
BAUXITE RESIDUE
VALORISATION AND
BEST PRACTICES
CONFERENCE
Leuven
5-7 October 2015

Selective recovery of scandium(III) from bauxite residue leachates by solvent extraction with a carboxyl-functionalized ionic liquid

Bieke Onghena*, Chenna R. Borra, Tom Van Gerven, Koen Binnemans

Department of Chemistry, KU Leuven
Department of Chemical Engineering, KU Leuven

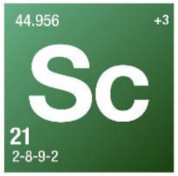
*bieke.onghena@chem.kuleuven.be

Content

- Recovery of scandium from red mud
- Introduction to solvent extraction with ionic liquids
- Results and discussion of experimental work
- Future prospects

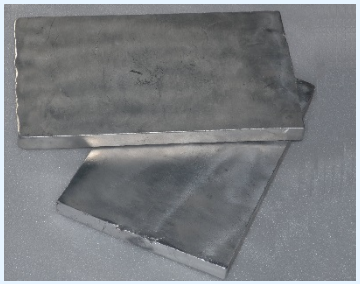
KU LEUVEN

Recovery of Sc from bauxite residue (red mud)

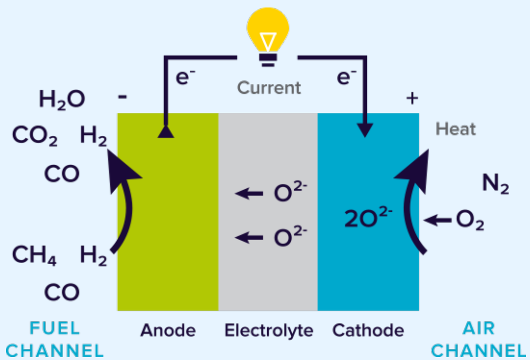


Applications of scandium

Scandium-aluminium alloy



Solid oxide fuel cells



+ ceramics, electronics, lasers, lighting, radioactive isotopes

Price in USD/kg (2013)

(source: USGS)

Sc oxide 99.99%	5000
Sc metal (ingot)	175 000

Bauxite residue contains

0.02 wt% Sc

3 billion tons BR stockpiled

= 0.6 million tons Sc stockpiled

120 million tons BR/year

= 24 000 ton Sc/year

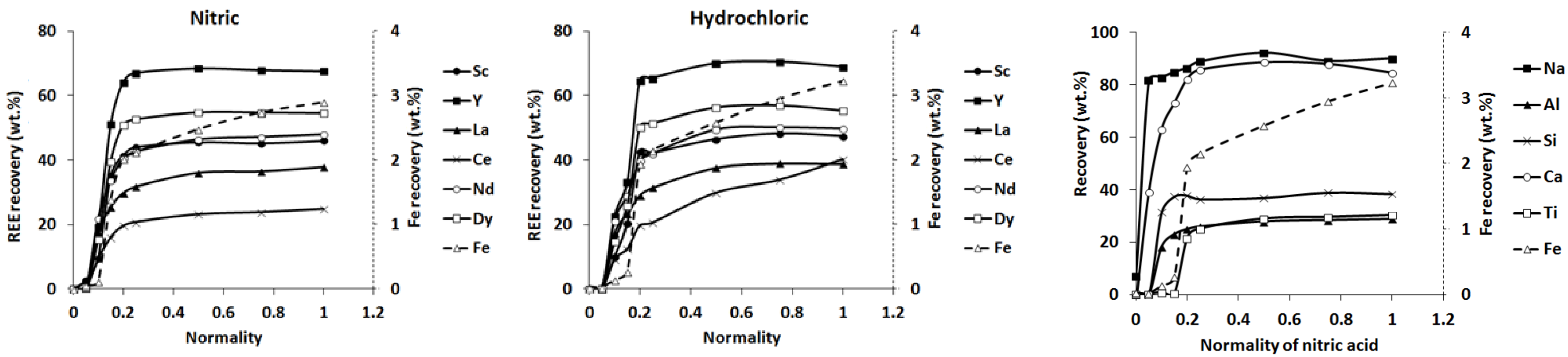
= 4 200 billion USD/year worth of Sc

KU LEUVEN

Direct leaching of bauxite residue

Chenna R. Borra *et al*. Minerals Engineering 76 (2015) 'Leaching of rare earths from bauxite residue (red mud)'

Selective dissolution of valuable REEs from red mud



Example: HCl leaching, 0.2 N, 50:1 L/S, 24 h, 25 °C

Composition red mud sample (Aluminium of Greece)			
Fe_2O_3	44.6 wt%	TiO_2	5.7 wt%
Al_2O_3	23.6 wt%	Na_2O	2.5 wt%
CaO	11.2 wt%	ΣREE (incl. Y)	788.5 ppm
SiO_2	10.2wt%	Sc	121 ppm

HCl leachate (mg/L)			
Fe(III)	109	Ti(IV)	134
Al(III)	520	Na(I)	396
Ca(II)	1040	ΣREE(III) (incl. Y)	~ 4
Si(IV)	361	Sc(III)	~ 1

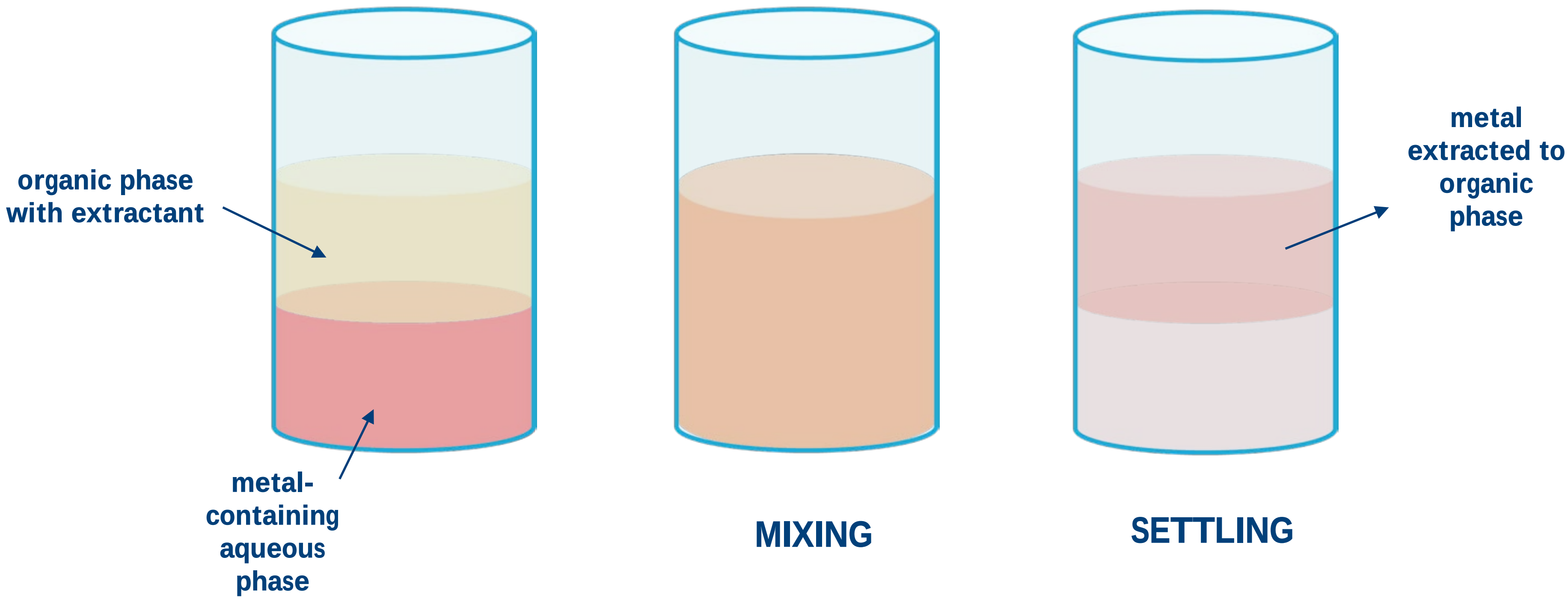
Goal

Recovery of Sc(III) from bauxite residue by selective extraction and purification of **bauxite residue leachates** using **solvent extraction** (liquid-liquid extraction) with an **ionic liquid** as the extracting phase

Solvent extraction

SOLVENT EXTRACTION:

preferential distribution of a solute between two mutually immiscible phases

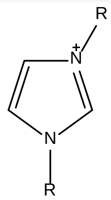


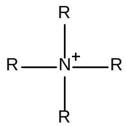
$$D = \frac{[M]_{IL}}{[M]_{aq}} \qquad \%E = \frac{n_{IL}}{n_{IL} + n_{aq}} \cdot 100\% \qquad \alpha_B^A = \frac{D_A}{D_B}$$

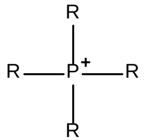
Ionic liquids (ILs) in solvent extraction

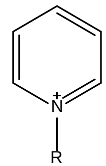
IONIC LIQUID = liquid that consists entirely of ions + low melting point (< 100 °C)

cations

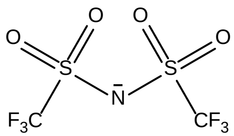








anions



PF_6^-

Cl^-

NO_3^-

<u>Properties:</u> low flammability, low volatility, broad liquidus range, tunable depending on structure (hydrophobic/hydrophilic), …

Use in solvent extraction as replacement for volatile solvents (e.g. kerosene):

→ more environmentally friendly
→ safer
→ higher metal loading
→ different mechanism

→ generally high viscosity
→ high price

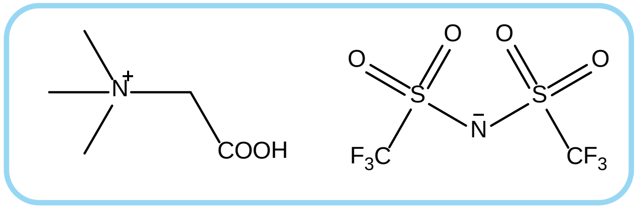
Results and discussion of experimental work

Recovery of Sc(III) from red mud leachates with the ionic liquid [Hbet][Tf_2N]

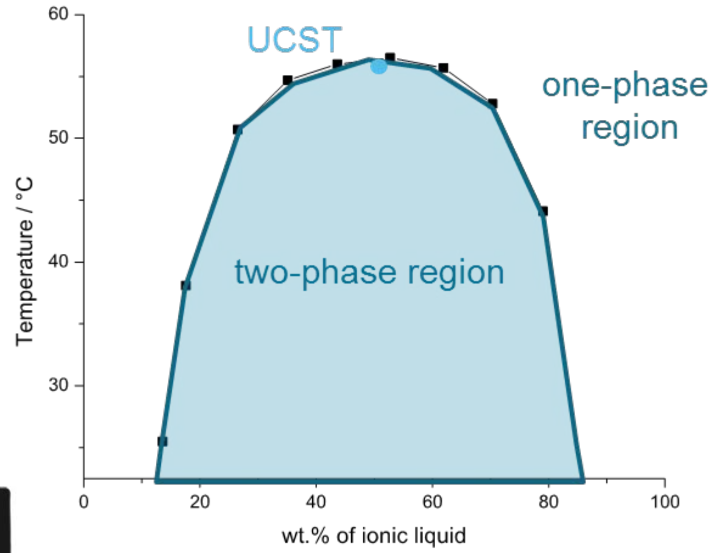
KU LEUVEN

Betainium bis(trifluoromethylsulfonyl)imide [Hbet][Tf_2N]

cation = natural product, commercially available



hydrophobic anion



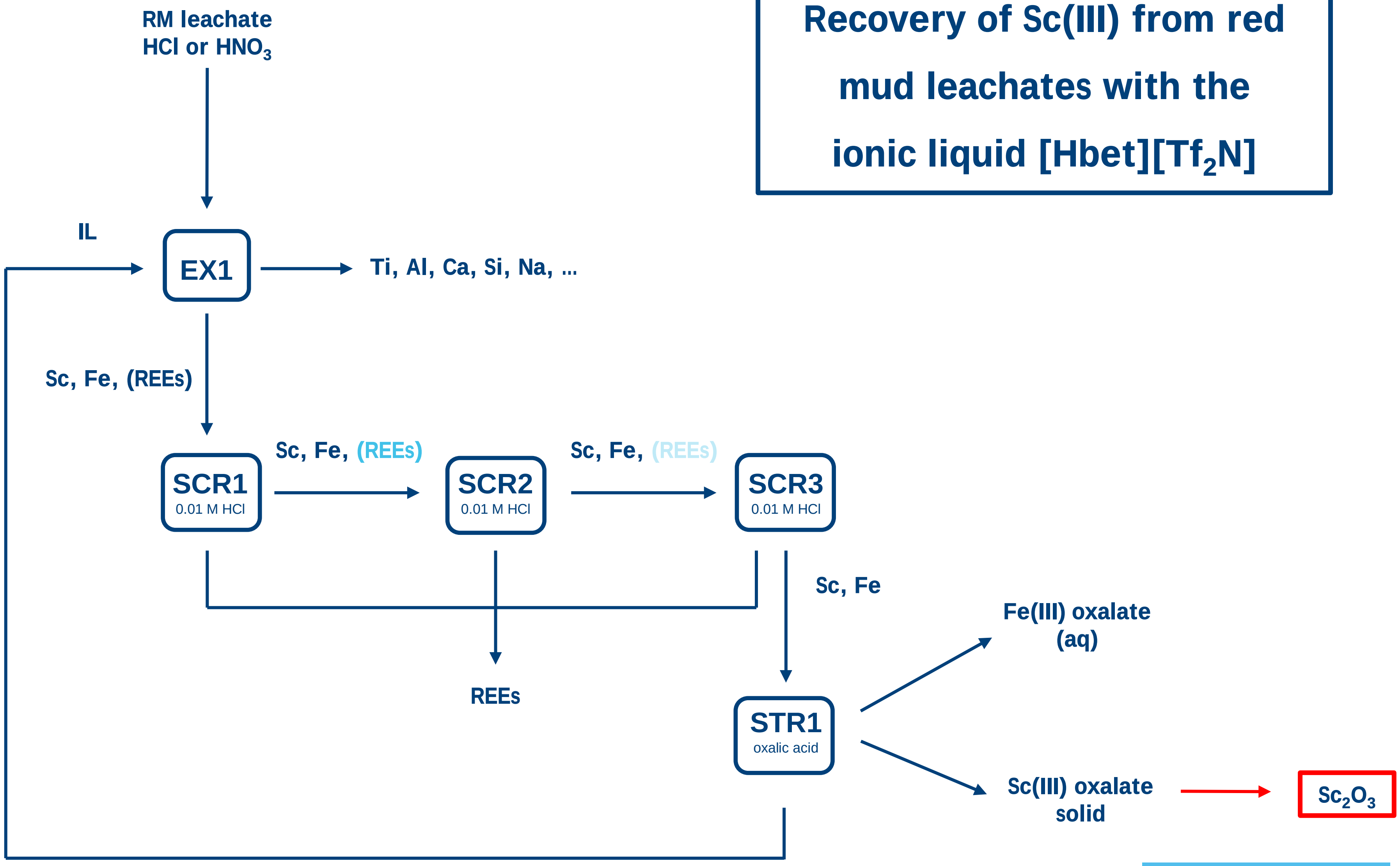
<u>Properties:</u>

- hydrophobic
- high solubility in water (14 wt%), high uptake of water (13 wt%)
- thermomorphic behavior in water (UCST = 55 °C)
- pH dependent phase behavior
- carboxyl function on cation
- acidic extractant: extraction is pH dependent
- betaine coordinates to metal ions

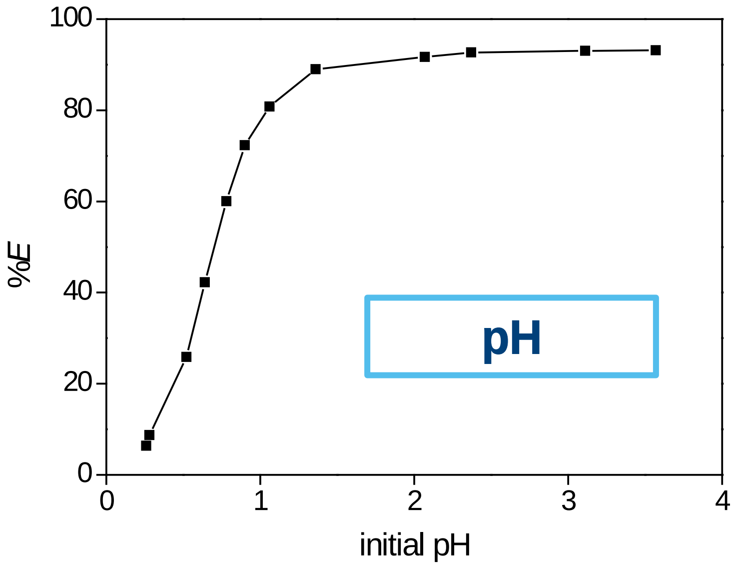
KU LEUVEN

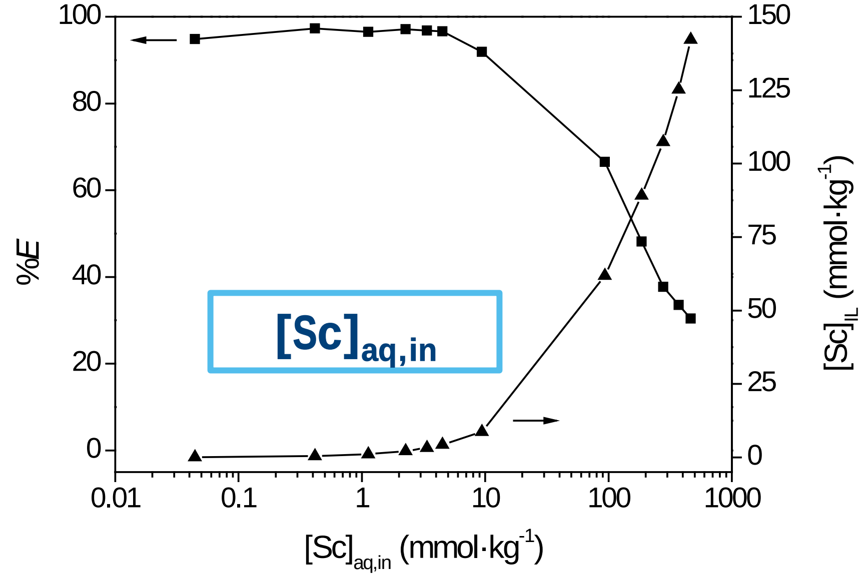
Conceptual flow sheet

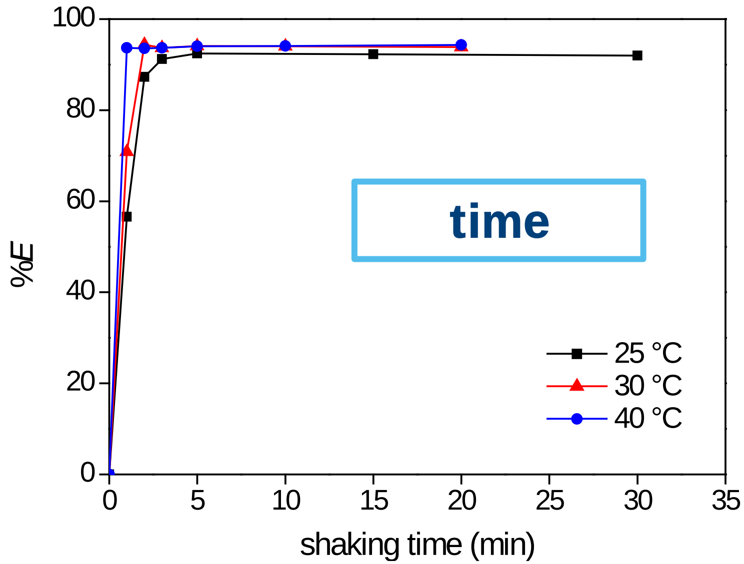
Recovery of Sc(III) from red mud leachates with the ionic liquid [Hbet][Tf_2N]

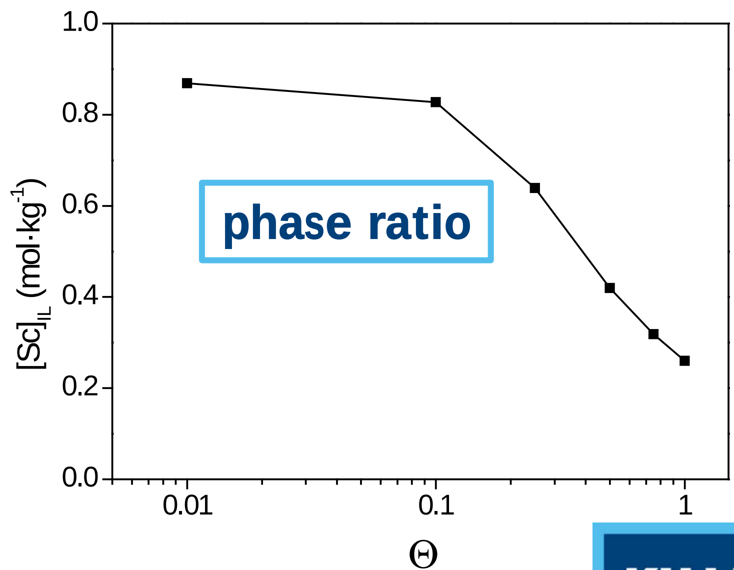


Extraction of Sc(III) with [Hbet][Tf_2N]



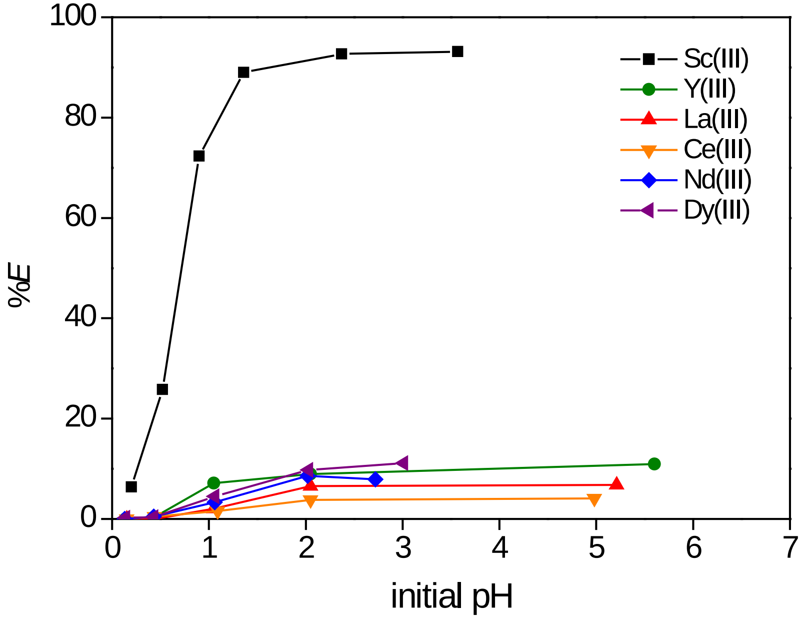


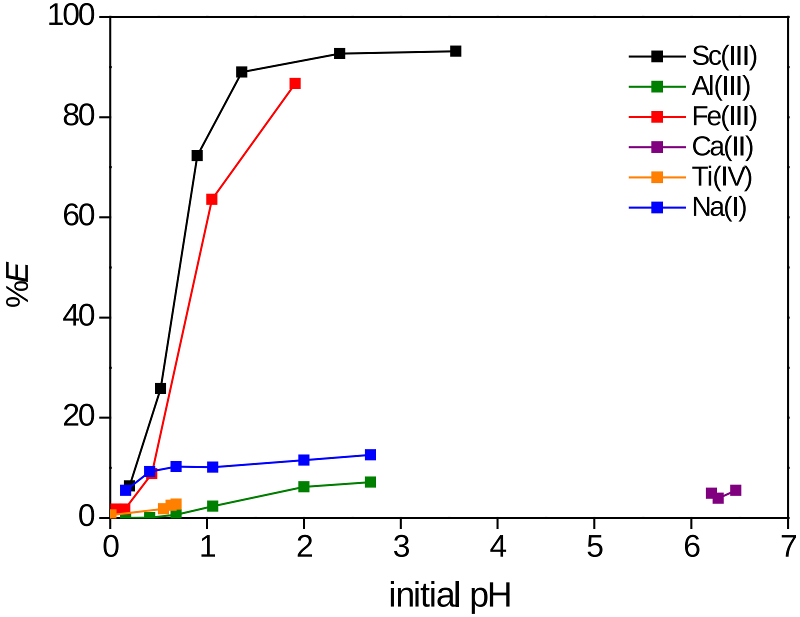




KU LEUVEN

Separation of Sc(III) from synthetic solutions





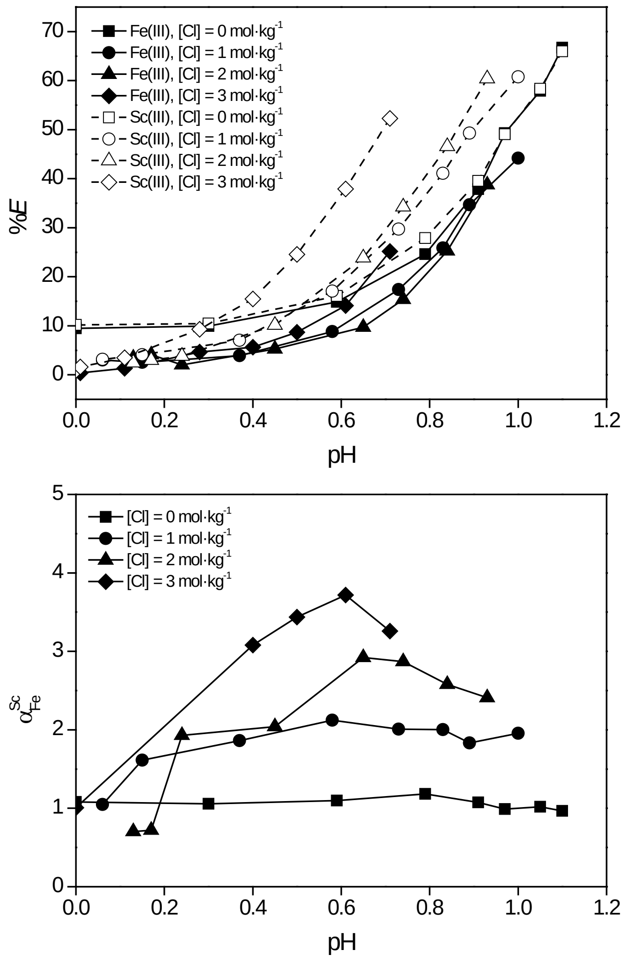
- Initial concentration: 10 mmol/g for each metal ion
- pH adjusted with HCl
- 15 min shaken, 25 °C

- Initial concentration: 10 mmol/g for each metal ion
- pH adjusted with HCl
- 15 min shaken, 15 °C

KU LEUVEN

Improving the Sc-Fe separation

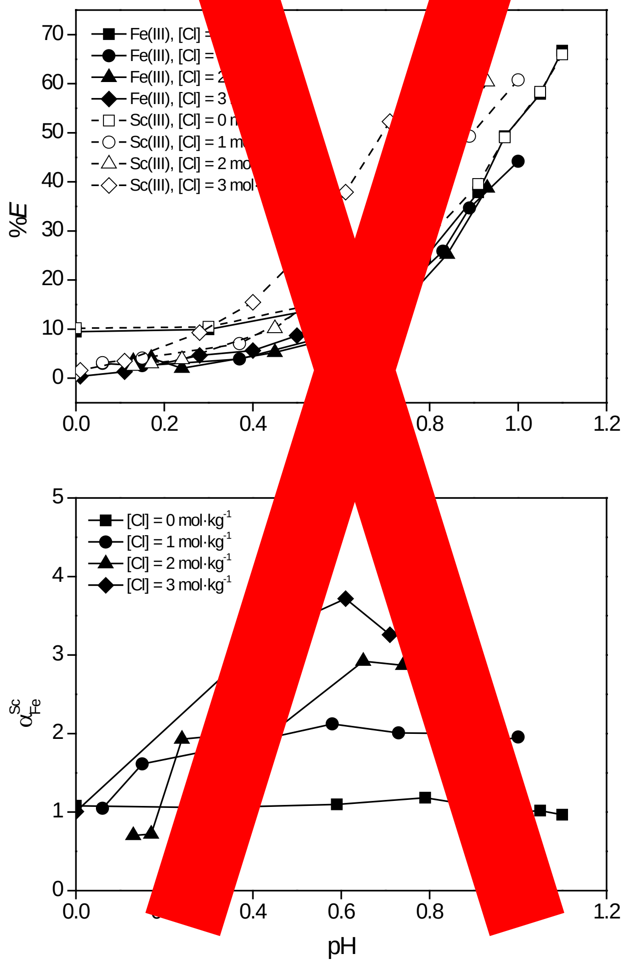
Addition of chloride to aqueous phase during extraction



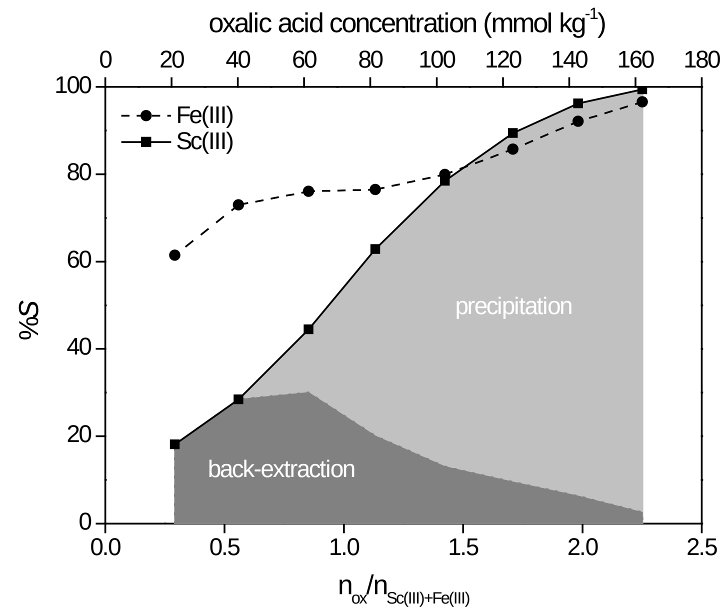
KU LEUVEN

Improving the Sc-Fe separation

Addition of chloride to aqueous phase during extraction



Precipitation stripping with oxalic acid



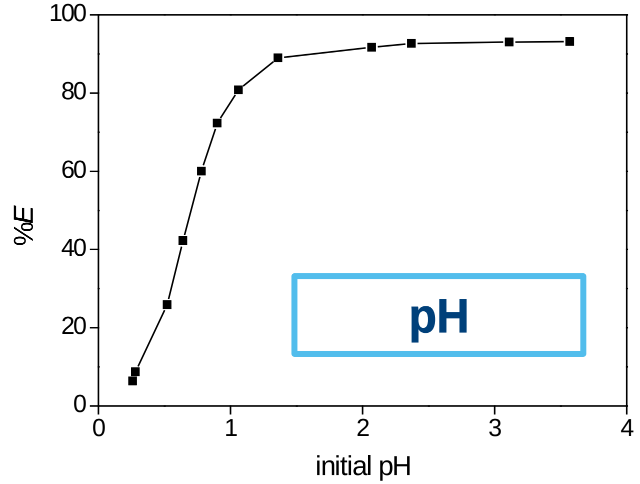
KU LEUVEN

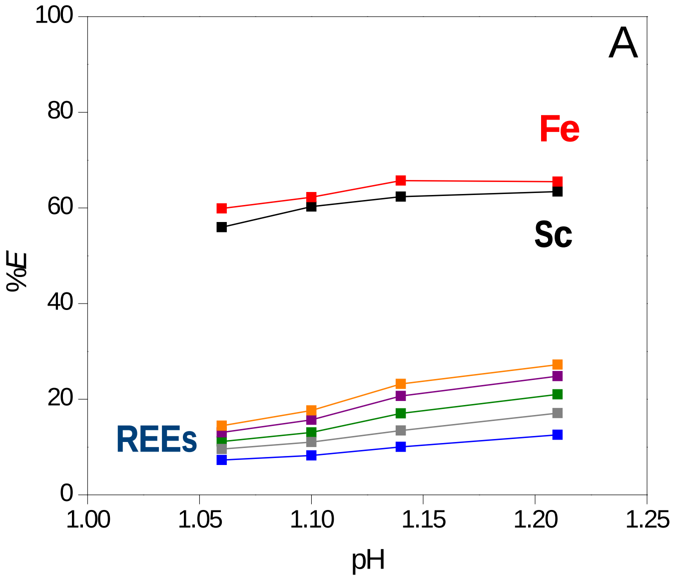
Sc/Fe separation from real RM leachates

Addition of base

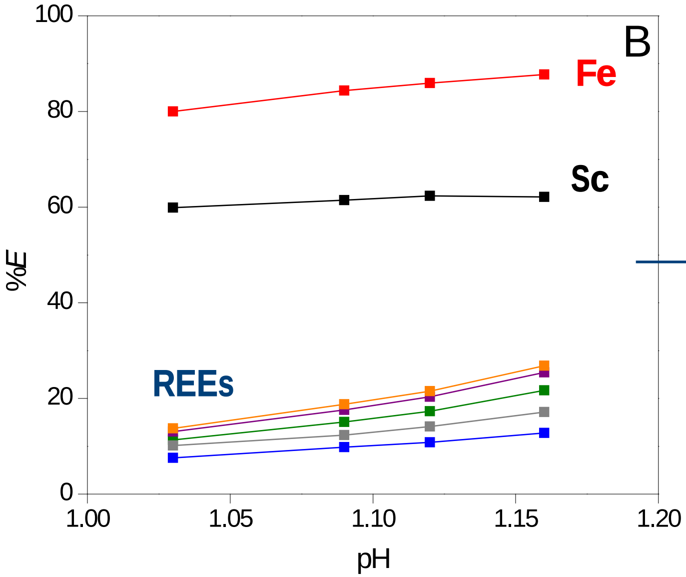
The leachates have a pH of around 1, which is not within the optimal range of extraction.

Addition of base may increase the pH and increase extraction.





HCl leachate



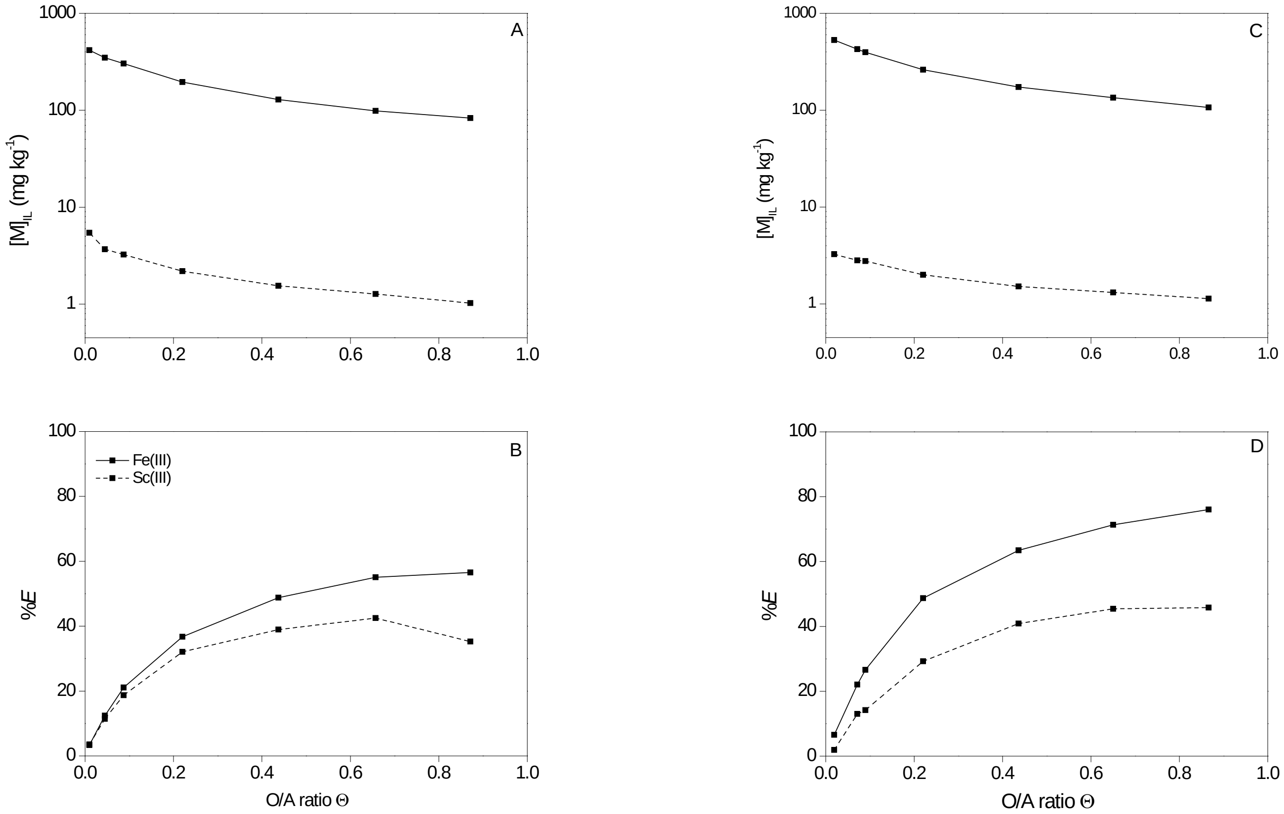
HNO_3 leachate

→ **limited effect**

Sc/Fe separation from real RM leachates

Influence of phase ratio A/O

In principle, by lowering the phase ratio, the metal concentration in the IL phase will increase

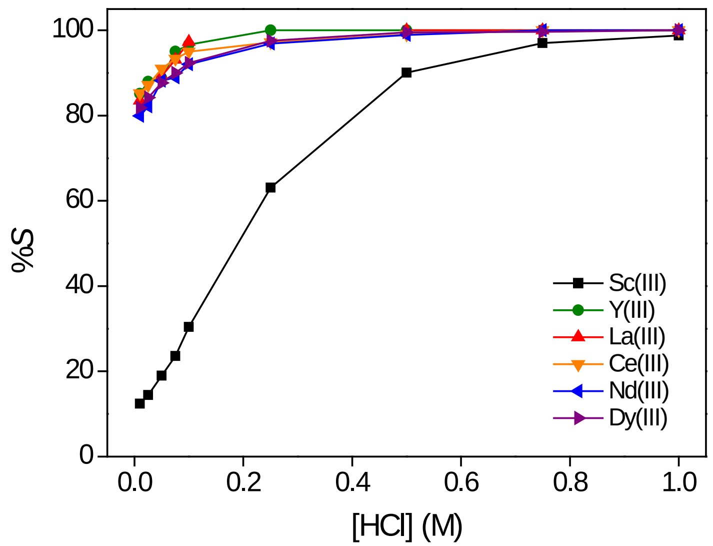


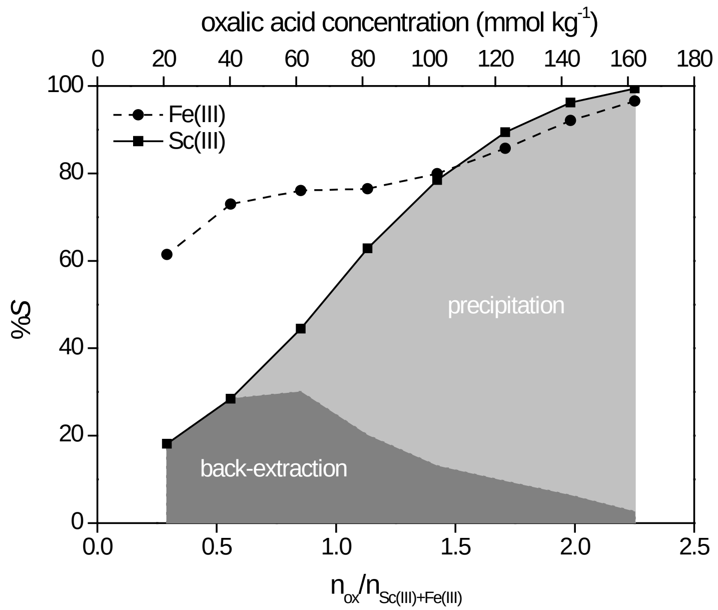
HCl leachate **HNO_3 leachate**

KU LEUVEN

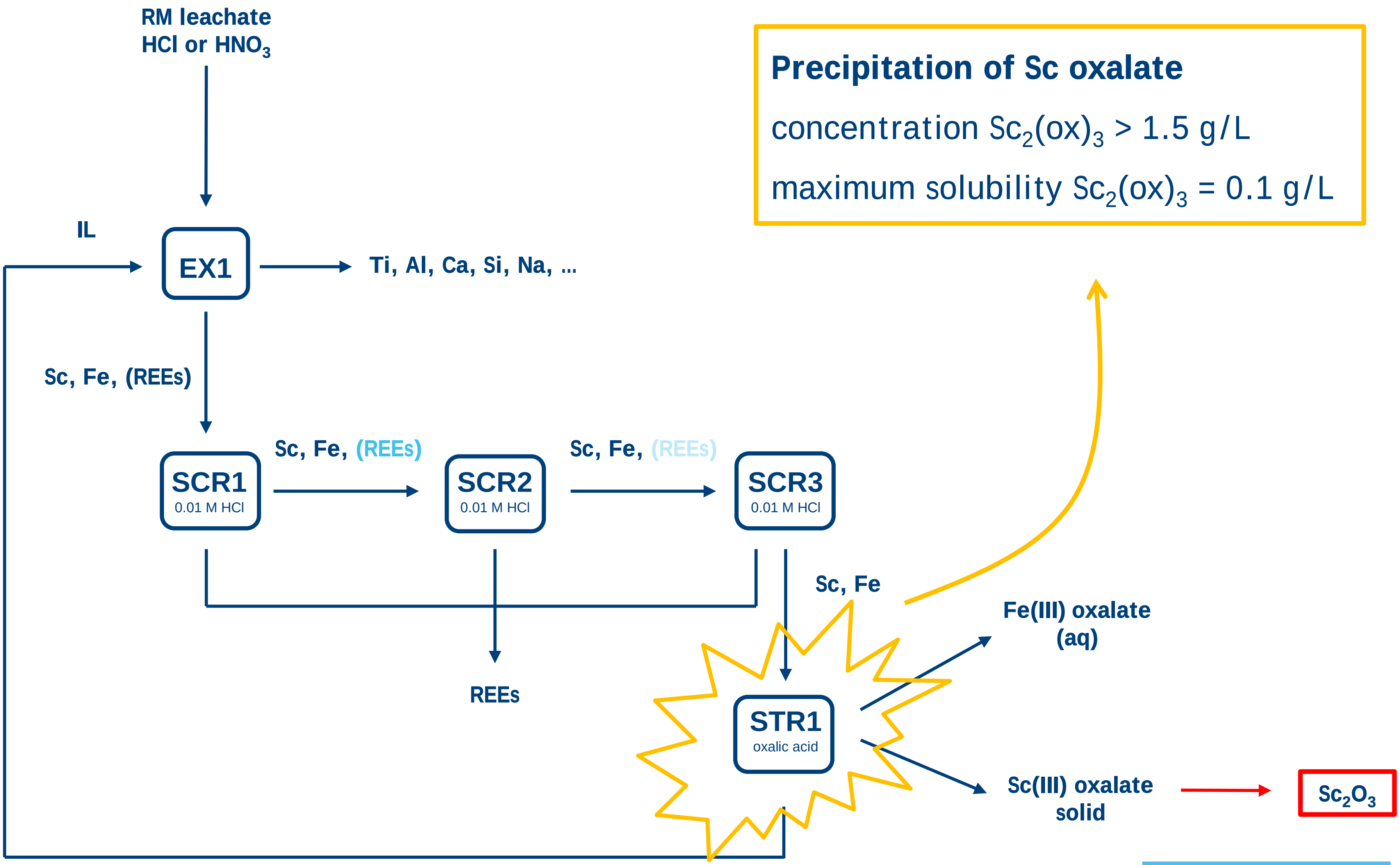
Scrubbing and stripping

1. Scrubbing with mineral acid (HCl/HNO_3) to remove coextracted REE
2. Oxalic acid precipitation stripping to strip Fe and Sc and selectively precipitate Sc





Application of process to real RM leachates



Precipitation of Sc oxalate

concentration $Sc_2(ox)_3$ > 1.5 g/L

maximum solubility $Sc_2(ox)_3$ = 0.1 g/L

Application of process to real RM leachates

+

- No extraction of Ca, Al, Na, Ti, Si
- Good separation of Sc and REE
- Easy stripping
- Fast kinetics
- ...

-

- Low concentrations in leachates:
  - oxalic acid stripping = problematic
  - SX less suitable for metal recovery
- Only moderate %E of Sc(III) with [Hbet][Tf_2N]
- Bad Sc/Fe separation
- No pH adjustment possible
- Loss of IL to aqueous phase
- ...

KU LEUVEN

Future prospects

- Increasing the Sc(III) concentration in the leachate → better solvent extraction
- Less consumption of acid by trying to avoid leaching of Al-Na-Ca-Si-matrix
- Implementation of Sc recovery in bigger picture
- Trying other IL systems to improve Sc/Fe separation

KU LEUVEN

Acknowledgments

Laboratory of Inorganic Chemistry, KU Leuven

Prof. Koen Binnemans

Chenna R. Borra and Prof. Tom Van Gerven (Chemical Engineering, KU Leuven)

IWT, FWO and KU Leuven for funding

EU MSCA-ETN REDMUD

For more info, check:

http://www.kuleuven.rare3.eu/

KU LEUVEN