Chalmers University of Technology,
Department of Chemistry and Chemical Engineering

Nuclear Chemistry and Industrial Materials Recycling

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environmentally friendly and efficient methods for extraction
of rare earth elements from secondary sources

ERA-MIN
NETWORK ON THE INDUSTRIAL HANDLING
OF RAW MATERIALS FOR EUROPEAN INDUSTRIES

Recovery of rare earth elements from mine tailings

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- ERA-MIN 2nd Joint Call Project. Launched in January 2015 and planned for 3.5 years.
- 11 partners from 8 countries. Coordinated by Chalmers University of Technology, Sweden.

AVANCEZ 1829
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AGH

SAVONA PROJECT
energy & environment

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ALEXANDRU IOAN CUZA
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brgm

Council for Geoscience

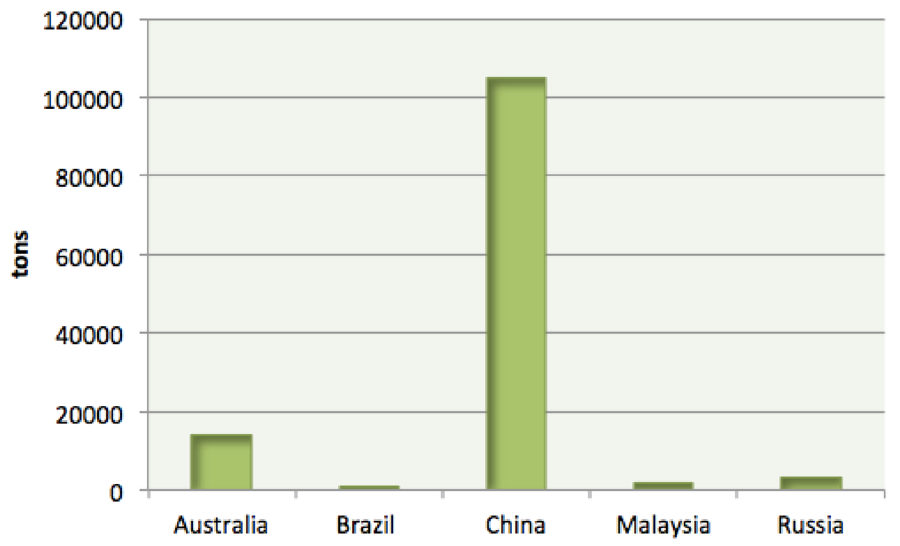
Primus.inter.pares AS

edm
Empresa de Desenvolvimento Mineiro, SA

Processing of secondary sources

- **No REEs production in currently located in the EU. There are, however, some plans for development, e.g. Norra Kärr (SE).**
- **Recent focus: the possibility to recover critical raw materials from secondary sources:**
  - Fluorescent lamps, permanent magnets (e.g. from HDDs) and NiMH batteries are attractive urban mining sources for REEs.
  - Tailings and other by-products from previous mining activities in the EU can hold significant amounts of critical raw materials, not just REEs but also W, P etc.

REMs supply in 2016



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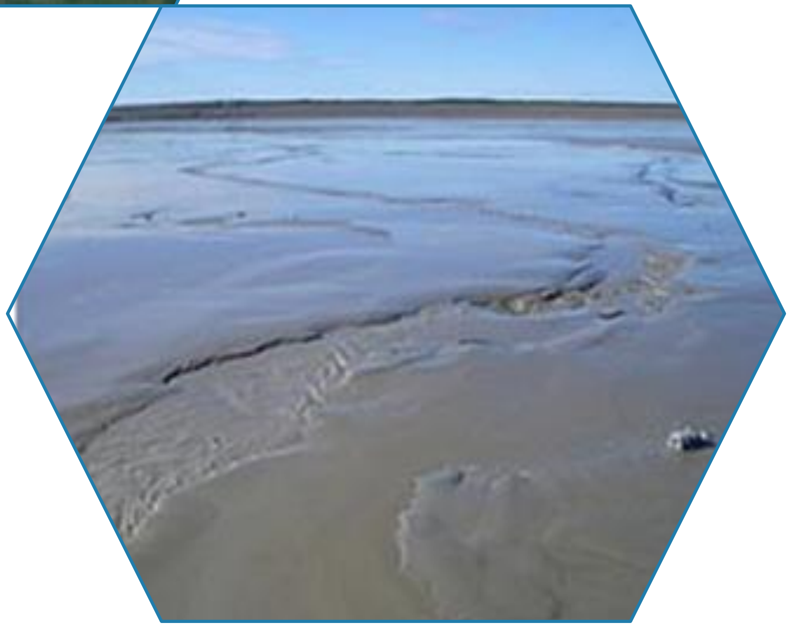
Mine tailings

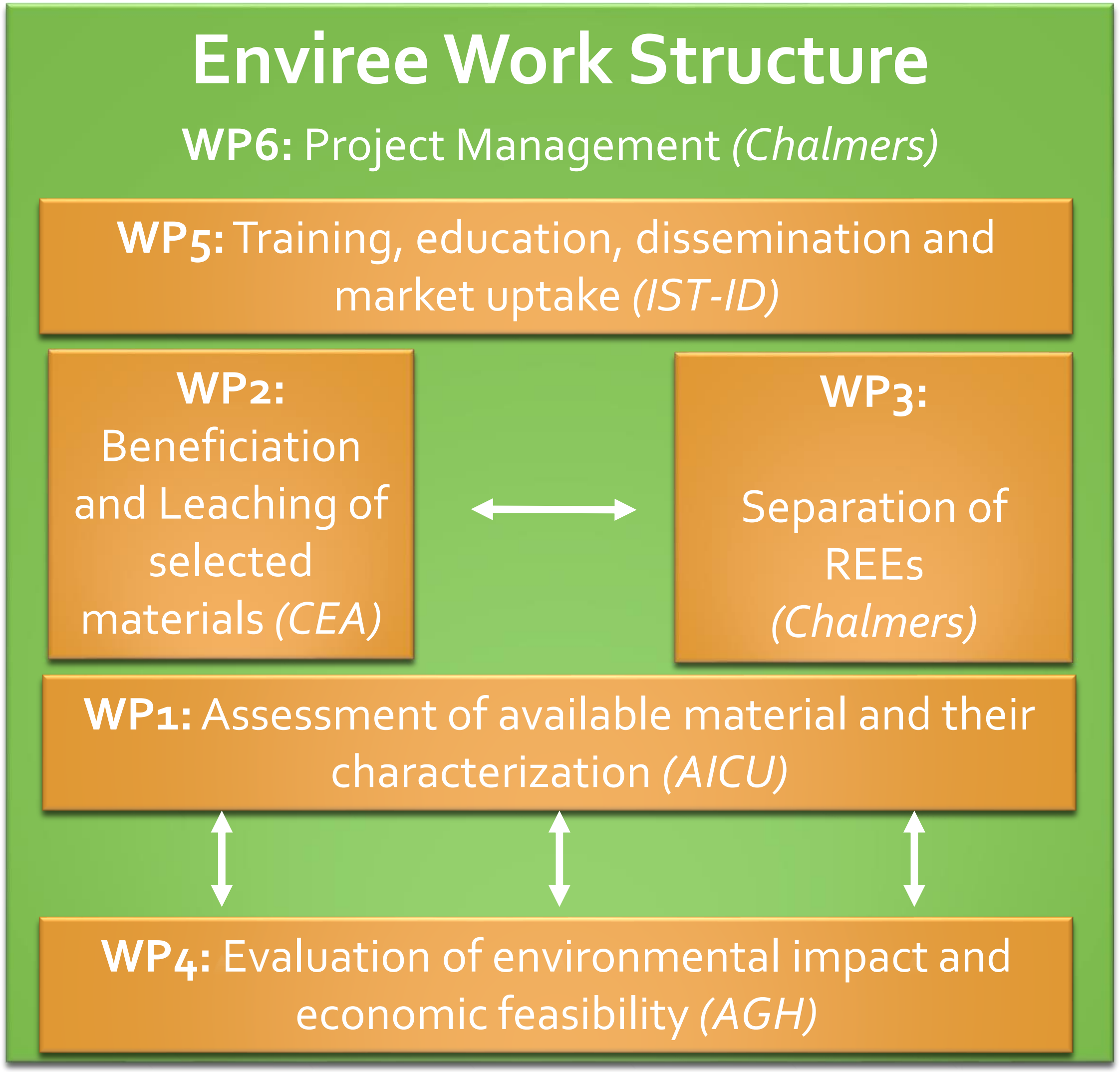
- Rock waste from the mining industry.
- When the ore has been stripped of its valuable minerals, it is piled up into tailings.
- Tailings can reach immense proportions, appearing in the form of large hills (or sometimes ponds) on the landscape.
- Secondary source of valuable metals.





Research topics

- Extraction: Integrated processes and system approach, and innovative waste management.
- Mineral processing: Processing of low grade and complex materials in efficient ways.
- Metallurgy: Treatment of by-products and wastes with recovery of the contained metal value.



Enviree Work Structure

WP6: Project Management *(Chalmers)*

WP5: Training, education, dissemination and market uptake *(IST-ID)*

WP2: Beneficiation and Leaching of selected materials *(CEA)*

WP3: Separation of REEs *(Chalmers)*

WP1: Assessment of available material and their characterization *(AICU)*

WP4: Evaluation of environmental impact and economic feasibility *(AGH)*

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Target materials

Material provider	Type of material provided
Boliden, Sweden	Tailing containing REE
Council for Geoscience, South Africa	Different secondary materials and mine residues from South Africa mines and processing plants where REE has been identifies as potential by-product
EDM, Portugal	Waste rock and tailing potentially containing REE
Rio Tinto, Australia	By-product from the mineral sand operations with potentially hight content of REE and Th
ZNP SAV s . r . o . Slovakia	Red mud from abandoned alumina production (from bauxite)
DIAMO-GEAM a.s., Czech Republic	a) samples from uranium production b) samples from tailing ponds c) mine water from Zlate hory area d) samples from waste rock pile
Hellenic copper mines LTD, Cyprus	Tailings from copper mining and processing
AGH, Poland	Tailings from copper ore processing – post flotation waste
	Tailings from zinc and lead ore processing – post floation waste
	Tailings from sculpture ore processing – post flotation waste
TERAMED Ltd., Czech Republic	Mining waste from different locations in the Czech Republic

- Tailings from lead, zinc, copper, sulfur, phosphate ores mining and treatment
- Red mud.
- Waste rock from other mining activities, possibly enriched with REEs.

Selected samples

- Tailings from sulphide flotation stage of the Boliden concentrator for gold mining, New Kankberg (Sweden)
  - Phosphates present as monazite and apatite, with minor amounts of xenotime and berlinite

Sulfides flotation tailings
170 ppm Ce
90 ppm La
70 ppm Nd
0.17% P_2O_5

- Tailings from underground tungsten mining (1954-1984), Covas (Portugal)
  - W: mainly scheelite and minor wolframite

Covas tailings
32 ppm Ce
16 ppm La
15 ppm Nd
1900 ppm W

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New Kankberg tailings

- The tailing pond area is around 5 km wide and 10 km long.
- Roughly **700 Mton** has so far been stored in the tailing pond.
- Around **1300 Mton** more is currently planned to be stored until year 2045.

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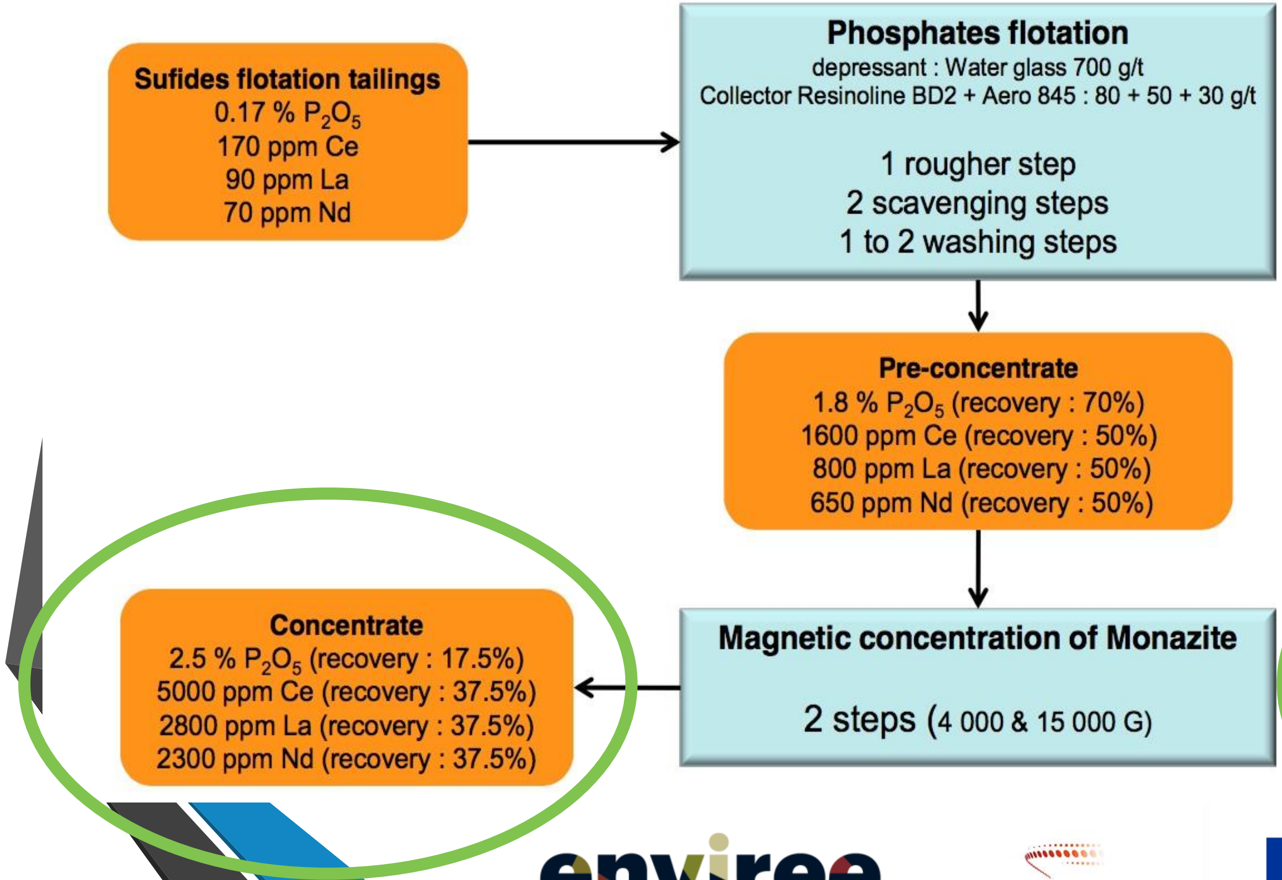
Beneficiation

New Kankberg tailings



Sufides flotation tailings
0.17 % P_2O_5
170 ppm Ce
90 ppm La
70 ppm Nd

Phosphates flotation
depressant : Water glass 700 g/t
Collector Resinoline BD2 + Aero 845 : 80 + 50 + 30 g/t

1 rougher step
2 scavenging steps
1 to 2 washing steps

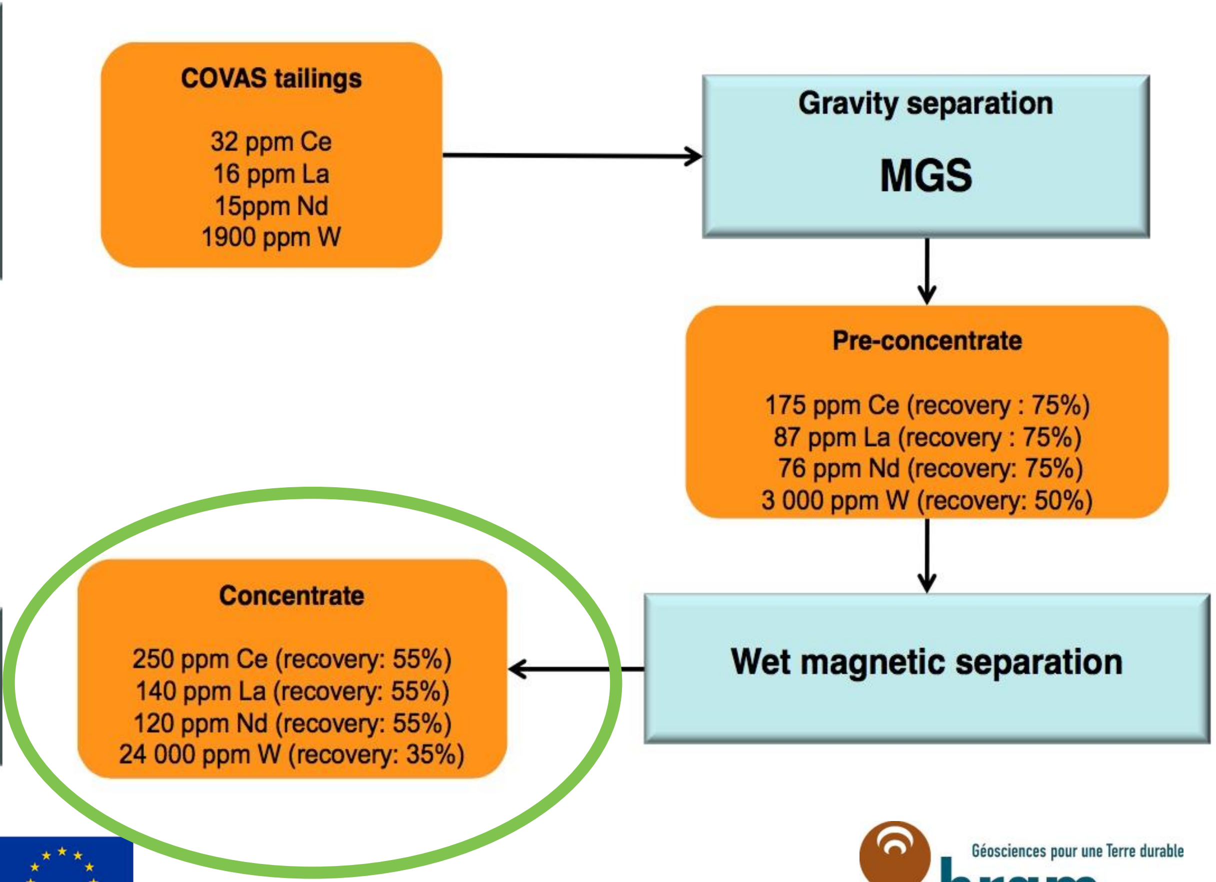
Pre-concentrate
1.8 % P_2O_5 (recovery : 70%)
1600 ppm Ce (recovery : 50%)
800 ppm La (recovery : 50%)
650 ppm Nd (recovery : 50%)

Magnetic concentration of Monazite

2 steps (4 000 & 15 000 G)

Concentrate
2.5 % P_2O_5 (recovery : 17.5%)
5000 ppm Ce (recovery : 37.5%)
2800 ppm La (recovery : 37.5%)
2300 ppm Nd (recovery : 37.5%)

Covas tailings



COVAS tailings

32 ppm Ce
16 ppm La
15ppm Nd
1900 ppm W

Gravity separation

MGS

Pre-concentrate

175 ppm Ce (recovery : 75%)
87 ppm La (recovery : 75%)
76 ppm Nd (recovery: 75%)
3 000 ppm W (recovery: 50%)

Wet magnetic separation

Concentrate

250 ppm Ce (recovery: 55%)
140 ppm La (recovery: 55%)
120 ppm Nd (recovery: 55%)
24 000 ppm W (recovery: 35%)

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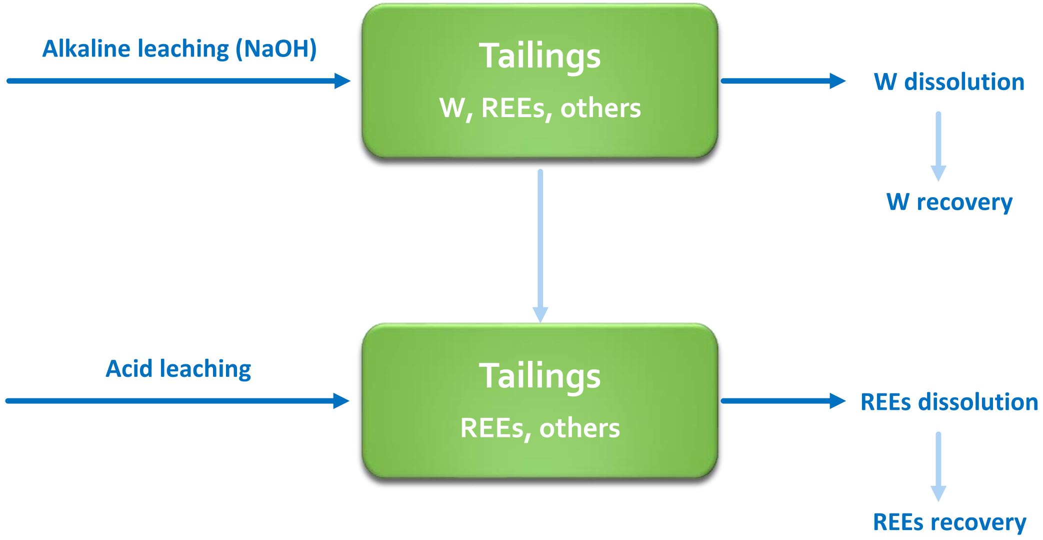
Leaching

- Low solubility of REEs phosphates:
  - acidic leaching
  - heating/conversion of phosphates required for efficient leaching

Covas concentrate
250 ppm Ce
140 ppm La
120 ppm Nd
24000 ppm W

New Kankberg concentrate
5000 ppm Ce
2800 ppm La
2300 ppm Nd
2.5% P_2O_5

- Leaching selectivity between REEs/W for Covas tailings
- Potential for P recovery from New Kankberg feed



Solvent extraction of REEs

- Study the solvent extraction of metals from *Covas* and *New Kankberg* synthetic feeds;
- HNO_3, HCl, and H_2SO_4 media (starting pH 0)
- Separate the contained REEs. Study the influence of impurities (Fe^{3+}, Cu^{2+}, PO_4^{3-}) and nature of the aqueous phase (acid type) on the separation process.

Covas feeds

Ion	content (mg/L)
Ce^{3+}	50
Nd^{3+}	25
La^{3+}	25
Dy^{3+}	5
Fe^{3+}	10000
Cu^{2+}	1000
pH	0

All solutions are stable after 3 months.

New Kankberg feeds

Ion	content (mg/L)
Ce^{3+}	1000
Nd^{3+}	500
La^{3+}	500
Dy^{3+}	100
$(PO_4)^{3-}$	10000
pH	0

The HNO_3 and HCl solutions are stable after 3 months.

The H_2SO_4 solution was not stable over time. One month later, Ce, Nd, and La concentrations were 20-25 % of their initial values.

Dy and P were not affected much.

Solvent extraction of REEs

Finding extraction systems that perform satisfactory in various acidic media (high phosphate, Fe, Cu concentrations)

- Diglycolamides (TODGA and analogues of TODGA)

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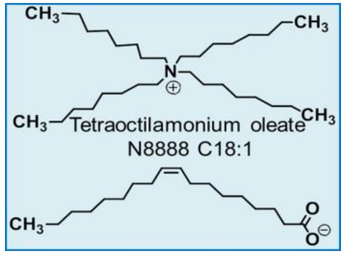
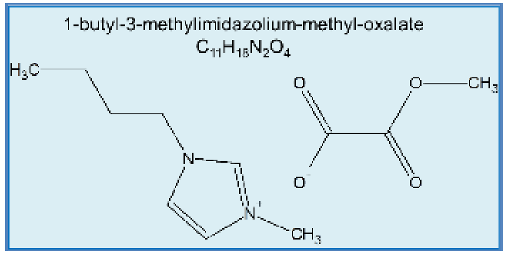
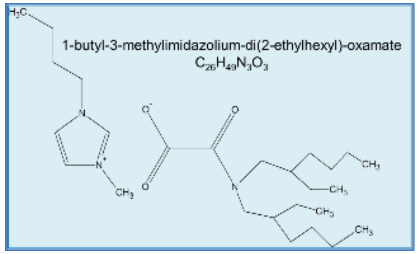
- Ionic liquids







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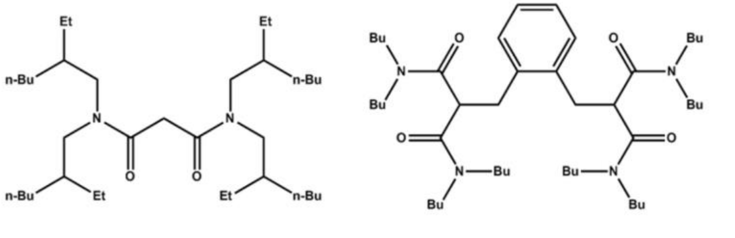
- New malonamides



a b

Figure 4.1-1: Molecular structures of: a - N,N,N',N'-tetrakis(2-ethylhexyl)malonamide (TiOMA); b - 2,2'-(1,2-phenylenebis(methylene))bis(N,N,N',N'-tetrabutylmalonamide) (B-BMA)

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- Membrane separation

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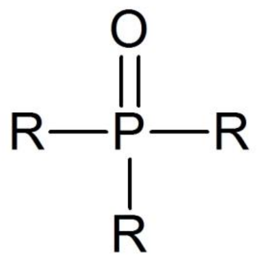
Solvent extraction of REEs

- Commercial extractants



$R = -C_8H_{17}$ or $-C_6H_{13}$

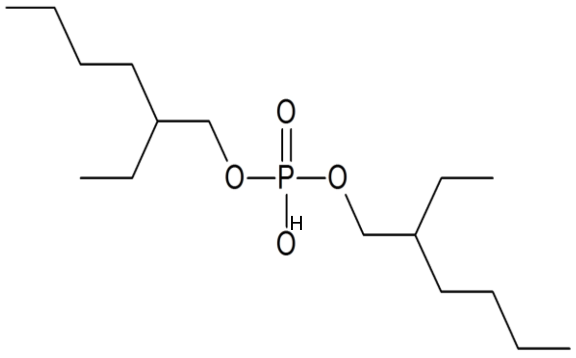
Cyanex 923

mixture of trialkyl-phosphine oxides:

$R_3P(O)$, $R_2R'P(O)$, $RR'_2P(O)$, $R'_3P(o)$

$R = [CH_3(CH_2)_7]$ - normal octyl,

$R' = [CH_3(CH_2)_7]$ - normal hexyl



D2EHPA

Di-(2-ethylhexyl) phosphoric acid

50 % vol. Cyanex 923 (1 min)

New Kankberg

C923

	Ce	Nd	La	Dy	P
HNO_3	>100	>100	58.2	>100	0.1
HCl	<0.05	<0.05	<0.05	<0.05	0.6
H_2SO_4	<0.01	<0.01	<0.01	<0.01	0.5

Good REEs extraction in HNO_3 media (not suitable for HCl, H_2SO_4)

P extraction in HCl, H_2SO_4 media

Covas

C923

	Fe	Cu	La	Ce	Nd	Dy
HNO_3	<0.01	<0.01	19.9	50.5	46.5	51.0
HCl	7.6	<0.01	<0.01	<0.01	<0.01	0.0
H_2SO_4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
D stripping 4 M HCl						
HNO_3			7.4	2.9	1.4	0.6
HCl	<0.01					
D stripping 4 M HNO_3						
HNO_3			9.5	2.7	1.4	0.2
HCl	0.5					

Good REEs extraction in HNO_3 media;

Not suitable for HCl, H_2SO_4 media

Possible co-extraction of Fe (time dependent);

Selective stripping possible

Screening of Acidic extractants (DEHPA, Cyanex 572

- Good selectivity, that allows for individual REEs separation
- Require pH control

- Adjustment of pH was problematic for the *New Kankberg* feed (precipitation even at low pH, 0.5-1, especially in H_2SO_4 media)

- The *Covas* feed is more stable and the pH can be increased >1

1 M DEHPA (30 min)

New Kankberg

	pH eq	Ce	Nd	La	Dy	P
HNO_3	0.8	47.0	61.6	21.1	>100	<0.01
HCl	0.74	15.0	22.9	5.2	>100	<0.01
H_2SO_4	precipitation issues					

Extraction works from all media, but it is best in HNO_3

pH control can be a problem, especially in H_2SO_4 media (precipitation)

P was not extracted

Covas

	pH eq	Fe	Cu	La	Ce	Nd	Dy
HNO_3	0.88	56.2	<0.01	0.2	0.6	1.0	>100
HCl	0.4	4.5	<0.01	0.1	0.2	0.4	47.6
H_2SO_4	0.77	5.7	<0.01	0.2	0.2	0.2	75.3
D stripping HCl							
HNO_3		<0.01		2.5	>100	>100	0.4
HCl		<0.01		1.2	>100	>100	0.7
H_2SO_4		<0.01			2.9	13.3	0.4

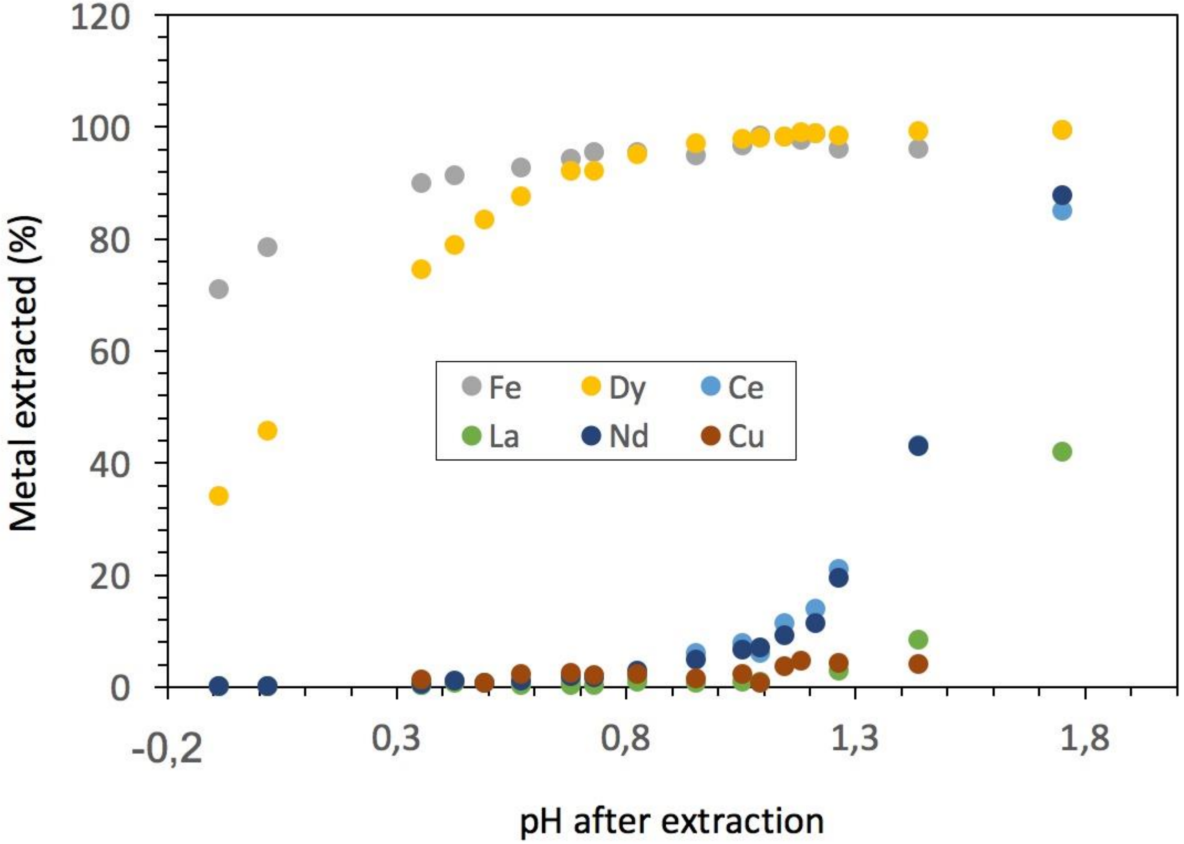
Fe is co-extracted in all cases

Selective stripping of REEs from Fe with diluted HCl

Extraction from H_2SO_4 media possible

H_2SO_4 *Covas* feed/ 1 M DEHPA: pH dependency

- pH_{in} = 0. The pH was increased with NaOH;
- Fe co-extracts even at low pH;
- Copper was not significantly extracted;
- Good extraction selectivity between HREEs and LREEs;
- HREEs (Dy) can be selectively extracted at low pH, together with Fe. No addition of NaOH is needed for this;
- Further recovery of the other REEs requires pH > 1;
- Poor Ce/ Nd selectivity.

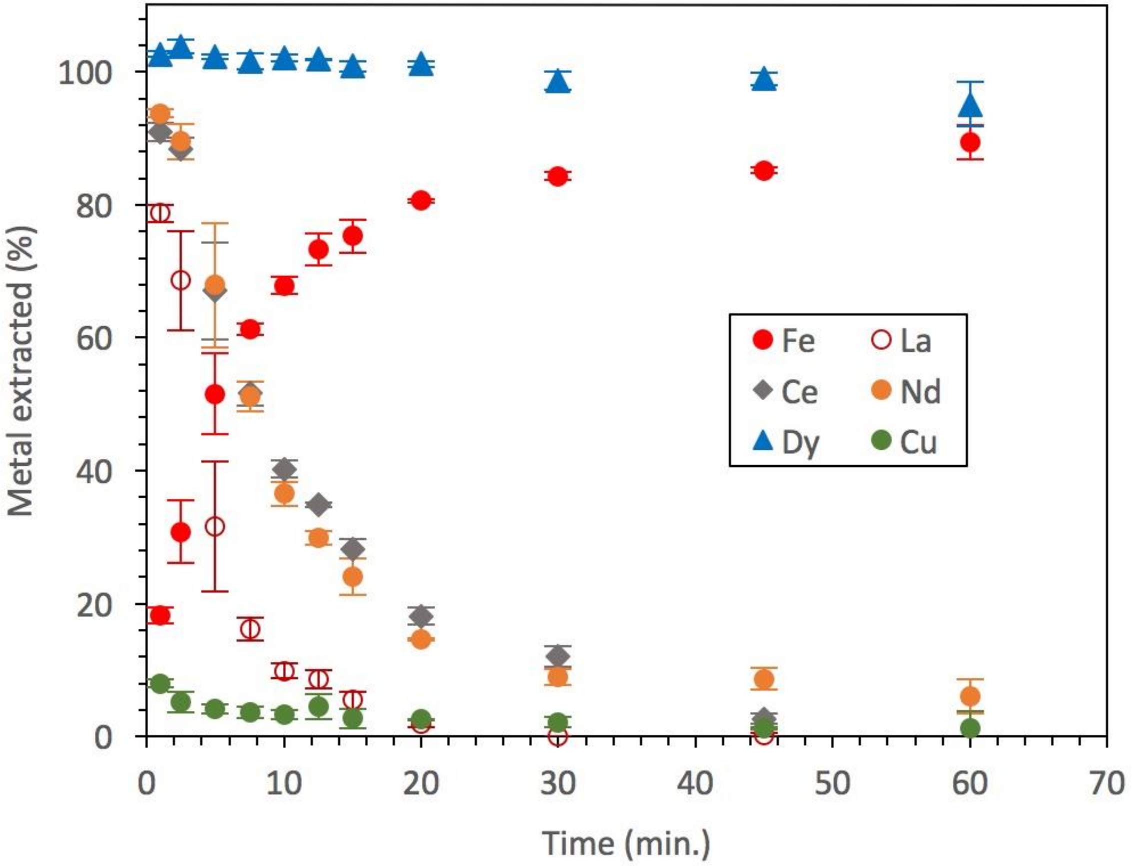


Distribution ratios as a function of pH after extraction of the Covas feed (sulfuric acid media) with 1 M DEHPA in Solvent 70. Conditions: O:A 1:1, 30 min. at 1500 vpm, 21 °C.

H_2SO_4 *Covas* feed/ 1 M DEHPA: kinetics

- Partially neutralized feed (pH 1.65);
- Fe is slowly extracted over time (90 % in 1 h);
- The aqueous pH changes during uptake of iron (liberation of H^+ from the extractant). This affects D_{REEs};
- As iron continues to extract, the pH goes down and the LREEs are back-extracted (their extraction is favored at higher pH);
- A short contact time between the two phases is recommended (lower D_{Fe} and higher D_{REEs}).

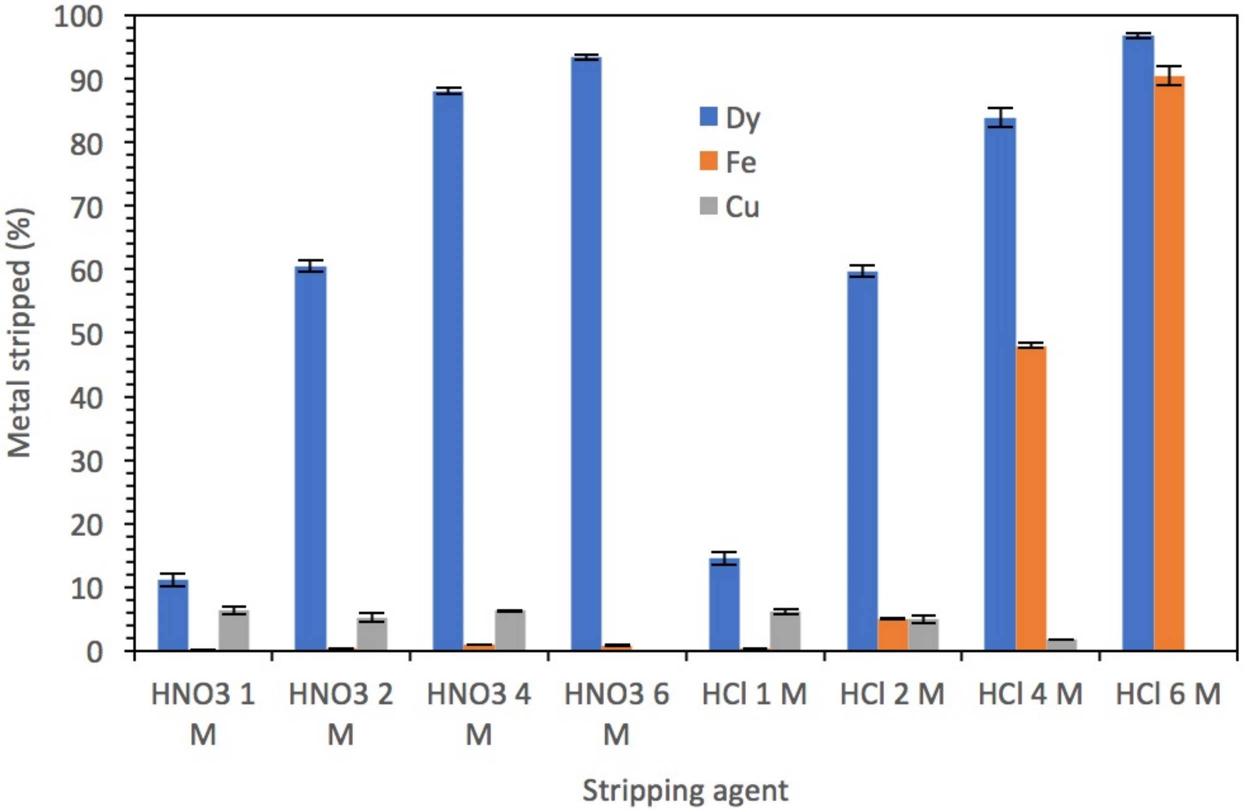
$$M^{3+}{}_{(aq)} + 3\,(HA)_{2\,(org)} \leftrightarrow M(HA_2)_{3\,(org)} + 3\,H^+{}_{(aq)}$$



Distribution ratios as a function of time for the extraction of Covas feed (sulfuric acid, initial pH 1.65) with 1 M DEHPA in Solvent 70. Conditions: O:A 1:1, 1500 vpm, 21 °C. Calculations using mass balance, triplicate test.

Selective stripping

- Aqueous feed (pH 1.65) + 1 M DEHPA (1 min shaking, 7 min phase disengagement). pH_{after} 1.15;
- Stripping of the resulting organic phase was investigated with HNO_3, HCl, and 0.5 M citric acid;
- Poor stripping with citric acid;
- Fe was not striped in significant amounts with HNO_3 or with low concentrated HCl.



Stripping of dysprosium and impurities after the extraction of Covas feed (sulfuric acid, initial pH 1.65) with 1 M DEHPA in Solvent 70. Conditions: O:A 1:1, 1500 vpm, 21 °C. Copper data for the 6 M systems not included. Calculations using mass balance, triplicate test .

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Conclusions

- REEs still have the highest supply risk among raw materials needed by the EU.

- Tailings and by-products from previous mining activities can be a source of critical raw materials, REEs included.

  - Tailings from sulphide flotation, New Kankberg (Sweden) – REEs, P
  - Tailings from W mining, Covas (Portugal) – REEs, W

- Hydrometallurgy (leaching and solvent extraction) can be employed to recover critical raw materials.

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Conclusions

- Extraction behavior of metal ions with DEHPA was governed by phase contact time and pH;
- A low contact time between the phases is recommended to minimize Fe co-extraction and get higher D_{REEs};
- Selective extraction of Dy and Fe can be carried out at low pH, then selectively stripped with nitric acid;
- Subsequent processing of the resulting aqueous solution, after pH increase, can lead to the recovery of the other REEs.

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