RECOVERY OF RARE EARTH ELEMENTS AND SCANDIUM FROM EUROPEAN DEPOSITS BY SOLVENT EXTRACTION

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OUTLINE

- Introduction of MEAB Company
- Aim of EC funded EURARE Project:

  Duty of MEAB: Initial lab. tests and construction/operation of a flexible mini-pilot SX plant for separation/purification of REE's
- Result and Discussion
  - REE Carbonates
  - Proposed Flowsheet
  - Laboratory Test
  - Demonstration Scale
- Conclusions

MEAB Chemie Technik GmbH

- German consulting and trading company founded in 1999.
- Active in the hydrometallurgical field especially in SX.

Experience:

- Conduct Lab. Tests and Pilot Scale SX Operations
- Support chemical and technical information
- Provide necessary process engineering and complete equipments list for customers

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MEAB Chemie Technik GmbH - Networking

- Chemical And Metallurgical RTD — RWTH AACHEN UNIVERSITY
- Mineral Processing — mbe — MBE COAL & MINERALS TECHNOLOGY GMBH
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- Bio-leaching — brgm — Géosciences pour une Terre durable
- Solid-liquid Separation — ANDRITZ
- Solvent Extraction, Ion Exchange And Chemical Precipitation — MEAB www.meab-mx.com
- Evaporation, Crystallization, Stripping — GEA Kestner

INTRODUCTION

- The need for REEs in the market is growing due to lots of potential applications.

- Owing to chemical similarities of REE’s, individual seperation of REE’s are quite complicated.

- For industrial Scale, SX is advantageous for selective seperation and concentration of REE’s.

- Europe has significant REE’s resources and historically most of the REE’s were discovered in Scandinavia.

- Recently new deposits were discovered especially in Greenland, Sweden and Norway.

- To decrease the outer REE’s source dependency, new initiatives were started in EU countries.

INTRODUCTION

- To develop the REE industry in Europe, European Council started the project called EURARE.
- The main aims of this project are:
  - Mapping, characterization, technological and economic evaluation of the REE resources in Europe.
  - Developing and optimizing innovating technologies for European REE resources with minimal impact to environment.
  - Training of experts and scientists about REE production.
- **23 Academic and industrial partners from 10 EU country**

RESULTS - Sources of REEs Carbonates

The project involves ores from four different European Rare Earth resources:

- **Steenstripine from Kvanefjeld deposit in Greenland,**
- Eudialyte from Norra Kärr deposit in Sweden,
- Eudialyte from TANBREEZ project in Greenland,
- Bastnasite from Rødberg ore in Norway.

The ore from Kvanefjeld deposit in Greenland was pre-concentrated in the form of REE carbonates and delivered to MEAB for separation and recovery by SX.

RESPONSIBILITY of MEAB

- Selection of reagents for SX,
- Investigation of SX parameters (e.g. Distribution coefficient, extraction rate, selectivity),
- Determination of scrubbing and stripping liquors and conditions,
- Determination of Equilibrium curves for extraction and stripping,
- Novel flowsheet development,
- Scaling up the laboratory tests as a demonstration plant,
- Operation and optimization of a continuous solvent extraction process,

RESULTS - LAB TESTS

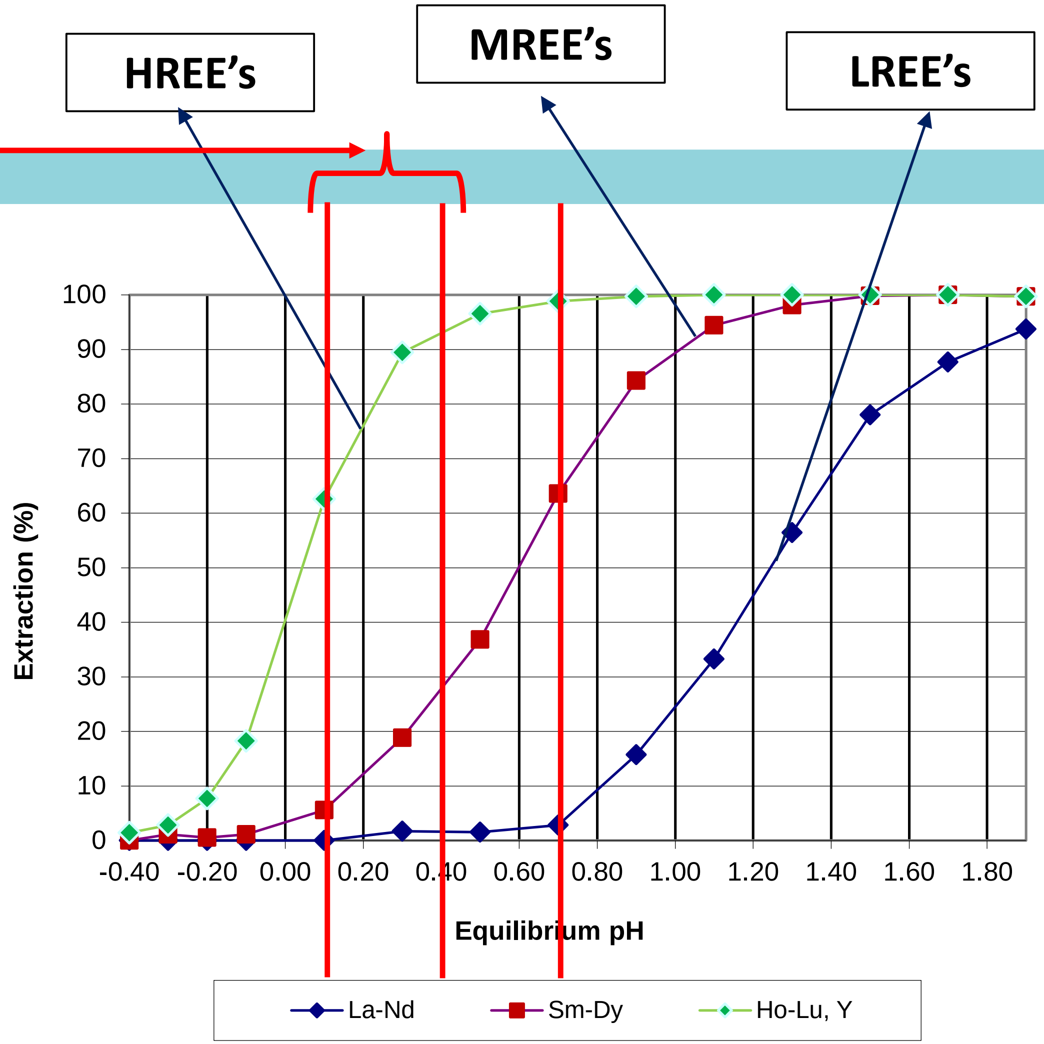
- The extraction of REEs are dependent on the hydrogen ion concentration so it is controlled by pH.

$REE^{3+} + 3\ HR \longrightarrow [REE * R_3] + 3\ H^+$

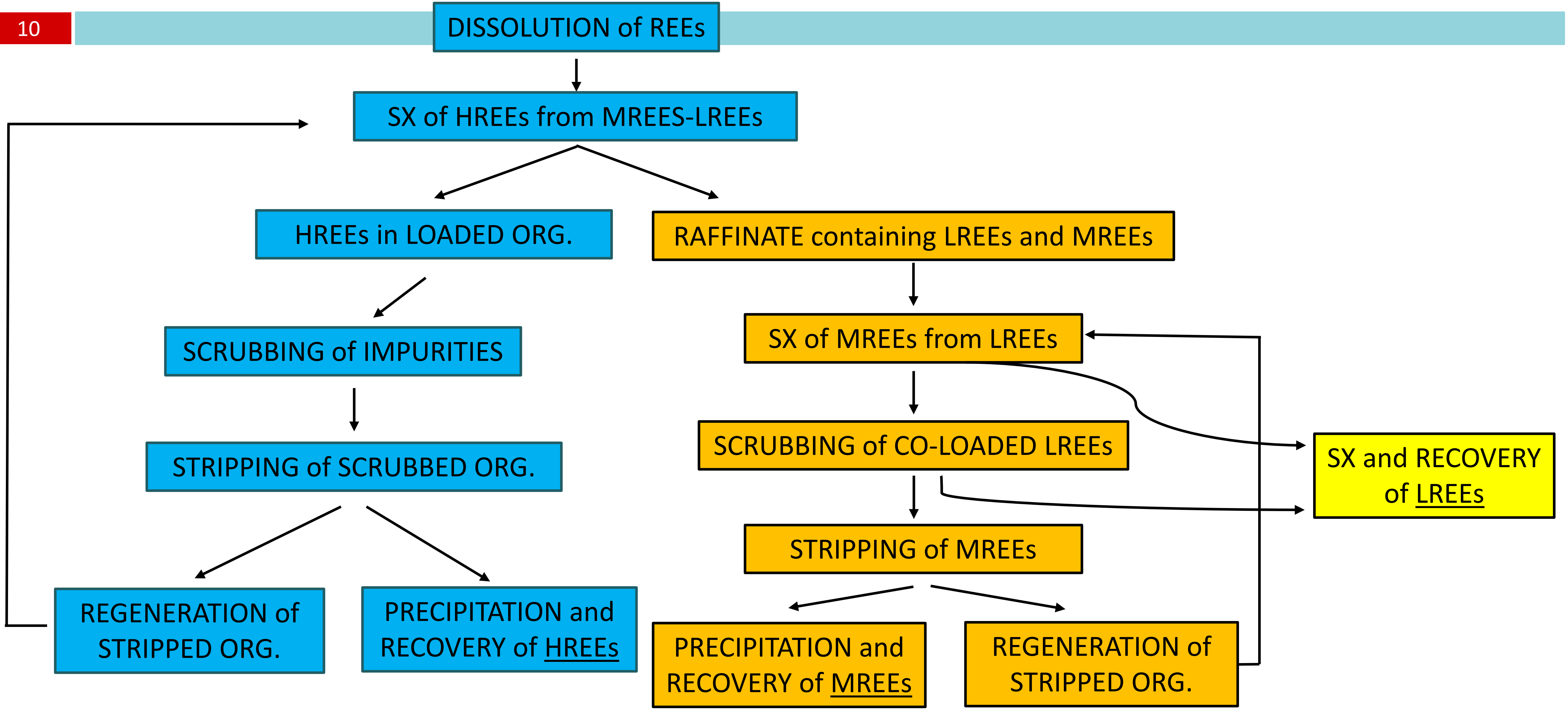
- pH isotherms obtained in lab experiments by Ionquest 801 diluted in aliphatic kerosene (Ketrul D85) with no modifier.

- pH between 0.1 and 0.4 is the best for the separation of HREEs from LREEs and MREEs.

- pH 0.7 is the best for the separation of MREEs from LREEs.



GENERAL PROCESS FLOW DIAGRAM



RESULTS - LAB TESTS

Composition of PLS in Chloride Media (g/L)

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
32	56	6.4	19	2.7	0.2	1.6	<0.1	1.7	0.2	0.5	<0.1	0.2	0.02	8.7

- The extraction of REEs from chloride media using 40 vol.-% Ionquest 801 was investigated btw pH 0.1 to pH 1.0.

- pH between 0.1 and 0.4 is the best for the separation of HREEs from LREEs and MREEs.

pH	La (LREE's)	Ce (LREE's)	Pr (LREE's)	Nd (LREE's)	Sm (MREE's)	Eu (MREE's)	Gd (MREE's)	Tb (MREE's)	Dy (MREE's)	Ho (HREE's)	Er (HREE's)	Tm (HREE's)	Yb (HREE's)	Lu (HREE's)	Y (HREE's)
0.1	0.1	0.4	0.7	1.1	4.3	7.3	11	19	36	73	68	75	32	88	52
0.4	0.2	0.4	1.0	1.5	6.0	11	15	20	40	88	75	79	49	95	72
1.0	0.9	6.4	15	20	51	66	66	40	51	89	84	98	98	98	79

Extraction behaviour of the REEs by changing pH:

RESULTS - LAB TESTS

- The extraction behaviour of LREEs and MREEs in a narrower pH range from synthetically prepared solution using 40 vol.-% Ionquest 801 was investigated further between pH 0.6 to pH 1.1.
- Co-extraction of LREEs starts to increase tramendously by increasing the pH from 0.6 to 0.8.

	LREE's				MREE's		
pH	La	Ce	Pr	Nd	Sm	Eu	Gd
0.6	1.5	8.0	8.1	17	53	50	49
0.8	2.7	15	16	31	64	56	53
1.1	3.7	22	22	41	69	57	54

Extraction behaviour of LREEs and MRREs by changing pH

RESULTS – DEMONSTRATION SCALE

To confirm the laboratory batch results, a mixer-settler demonstration plant was operated in a continuous mode:

- Active mixer volume: 0.12 l
- Active settler volume: 0.48 l
- Active settler loading surface: 0.006 m^2
- Total capacity (aq + org + rec) at 1.5 m/h surface loading: 10 l/h
- A modified McCabe-Thiele construction based on the batch experiment equilibrium data was used to determinate the number of mixer settler stages required in the demonstration plant.

RESULTS – DEMONSTRATION SCALE - HREEs

- **Section 1: HREE Separation.** Extraction of HREE from LREE and MREE using di(ethylhexyl)phosphonic acid (Ionquest 801) in kerosene (D85) at pH 0.4
- **Section 2: MREE+LREE Removal.** Scrubbing of LREE and MREE from the loaded organic by using 1.5 M HCl
- **Section 3: HREE Recovery.** Stripping of HREE from the scrubbed organic solution by using 4-5 M HCl.

  Precipitation of the resulting HREE from the strip solution by using sodium carbonate

RESULTS – DEMONSTRATION SCALE - HREEs

Extraction Stage

Extractant: 40 vol.% Ionquest 801
Diluent: Kerosene (D85)
Stages: 4,
pH: 0.4
Scrubbing: 1.5 M HCl
Stages: 6
Stripping: 4-5 M HCl
Stages: 5+1

Metal	Aqueous feed (g/L)	Raffinate (g/L)	Extraction efficiency (%)
Dysprosium	0.73	0.020	98
Holmium	0.07	0.006	92
Erbium	0.24	0.019	92
Ytterbium	0.12	0.001	99
Yttrium	4.40	0.008	>99
HRE (Dy - Yb, Y)			96

Strip Solution (g/l)

La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Y
<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	4.5	0.9	2.2	0.7	38

LREE's MREE's HREE's

Raffinate (g/l)

La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Y
15.2	25.6	5.9	8.7	0.8	0.07	0.04	0.02	0.006	0.030	0.001	0.008

RESULTS – DEMONSTRATION SCALE - MREEs

- **Section 1: MREE Separation.** Extraction of MREE from LREE by using di(ethylhexyl)phosphonic acid (Ionquest 801) in kerosene (D85) at pH 0.7

- **Section 2: LREE Removal.** Scrubbing of LREE from the loaded organic by using 1M HCl

- **Section 3: MREE Recovery.** Stripping of MREE from the scrubbed organic solution by using 3-4 M HCl

RESULTS – DEMONSTRATION SCALE - MREEs

Extraction Stage

Extractant: 40 vol.% Ionquest 801
Diluent: Kerosene (D85)
Stages: 6,
pH: 0.7
Scrubbing: 1.0 M HCl
Stages: 6
Stripping: 3-4 M HCl
Stages: 5

Metal	Aqueous feed (g/L)	Raffinate (g/L)	Extraction efficiency (%)
Samarium	0.80	0.010	90
Europium	0.07	0.011	95
Gadolinium	0.40	<0.002	>99
Dysprosium	0.02	<0.002	>99
MREE (Sm-Dy)			96

Strip Solution (g/l)

La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Y
<0.05	0.5	0.6	5.0	7.1	0.7	4.0	0.2	<0.01	<0.01	<0.01	<0.01

LREE's **MREE's** **HREE's**

Raffinate (g/l)

La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Y
15.0	24.9	5.5	8.3	0.010	<0.005	<0.002	<0.002	<0.001	<0.001	<0.001	<0.001

CONCLUSIONS

- Separation of Heavy, Medium and Light REEs resulting from Kvanefjeld Rare Earths carbonate feed stock was investigated by MEAB.

Lab. tests and continuous extraction demonstration tests showed that;

- More than 95 % of the heavy REEs and Y were extracted in 4 stages at pH 0.4.
- More than 99 % of the co-extracted light and medium REEs were scrubbed by 1.5 M HCl in 6 stages.
- Heavy REEs and Y were stripped from the scrubbed organic by 4-5 M HCl in 5+1 stages.

- More than 90 % of the medium REEs were extracted in 6 stages at pH 0.7.
- More than 90 % of the co-extracted light REEs were scrubbed by 1.0 M HCl in 6 stages.
- Medium REEs and Dy were stripped from the scrubbed organic by 3-4 M HCl in 5 stages.

CONCLUSIONS

Lab. and continuous extraction demo. tests using MEAB's MSU-0.5 mixer-settler equipment showed that; almost all heavy and medium REEs were extracted in a multi stage mixer settler arrangement by using the same organic extractant only by operating at different pH values in order to separate the REEs generated from European deposits.

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