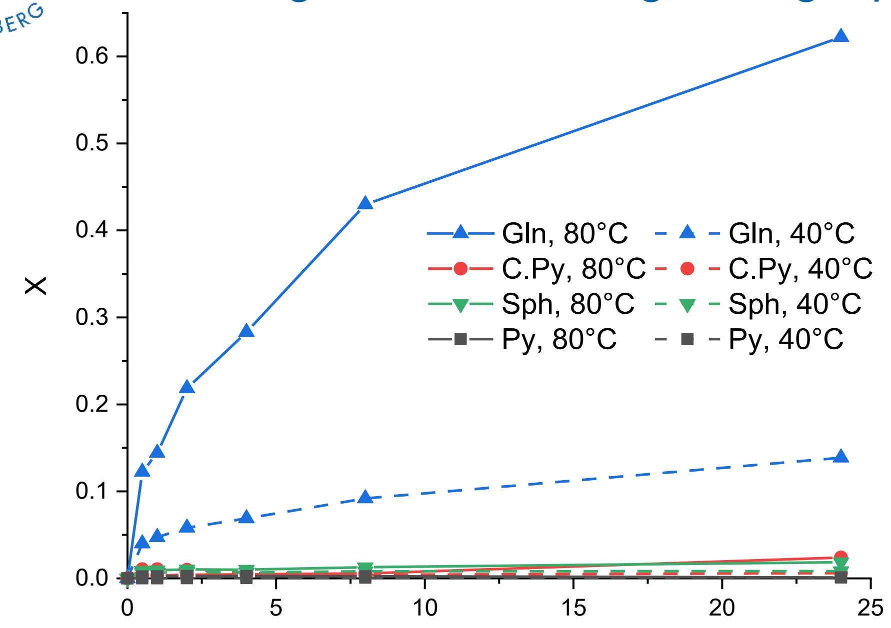
$$Au \xrightarrow{CuCl_2\ (Eth)} AuCl_2^-$$

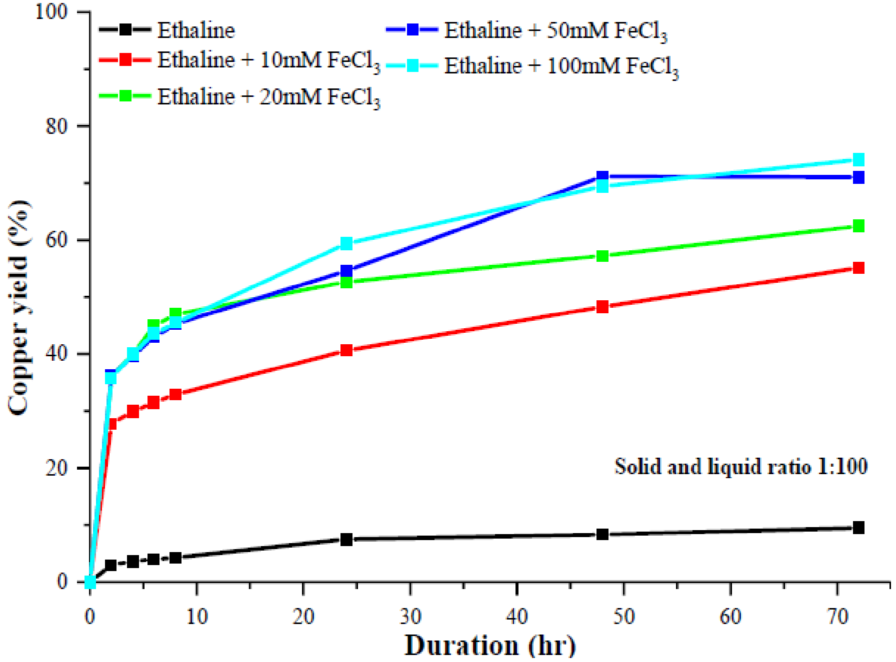
$$CuFeS_2 \xrightarrow{CuCl_2\ (aq)} \text{Passivation}$$

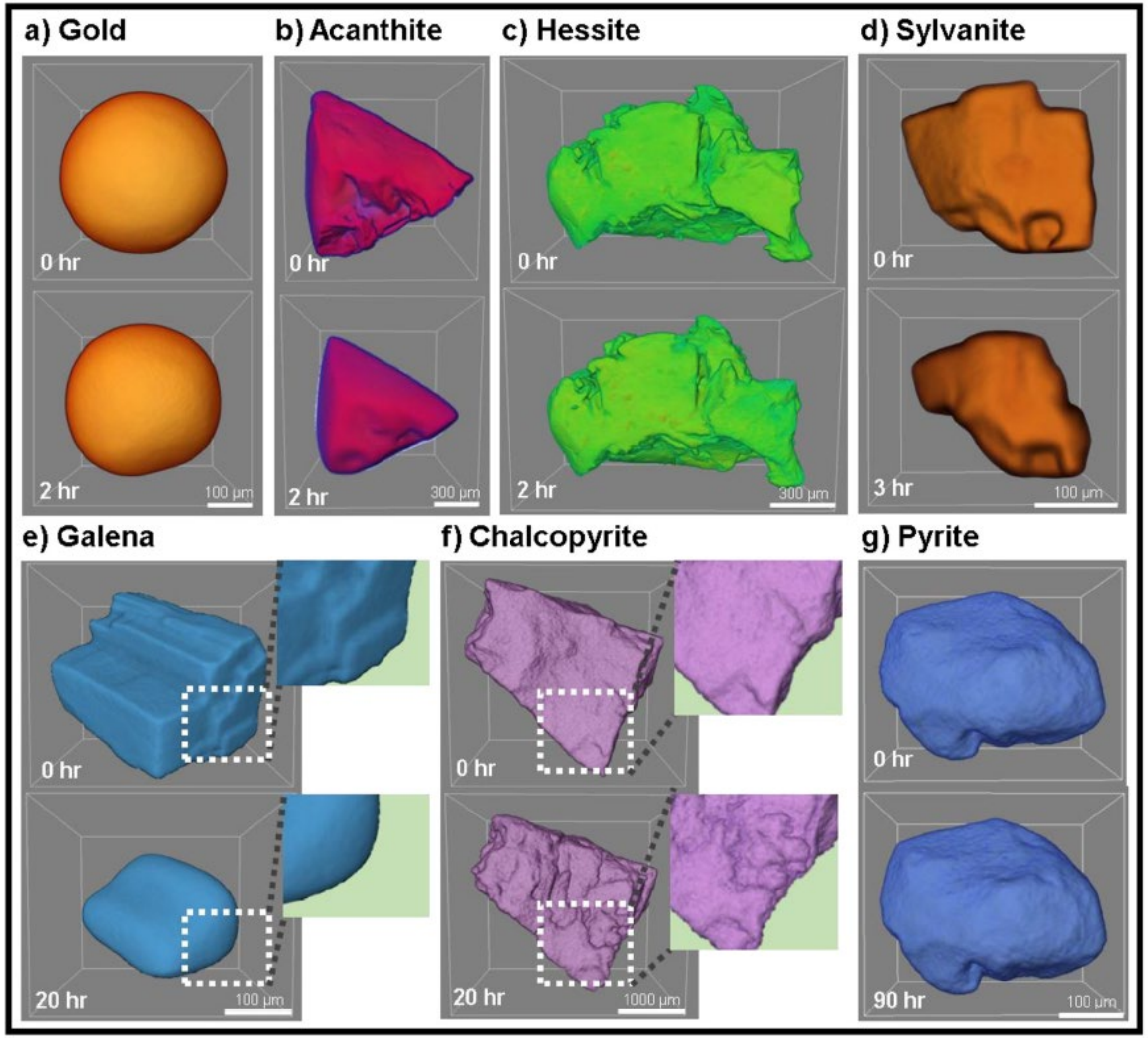
$$Au \xrightarrow{CuCl_2\ (aq)} \times$$



Leaching kinetics: looking at single particles



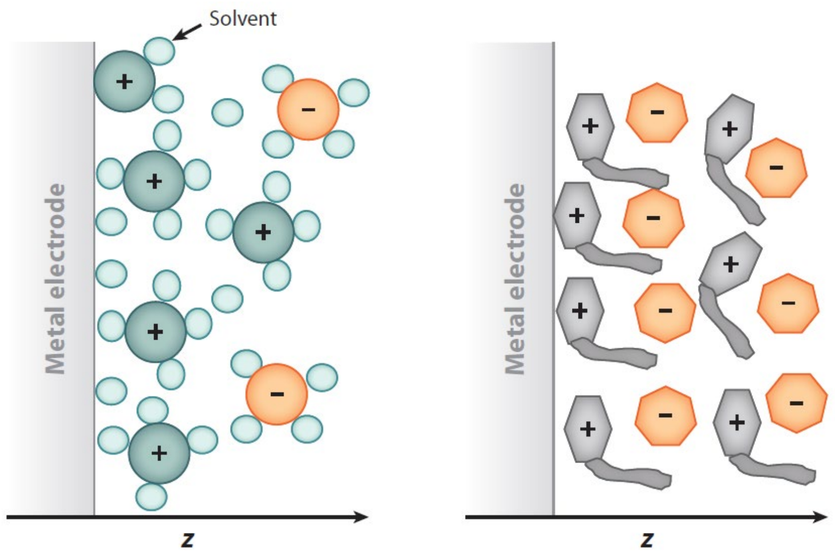




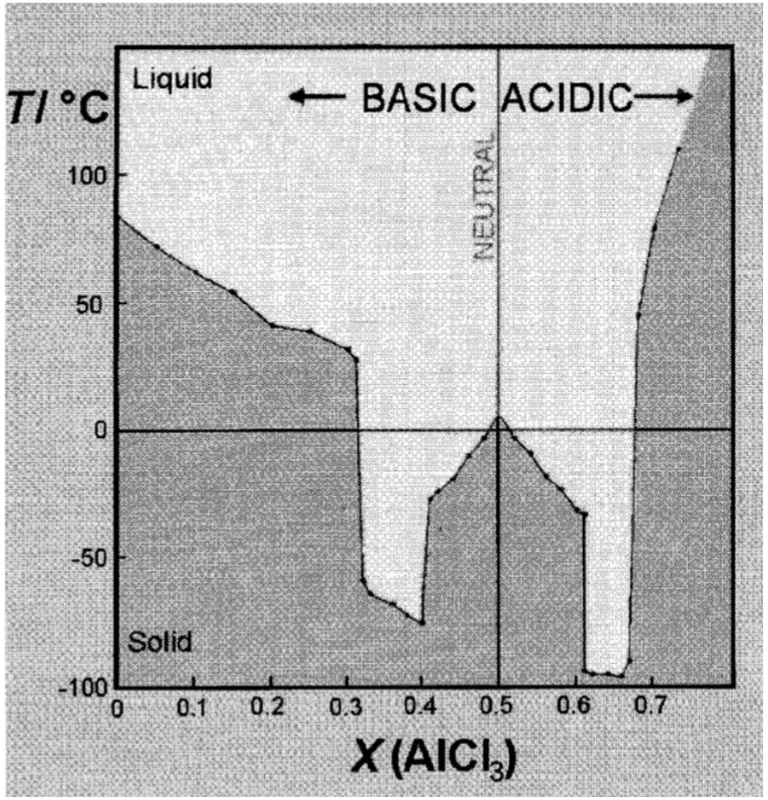
Hydrometallurgy **211**, 105869 (2022)

Problems in theory and practice

- High viscosity
- Role of residual water disputed
- Reversibility unclear
- Metal speciation barely investigated
- No viable solutions for IL recovery/recycling
- Anode reaction often not considered
- What happens on a molecular level?



Annu. Rev. Mater. Res. **43,** 335 (2013)



Endres, McFarlane, Abbott
Electrodeposition from Ionic Liquids
Wiley 2008

Thank you for your attention and interest!

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Salt & Mineral Chemistry

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