Extraction and separation of Rare Earths

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Rare Earths Systems
1. Solvent extraction is the only industrial technology for RE separation
2. Raw materials processing
3. Basics of Solvent Extraction
   • chemistry
   • technology
4. Examples of process flow sheet
5. Conclusions & Prospects
Separations: a key step in the value chain

Mining Operators
- Ore Beneficiation
- Mine Concentrates

Separations
- Ore attack
- Rare Earths mix concentrate
- Salts & Oxides Specialties
- Metals & Alloys

Rare Earths Producers
- Ore attack
- Rare Earths mix concentrate
- Salts & Oxides Specialties
- Metals & Alloys

Rare earths users
- oil refining catalysts
- depollution catalysts
- phosphors
- glass and polishing
- ceramics and others
- magnets
- special alloys

End Users Markets
(cars, electronics, computers, lighting, glass, medical, energy, nuclear, communications, ...)

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Rare Earths are difficult to separate

- **Electronic structure**: $4f^{0-14} 5d^1 6s^2 \rightarrow$ Very similar chemical properties
  \[ \rightarrow \text{Physical properties} > \text{numerous applications} \]

- **Ionic radius**
  - Monotonic evolution from $\text{La}^{3+}$ to $\text{Lu}^{3+}$
    \[ r_{\text{La}^{3+}} = 1.16 \text{Å} \rightarrow r_{\text{Lu}^{3+}} = 0.7 \text{Å} \]
  - The regular variation of $\text{Ln}^{3+}$ ionic radii makes the separation between two ions very difficult and only possible by complexation.
  - **Exception for $\text{Ce}^{4+}$ and $\text{Eu}^{2+}$**
    - Proximity with uranides and alkaline earths beneficial for their separation
Since 1965-1970 solvent extraction is the only industrial technology for RE separation

Global production of Rare Earths (tpa REO)

- China (bastnaesite+ionics)
- USA (bastnaesite Molycorp)
- Others (incl. Monazite Solvay)

Solvent extraction

Fractionated crystallization
Selective precipitation (Ce)
Ion-exchange resins

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Where are the RE separation plants located today

For a global production of # 130.000 T/year REO
AGENDA

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   • chemistry
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## Raw materials
### Four main ore types are processed for RE production

#### Classical raw materials

<table>
<thead>
<tr>
<th>Monazite</th>
<th>Xenotime</th>
<th>Bastnaesite</th>
<th>Bastnaesite</th>
<th>Ionic Clay</th>
<th>Loparite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>USA MontainPass</td>
<td>China (In.Mongolia) Bayan Obo</td>
<td>China Xunwu</td>
<td>Russia</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La2O3</td>
<td>23,9</td>
<td>0,4</td>
<td>32</td>
<td>23</td>
<td>30</td>
</tr>
<tr>
<td>CeO2</td>
<td>47,6</td>
<td>1,4</td>
<td>50,5</td>
<td>50</td>
<td>7</td>
</tr>
<tr>
<td>Pr6O11</td>
<td>5,2</td>
<td>0,5</td>
<td>4,2</td>
<td>6,2</td>
<td>7,5</td>
</tr>
<tr>
<td>Nd2O3</td>
<td>18,1</td>
<td>1,2</td>
<td>12</td>
<td>18,5</td>
<td>7,5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Light RE</th>
<th>Medium RE</th>
<th>Heavy RE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La2O3</td>
<td>94,7</td>
<td>5,3</td>
</tr>
<tr>
<td>CeO2</td>
<td>3,5</td>
<td>96,5</td>
</tr>
<tr>
<td>Pr6O11</td>
<td>98,7</td>
<td>1,3</td>
</tr>
<tr>
<td>Nd2O3</td>
<td>23,9</td>
<td>0,03</td>
</tr>
<tr>
<td>Sm2O3</td>
<td>47,6</td>
<td>0,09</td>
</tr>
<tr>
<td>Eu2O3</td>
<td>5,2</td>
<td>0,25</td>
</tr>
<tr>
<td>Gd2O3</td>
<td>18,1</td>
<td>0,03</td>
</tr>
<tr>
<td>Tb4O7</td>
<td>1,4</td>
<td>6,6</td>
</tr>
<tr>
<td>Dy2O3</td>
<td>0,5</td>
<td>6,1</td>
</tr>
<tr>
<td>Ho2O3</td>
<td>12</td>
<td>2,5</td>
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<tr>
<td>Er2O3</td>
<td>0,01</td>
<td>6,1</td>
</tr>
<tr>
<td>Tm2O3</td>
<td>0,01</td>
<td>9</td>
</tr>
<tr>
<td>Yb2O3</td>
<td>0,03</td>
<td>0,01</td>
</tr>
<tr>
<td>Lu2O3</td>
<td>0</td>
<td>0,8</td>
</tr>
<tr>
<td>Y2O3</td>
<td>0,76</td>
<td>64,3</td>
</tr>
</tbody>
</table>

NB Loparite (a [RE-Ca-Nb-Ti]mix-oxide) is specifically used in Russia at low level production
New RE mining projects evaluate new minerals

- Number of new projects are based on minerals showing a very complex mineralogy
- Some of them contain not only RE (i.e. Zr, Nb, Ta, U),
- These complex minerals have never been processed and require specific and new process development.

<table>
<thead>
<tr>
<th>Rare earth mineral</th>
<th>Formula</th>
<th>Type of REE</th>
<th>Existing process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bastnaesite</td>
<td>fluocarbonate CeF CO₃</td>
<td>LRE</td>
<td>Yes</td>
</tr>
<tr>
<td>Monazite</td>
<td>phosphate (Ce,Y)PO₄</td>
<td>LRE</td>
<td>Yes</td>
</tr>
<tr>
<td>Xenotime</td>
<td>phosphate YPO₄</td>
<td>HRE</td>
<td>Yes</td>
</tr>
<tr>
<td>Fergusonite</td>
<td>(Y,U,Th)[Nb,Ta,Ti]O₄</td>
<td>HRE</td>
<td>No</td>
</tr>
<tr>
<td>Eudyalite</td>
<td>Na₄(Ca,Ce)₂(Fe,Mn,Y)ZrSi₈O₂₂(OH,Cl)₂</td>
<td>HRE</td>
<td>No</td>
</tr>
</tbody>
</table>

Formulae of major minerals containing rare earths
Raw materials - issues impacting separations

- All Rare Earths raw materials contain natural radioactivity (Thorium and Uranium)

<table>
<thead>
<tr>
<th></th>
<th>bastnaesite</th>
<th>monazite</th>
<th>pyrochlore</th>
<th>xenotime</th>
<th>apatite</th>
<th>eudyalite</th>
</tr>
</thead>
<tbody>
<tr>
<td>REO contents in deposit</td>
<td>0,5%-10%</td>
<td>3%-15%</td>
<td>1%</td>
<td>0,6%-6%</td>
<td>0,6%-0,8%</td>
<td>0,90%</td>
</tr>
<tr>
<td>Thorium / REO</td>
<td>0,50%</td>
<td>0,5%-15%</td>
<td>7%</td>
<td>3%</td>
<td>2%</td>
<td>0,15%-0,3%</td>
</tr>
<tr>
<td>Uranium / REO</td>
<td></td>
<td>0,05%-0,5%</td>
<td>2%</td>
<td>0,1%-0,2%</td>
<td>0,3%-0,8%</td>
<td>0,20%</td>
</tr>
</tbody>
</table>

- Radioactivity is a relatively complex technical challenge due to the fact that separation processes make cuts in radioactive families of Thorium and Uranium. The main isotopes to consider are:
  - $^{232}$Th family: $^{232}$Th, $^{228}$Ra, $^{228}$Th
  - $^{238}$U family: $^{238}$U, $^{234}$U, $^{230}$Th, $^{226}$Ra, $^{210}$Pb
  - $^{235}$U family: $^{235}$U, $^{227}$Ac.

Radioactive isotopes groups $[^{232}$Th$]$, $[^{228}$Th$]$, $[^{230}$Th$]$ $[^{238}$U$]$, $[^{234}$U$]$, $[^{235}$U$]$, $[^{228}$Ra$]$, $[^{226}$Ra$]$, $[^{210}$Pb$]$ and $[^{227}$Ac$]$ have a complex chemistry and are split according various behaviours during separations by precipitation or SX.
Two main process routes for ore cracking

(* *) different temperatures are used

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The principal ionic clays are muscovite and kaolinite $[(\text{Al,Si})\text{O}_x(\text{OH}^-)_3, (\text{RE}^{3+})]$.

**Process route for ionic ores**

- **Mining and concentration**
  - Ore concentrate
  - Ore craking $\text{H}_2\text{SO}_4$ or NaOH
- **Non RE purification**
  - Mix RE concentrate
- **RE cation adsorption clays**
  - Ammonium sulphate leaching
  - Mix RE carbonate
- **SX separations**
- **Ion exchange leaching**
  
  $$2 [(\text{Al,Si})\text{O}_x(\text{OH}^-)_3, (\text{RE}^{3+})] + 3 [(\text{NH}_4^+)_2\text{SO}_4^2] \rightarrow 2 [(\text{Al,Si})\text{O}_x(\text{OH}^-)_3, 3\text{NH}_4^+] + 2 (\text{RE})_2\text{SO}_4_3$$

**Ion exchange leaching**

- **Heap leaching**
  - Leaching solution
- **In situ leaching**
  - Injection of leaching solution
  - Leachate

**SOLVAY**

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   • chemistry
   • technology
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Basics of Solvent Extraction (*)

- Definitions
- Solvents
- Chemistry of solvent extraction
  - Extractant classes and selectivities
  - Case of non RE$^{3+}$ (Ce$^{IV}$ and Eu$^{II}$)
- Technology and process design
- Choice of a separation system

(*) SX
Or « Liquid-Liquid Distribution » according to IUPAC
Or Liquid-Liquid Extraction
Definitions

Equilibrium  Distribution of a specie between two immiscible phases

\[ \text{RE}_{\text{aq}} + \text{S}_{\text{org}} \rightleftharpoons \text{RE S}_{\text{org}} \]

- Equilibrium Constant  \( K_{\text{TR}} = \frac{[\text{RE S}]_{\text{org}}}{[\text{RE}]_{\text{aq}} \cdot [\text{S}_{\text{org}}]} \)
- Partition Coefficient  \( P_{\text{RE}} = \frac{[\text{RE S}]_{\text{org}}}{[\text{RE}]_{\text{aq}}} \)
- Separation Factor expresses the selectivity of the system, its faculty to separate two species \( \text{RE}_1 \) et \( \text{RE}_2 \)

\[ F = \frac{P_{\text{RE}_1}}{P_{\text{RE}_2}} \]
The solvent is the heart of the process

A « solvent » is an organic mixture which includes mainly

- **an extracting agent**, active player of the system, which chemically reacts with species to be extracted. It should be insoluble in water (alkyl chains C4 to C15). EA are usually viscous liquids (some are solids).

- **a diluent**, usually a mixture of aliphatic and/or aromatic hydrocarbons, it helps hydrodynamic, acting on solubility of the extracted species and giving a lower viscosity.

Sometime are added
- a **modifier** to improve some properties (solubility, viscosity/hydrodynamic, kinetics)
- a **synergistic agent** (or anti-synergistic) which modifies partition coefficients and/or selectivity.
The chemistry of Rare Earths extraction
3 classes of extracting agents

In hydrometallurgy it is convenient to consider 3 types of distribution systems (*). A large number of extractants are available for Rare Earths among the products especially designed for metal separation and purification purpose.

- **extraction by compound formation**
  Acidic and chelating extractants = cation exchangers
  \[
  \text{RE}^{3+} + 3(\text{HA})_{\text{org}} \rightleftharpoons (\text{REA}_3)_{\text{org}} + 3\text{H}^+ 
  \]

- **extraction by solvation**
  Neutral extractants = molecules exchangers
  \[
  \text{RE}^{3+} + 3\text{NO}_3^- + (\text{S})_{\text{org}} \rightleftharpoons (\text{S},\text{RE(NO}_3)_3)_{\text{org}} 
  \]

- **extraction by ion-pair formation**
  Basic extractants = anion exchangers
  \[
  \text{RE}^{3+} + 3\text{NO}_3^- + (\text{B}^+\text{NO}_3^-)_{\text{org}} \rightleftharpoons (\text{B}^+,\text{RE(NO}_3)_4^-)_{\text{org}} 
  \]

- For all of them the exchange equilibrium for 2 REE characterizes the selectivity
  \[
  \text{RE}_1 + \text{RE}_2_{\text{org}} \rightleftharpoons \text{RE}_2^+ \text{RE}_1^+_{\text{org}} 
  \]
  (separation factor \( F_{1/2} = k_{\text{TR}1}/k_{\text{TR}2} \))

(*) Y. Marcus

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1- Acidity extractants / cationic exchangers

- Strongly acidic
  - Alkylphosphoric derivatives

HDEHP, DEHPA, P204
- BIS(2-ethylhexyl) hydrogen phosphate
- PHOSPHORIC ACID BIS(2-ETHYLHEXYL)ESTER
  \[ C_{16}H_{35}O_4P \]

HEHEHP, HEHEHPA, PC88A, P507, Ionquest 801
- 2-ethylhexyl hydrogen-2-ethylhexyl phosphonate
- PHOSPHONIC ACID (2-ETHYLHEXYL)-MONO(2-ETHLHEXYL)ESTER
  \[ C_{16}H_{35}O_3P \]

Cyanex 272, P229
DI-ISOOCTYLPHOSPHINIC ACID
  \[ C_{16}H_{35}O_2P \]
Ionquest 290
BIS (2,4,4-TRIMETHYL-PENTYL) PHOSPHINIC ACID
1- Acidic extractants / cationic exchangers

**Weakly acidic**

- **Carboxylic acids**  \( R-(C=O)-O-H \)
  
  - Versatic acids
    - \( R_1+R_2=C7, \text{versatic 10} \)
    - \( R_1+R_2=C6-C8, \text{versatic 911} \)
  
  - Naphtenic acids
    - \( R_1-R_4= \text{alkyl} \)
    - Ex: NOR 180

- **Chelating extractants** which have been developed for hydrometallurgy show no real interest for RE separations
  
  - Oxime series i.e. LIX 860
    - 5-dodecyl-2-hydroxybenzaldehyde oxime
  
  - Kelex 100
    - 7-(4-ethyl-1-methylocty)-8-hydroxyquinoline
  
  - \( \beta \)-diketone LIX 54

**CA-100**
- Sec-Nonylphenoxyacetic acid
- \( C_{17}H_{26}O_3 \)
- M 278.39

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1- Extraction by acidic extractants

The general reaction is

\[ \text{RE}^{3+} + 3 \text{(HL)}_{\text{org}} \rightleftharpoons (\text{RE} \text{L}_3)_{\text{org}} + 3 \text{H}^+ \quad (k_{\text{RE}}) \]

1) Alkylphosphoric acids \((R^*)(R^*)(P=O)O-H\)

- **Strong extractants and associated in organic diluant in a dimeric form**

\[
\begin{align*}
R^* & \quad \text{P} & \quad \text{O} & \quad \cdots \cdot \quad \text{H} \quad \cdots \cdot \quad \text{O} & \quad \text{P} & \quad \text{<} & \quad R^* \\
\text{O-H} & \quad \cdots \cdot & \quad \text{O} & & & & \\
\end{align*}
\]

> only 1 H\(^+\) can be exchanged by a dimer

\[(H_2L_2)_{\text{org}} \rightleftharpoons (HL)_2_{\text{org}} + \text{H}^+\]

- **Extract RE in acidic medium**

\(P_{\text{RE}}\) is strongly dependent on acidity of the aqueous phase.

With the less acidic extractants a saponification is required to extract REE

\[ \text{RE}^{3+} + 3\text{OH}^- + 3 \text{(HL)}_{\text{org}} \rightleftharpoons (\text{RE} \text{L}_3)_{\text{org}} + 3 \text{H}_2\text{O} \]

- **Extraction mechanism varies with diluent (for HDEHP)**

  - aromatic

\[ \text{RE}^{3+} + 3 (H_2L_2)_{\text{org}} \rightleftharpoons [\text{RE} (HL_2)_3]_{\text{org}} + 3 \text{H}^+ \]

\[k_{\text{RE}} = P_{\text{RE}} [\text{H}^+]^3/[H_2L_2]^3\]

  - aliphatic

\[ \text{RE}^{3+} + 2.5 (H_2L_2)_{\text{org}} \rightleftharpoons [\text{RE} \text{L(HL}_2)_2]_{\text{org}} + 3 \text{H}^+ \]

\[k_{\text{RE}} = P_{\text{RE}} [\text{H}^+]^3/[H_2L_2]^{2.5}\]

and equilibrium constant \(k_{\text{RE}}\) is linked to the dielectric constant of the diluent, \(k_{\text{RE}}\) decreases when \(\varepsilon\) increases (\(k_{\text{RE}}\) kerosene > \(k_{\text{RE}}\) cyclohexan > \(k_{\text{RE}}\) benzene > \(k_{\text{RE}}\) chloroform)

- **Polymerisation of extracted species** occurs for concentrated solutions and can generate some gel formation which gives limitations in use.
1- Extraction by acidic extractants

2) carboxylic acids \( R(C=O)O-H \)

Extraction reactions are similar to that of strongly acidic extractants

- **They are associated in a dimer form** (but all \( H^+ \) can be exchanged)
  \[
  \text{RE}^{3+} + \frac{3}{2}(H_2L_2)_{org} \rightleftharpoons [\text{RE}L_3]_{org} + 3 \, H^+ 
  \]

- Much less acidic than phosphorous acidic extractants they extract in neutral aqueous solutions
  - Versatic extracts RE in pH 4-6 range.
  - Naphtenic have been widely used but the composition of the extractant is often not stable
  - CA-100 extracts at lower pH value than Versatic.

- Extracted species are often solvated by extractant molecules \( (REL_3\times HL) \), concentrated organic solutions are viscous and can generate some gel formation especially with HRE.

- **Low cost extractants** but some losses by solubility and high viscosity with HRE.
1- Extraction by acidic extractants

- The extraction power depends on the acidity of the extractant

  alkylphosphoric > alkylphosphonic > alkylphosphinic >>> carboxylic acids

  \[(RO)_2PO-OH\] > \[(RO)RPO-OH\] > \[R_2PO-OH\] > \[R(CO)OH\]

- Alkyl-phosphoric are the stronger extractants but more difficult to back-extract (increasing reactant costs in processes).

Comparative extraction power for acidic extractants

- Extraction by acidic extractants

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1- Extraction by acidic extractants - Selectivity

- **Alkylphosphoric acids**
  - Extraction increases with the atomic number of REE.
  - Y is between Ho and Er (F_Y/Ho #2) in accordance with its atomic number.
  - Among SX extractants they have the highest selectivity for the RE family.
  - Extented scale is 10^5-10^6 units and the mean separation factor is #2,4-3.
  - Anions and diluents have a very limited impact on selectivity.

HEHEHP is a bit more selective than HDEHP. Its main advantage comes from its lower extraction constant for REE

\[ \Delta pK_{E\#} = 2\pm0.5 \]
Carboxylic acids

The selectivity of is rather low (extended scale <20) and HRE are at the same level with no possible separation.

But Y shows a special behavior being moved towards LRE. This behavior has been used for some process design.

With CA-100 Y is with HRE.

For Yttrium production Naphtenic and Versatic are used in separation schemes.
1- Selectivity of acidic extractants towards non-REE

Important to consider for
- purification of RE against impurities of the raw materials (i.e. ores)
- recovery of RE in recycling processes (end-of-life products or scraps).

Table from Marcus & Kertes
Ion Exchange & solvent Extraction of Metal Complexes 1969

Extraction of various cations by HDEHP 50% in toluene in HCl medium

<table>
<thead>
<tr>
<th>Metal</th>
<th>HCl (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
</tr>
</tbody>
</table>

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2- Neutral extractants / molecular extractants

- **Phosphorous derivatives**
  - TBP
    - Tri-n butyl phosphate
    - $C_{12}H_{27}O_4P$
  - DBBP
    - Dibutyl butyl phosphonate
    - $C_{12}H_{27}O_3P$
  - TOPO, Cyanex 921
    - Trioctylphosphine oxide (solid)
    - $C_{24}H_{51}OP$
  - Cyanex 923 & 925
    - Liquid mixture of four trialkylphosphine oxides

They extract RE nitrate – no or limited extraction of RE chloride or sulfate

- **Others**
  - Ethers R-O
  - Alcohols R-OH
  - Ketones R-(C=O)-R
  - i.e. isopropylether
  - i.e. isobutanol
  - i.e. MIBK

Increasing acidity
2- Extraction by neutral extractant - TBP

The most important is TBP which extracts RE nitrate salts

$$TR^{3+} + 3 NO_3^- + 3 (TBP)_{org} \rightleftharpoons ((TBP)_3, TR(NO_3)_3)_{org}$$

- Partition coefficients are highly dependant of nitrate concentration
  $$P_{TR} = k_{TR} \cdot [NO_3^-]^3 \cdot [TBP]^3.$$ 
- Extraction can be increased by a salting out effect with non-extracted salts (i.e. Na or NH$_4$ nitrate).
- HNO$_3$ is extracted and decreases partition coefficients.
- Back-extraction is achieved by water.

![Graph 1: PCe function of NH$_4$NO$_3$ (M)](image1)

- Ce$_{aq}$ 0.35 mol.l$^{-1}$
- TBP 60-kerosene 40 vol%

![Graph 2: PCe function of HNO$_3$ (M)](image2)

- Ce$_{aq}$ 1.7 mol.l$^{-1}$
- TBP 75-kerosene 25 vol%
2- Extraction by neutral extractant - TBP selectivity

- **TBP selectivity** is relatively low and highly influenced by RE concentration in aqueous phase
  - LRE selectivity increases with the REO concentration
  - Y moves towards LRE when REO decreases
  - for HRE poor selectivity

Separation factors with aqueous conc. of RE nitrates
(TBP 50 vol% in Shellsol A)

Variation of the selectivity with aqueous conc. of RE nitrates
(TBP 50 vol% in Shellsol A)
2-Selectivity of neutral extractants towards non-REE

Tables from Marcus & Kertes in Ion Exchange & solvent Extraction of Metal Complexes 1969

Partition coefficient

Undiluted TBP in HNO₃ medium

Partition coefficient

Undiluted TBP in HCl medium

Extraction and separation of Rare Earths
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3- Basic extractants / anion exchangers

- Alkylamines
  - Primary amines
    - PRIMENE™ JM-T
      (C16-22)-terC –alkyl amine
    - N1923
      SecC-alkyl amine
      R₂CNH₃R
  - Quaternary ammonium salts
    - ALIQUAT 336, ADOGEN 464
      Tricaprylmethylammonium chloride
      CH₃N[(CH₂)₇CH₃]₃Cl

- Primary amines extract RE sulphate
- Quaternary ammonium salts extract RE nitrate or RE thiocyanate
- No extraction occurs in chloride medium
3- Extraction by basic extractants - Amines

1) Primary amines

They extract RE sulphates, but no extraction occurs in chlorure or nitrate solution

\[
\begin{align*}
H_2SO_4 + 2 (RNH_2)_org & \rightleftharpoons (RNH_3)_2(SO_4)_org \\
2 RE^{3+} + 3 SO_4^{2-} & \rightleftharpoons 2 RE(SO_4)_3^{3-}
\end{align*}
\]

\[
2 RE(SO_4)_3^{3-} + 3[(RNH_3)_2 SO_4]_org \rightleftharpoons 2[(RNH_3)_3,RE(SO_4)_3]_org + 3 SO_4^{2-}
\]

Primary amines are efficient extractant to separate Th from U and RE. They have been studied in that purpose from solutions obtained after sulfuric attack of the monazite (ORNL 1959). The selectivity between adjacent RE is rather low \((F=1,2-1,9)\) and not really large enough for separations.

Table from Marcus & Kertes in Ion Exchange & Solvent Extraction of Metal Complexes 1969

Extraction and separation of Rare Earths
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3- Extraction by basic extractants - Amines

2) Quaternary ammonium salts

- they extract RE-thiocyanates and RE-nitrates, by the simplified reaction (i.e. NO$_3^-$)

$$\text{RE}^{3+} + 3 \text{NO}_3^- + (R_4N^+NO_3^-)_{\text{org}} \leftrightarrow (R_4N^+,RE(\text{NO}_3^-)_4)_{\text{org}}$$

- anion concentration is the key parameter for partition coefficients

$$P_{\text{RE}} = k_{\text{RE}} \cdot [\text{NO}_3^-]^3 \cdot [R_4N^+NO_3^-]$$

- back-extraction is achieved by water.

Influence of ammonium nitrate on Y nitrate extraction by ALIQUAT 336
Aliquat 0.5M
Y(NO$_3$)$_3$ 0.5 mol.l$^{-1}$
Amine extraction is a complex chemistry:

- in organic phase associated species and water molecules are involved in the extraction mechanism which is slightly different for LRE and HRE
  For Aliquat 336:

  - **Light RE extraction**
    \[
    \text{RE}^{3+} (\text{H}_2\text{O})^t + 3\text{NO}_3^- + \frac{3}{2} [(\text{R}_4\text{N}^+\text{NO}_3^-)_2(\text{H}_2\text{O})_y]_{\text{org}} \Leftrightarrow [(\text{R}_4\text{N}^+)_3\text{RE}^{3+}(\text{NO}_3^-)_6,v\text{H}_2\text{O}]_{\text{org}}
    \]

  - **Heavy RE extraction**
    \[
    \text{RE}^{3+} (\text{H}_2\text{O})^v + 3\text{NO}_3^- + [(\text{R}_4\text{N}^+\text{NO}_3^-)_2(\text{H}_2\text{O})_y]_{\text{org}} \Leftrightarrow [(\text{R}_4\text{N}^+)_2\text{RE}^{3+}(\text{NO}_3^-)_5,v\text{H}_2\text{O}]_{\text{org}}
    \]

- At high concentration in organic phase, aggregation and strong association lead to polymer evolution with precipitation and/or an increase of viscosity. Adding a modifier could change these complex reactions but often decreases the extraction efficiency.
3- Extraction by basic extractants
Aliquat 336 selectivity

Characteristics for Aliquat 336

- **Medium selectivity**
  - an extended scale of # 100-150
  - F #1,4-1,5 between adjacent RE

- **Reverse evolution** in the extraction order for RE
  - in nitrate medium \( P_{\text{La}} < P_{\text{Lu}} \)
  - in thiocyanate \( P_{\text{La}} > P_{\text{Lu}} \)

- **Y has a special behavior**
  - Y # HRE in nitrate
  - Y # LRE in SCN.
The chloride medium in which the rare earths are not extracted offers possibilities for separation of non-RE elements by amine extractants.

Example: Tri-isooctylamine in HCl medium

Table from Marcus & Kertes
Ion Exchange & solvent Extraction of Metal Complexes 1969

3- Selectivity of amine extractant towards non-REE
Separation factor
\[ F_{2/1} = \frac{P_{RE2}}{P_{RE1}} \]

Yttrium shows a particular behavior - link to the ionic radius - link to the complex formation chemistry

SELECTIVITY Overall Comparison of extractants for RE
Ce⁴⁺ and Eu²⁺ can be separated by Solvent Extraction with a very high selectivity

Ce⁴⁺ can be oxidized to Ce(OH)₄, insoluble in acidic medium:

\[
\text{Ce}^4+ \rightarrow \text{Ce(OH)}_4 \quad \text{insoluble in acidic medium}
\]

i.e. oxidation by Na-hypochlorite:

\[
2 \text{Ce}^3+ + \text{ClO}^- + 6 \text{OH}^- + \text{H}_2\text{O} \rightarrow 2 \text{Ce(OH)}_4 \downarrow + \text{Cl}^-
\]

Extraction is very efficient with acidic (alkyl phosphorous acids, carboxylic) or neutral extractants:

- In nitrate medium TBP gives a separation factor \( F(\text{Ce}^4+/\text{RE}^3+) > 10^5 \)

\[
\text{Ce}^4+ + 4 \text{NO}_3^- + 2 \text{TBP} \Leftrightarrow \text{Ce(NO}_3)_4 \text{(TBP)}_2
\]

The main issue is the back-extraction which necessarily requires a reducing agent (NaNO₂, formol, NaCl, méthanol, H₂O₂, Fe²⁺, hydroxylamine, hydrazine have been proposed)

Eu²⁺ can be reduced to Eu³⁺:

\[
\text{Eu}^3+ + e^- \rightarrow \text{Eu}^2+
\]

i.e. reduction by Zn:

\[
2 \text{Eu}^3+ + \text{Zn}^0 \rightarrow 2 \text{Eu}^2+ + \text{Zn}^{2+}
\]

and selective precipitation of EuSO₄.

Extraction of RE³⁺ vs Eu²⁺ is very selective with acidic extractants:

\[
F(\text{Sm}^3+/\text{Eu}^2+) > 10^6 \quad \text{with HDEHP or HEHEHP.}
\]
AGENDA

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**Equilibrium**  Distribution of a specie between two immiscible phases

\[ \text{RE}_{aq} + S_{org} \Leftrightarrow \text{RE} S_{org} \]

- Equilibrium Constant
  \[ K_{TR} = \frac{[\text{RE} S]_{org}}{[\text{RE}]_{aq} \cdot [S_{org}]} \]

- Partition Coefficient
  \[ P_{RE} = \frac{[\text{RE} S]_{org}}{[\text{RE}]_{aq}} \]

- Separation Factor
  \[ F_{1/2} = P_{RE1}/P_{RE2} \]

**Distribution** or Partition curve or partition isotherm
- different shapes
- \( P \) varies with concentration in aqueous phase
- maximum loading of organic phase

![Diagram](attachment:image.png)
McCabe & Thiele construction (principles)

**Extraction 1 stage**

**Counter-current Extraction 3 stages**

**Washing 2 stages**

**Back-extraction 4 stages**

---

Extraction and separation of Rare Earths
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**McCabe & Thiele construction for a separation battery**

*(general case)*

**Separation of two species RE$_1$>RE$_2$**

Two conditions are required to get an effective separation:

1. **extraction zone**
   - Extraction coefficient for RE$_1$ > 1
   \[ E_{RE_1} = \frac{P_{RE_1}.O}{(F+W)} > 1 \]

2. **washing or scrubbing zone**
   - Washing coefficient for RE$_2$ > 1
   \[ S_{RE_2} = \frac{1}{E_{RE_2}} = \frac{1}{(1/P_{RE_2}).W/O} > 1 \]
For Rare Earths separations the reaction is an exchange between 2 RE

The separation factor $F_{1/2} = \frac{k_{TR1}}{k_{TR2}}$ is the equilibrium constant of the exchange reaction ($F>1$) of RE between the two phases

$$\text{RE}_1 + \text{RE}_{2\text{org}} \rightleftharpoons \text{RE}_2 + \text{RE}_{1\text{org}}$$

For a counter-current operation

In a battery with $n$ stages
For Rare Earths separations
McCabe & Thiele construction applied to molar fractions

Operating line for scrubbing zone
slope $\text{SCR} = \left(\frac{1}{P_{\text{TOTAL}}}\right) \cdot \frac{v_s}{V_{\text{solvent}}}$

Operating line for extraction zone
slope $\text{EXT} = \left(\frac{1}{P_{\text{TOTAL}}}\right) \cdot \frac{(v_s + v_{\text{Feed}})}{V_{\text{solv.}}}$
To reach high purity for individual Rare Earths 99% up to 99,999%, the total number of stages required for one cut \((n_E + n_S + n_R)\) ranges from \(~30\) up to 100.
Proprietary softwares have been developed

- To make calculation of separation
- To drive the industrial batteries

Example 1: calculation for a binary mixture Ce 90:La10
Proprietary softwares have been developed.

Example 2: Separation $La, Ce, Pr, Nd / Sm, Eu, Gd, ... Y$

Feed

<table>
<thead>
<tr>
<th>Element</th>
<th>Feed Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>25.8%</td>
</tr>
<tr>
<td>Ce</td>
<td>46.0%</td>
</tr>
<tr>
<td>Pr</td>
<td>5.5%</td>
</tr>
<tr>
<td>Nd</td>
<td>14.7%</td>
</tr>
<tr>
<td>Sm</td>
<td>1.4%</td>
</tr>
<tr>
<td>Dy</td>
<td>0.8%</td>
</tr>
<tr>
<td>Y</td>
<td>3.6%</td>
</tr>
<tr>
<td>others HRE</td>
<td>1.4%</td>
</tr>
</tbody>
</table>

EXTRACTION AND SEPARATION OF RARE EARTHS
The mixer-settler is the only industrial choice for RE separation batteries.

**Technology**

**Unit operation**

- An organic immiscible solvent is added.
- Initial aqueous solution
- Mixing
- Settling separation

**Mixer-settler**

- Mixer
- Settler
- Emulsion separation
- Motor
- Solvent outlet
- Aqueous outlet

**Counter-current battery**

- Organic feed
- Aqueous exit
- Organic exit
- Aqueous feed

**DESCRIPTION D'UN ETAGE**

**Mixer-settler**

- Initial aqueous solution
- An organic immiscible solvent is added
- Mixing
- Settling separation

**Extraction and separation of Rare Earths**

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Technology
the mixer-settler is the only industrial choice for RE separation batteries

Solvay La Rochelle
Mixer-setters are
- relatively easy to design and flexible to run in operation (high capacity, phases ratio, stop and go)
- the efficiency of each stage is close to one theoretical stage.

Main advantages
- possibility to adjust the phase ratio in the mixer using internal recycling;
- possibility to control the emulsion by the mixing power;
- a relatively high contact time between phases.

Main drawbacks
- require a large surface area to be installed,
- the hold-up of the solvent could be important,
- could be difficult to run when solids particles exist in the phases.

Mixer-Settler design
Kinetic studies are required
- mixing during extraction
- phase separation for settling
Mixer-settler: sedimentation and coalescence

**The nature of the continuous phase is a key parameter for settling**

Water-in-oil or oil-in-water emulsion type determines separation behaviour.

**Ostwald Law**
3 domains to be considered with the Aqueous/Organic ratio:
- Continuous aqueous phase is the only possible
- Continuous organic phase is the only possible
- Ambivalence domain where both systems are possible

*Remark: the continuous phase can be identified by conductivity measurement*

- Continuous organic phase
- Not determined
- Continuous aqueous phase

<table>
<thead>
<tr>
<th>A/O Ratio</th>
<th>0.33</th>
</tr>
</thead>
</table>

Sedimentation front

Organic phase dispersed = aqueous continue o/w

Coalescence front

Case density of organic phase < density of aqueous phase

Extraction and separation of Rare Earths
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**Mixer-Settler design**

**Mixer**
Batch test in standardized tank with different turbines to reach equilibrium and create emulsion characteristics

**Settler**
Continuous test on a mixer settler unit model for sizing
Variation of the height of the emulsion band $H$ with the specific flow-rate $Q/S$ of the dispersed phase.

*Example:* Ryon lines

$$\log H = \log K + n \log Q/S$$

for 2 temperatures $T_1$ & $T_2$

<table>
<thead>
<tr>
<th>$m^3$</th>
<th>small</th>
<th>medium</th>
<th>large</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixer</td>
<td>&lt; 0.1</td>
<td>0.5 - 1</td>
<td>15</td>
</tr>
<tr>
<td>Settler</td>
<td>0.3 - 0.4</td>
<td>4</td>
<td>40</td>
</tr>
</tbody>
</table>

*Extraction and separation of Rare Earths*

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AGENDA

1. Solvent extraction is the only industrial technology for RE separation
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Select an extraction process

To define an extraction process two choices are to be considered

- the solvent
- the technology

in order to reach targeted objectives

- Purity and Yield
- Environment and safety
- Economy (capital investment CAPEX and operating costs OPEX)

Purity and yield are obtained by the definition of operating conditions (stages number, flow rates and reflux) when the selection of the solvent has been made.

Moreover in the case of Rare Earths separations a certain sequence of successive cuts must be considered.
Select a extraction process
is to find an optimum economic

OPEX
- Reactants: acid, base,…salts
- Energy (steam for concentration or T° adjustment)
  - Solvents losses
  - Effluent treatment
  - Taxes on discharge streams

CAPEX
- the battery
  - number and volume of stages
  - material
  - Annex equipments linked to the solvent characteristics
- Hold-up
  - Induced equipments
  - specific effluent treatment

The type of the solvent: cation or molecules
its solubility in water and eventual dégradation
its viscosity <> temperature to improve phase separation

the solvent is the first choice which determines for a great part the economy of the process

- selectivity of the solvent
- maximum loading of the solvent
- concentration of metal ions in aqueous phase
- hydrodynamic (> volume of stages)
- corrosion > material choice

(*) both dependent on local conditions

54 Extraction and separation of Rare Earths
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There are two industrial SX process routes for RE separation:

- **Nitrate route**
  - Lower OPEX
  - Higher CAPEX
  - Nitrate liquid effluent to deal with

- **Chloride route**
  - Lower CAPEX
  - Higher OPEX
  - N or NH\(_4\) chloride liquid effluent

- Chloride route is used by Chinese producers and new comers
- *Solvay* uses both routes chloride in its two Chinese plants and nitrate in its La Rochelle plant.
What process flow sheet for the refinery?

A lot of processes are possible for RE separations according to:
- raw material (ore, concentrate, ..)
- targeted products and purity (99% to 99,999%)
  - 

Ore attack

Separation Non-RE impurities Incl. R* / TREO

Mix-RE chemical concentrate

LRE / HRE

4 RE to separate

La / Ce,Pr,Nd

Ce / Pr,Nd

Pr / Nd

Or

La, Ce,Pr / Nd

La, Ce / Pr

La / Ce

11 RE to separate

HRE Separations

Sm/Eu/Gd/Tb/Dy/Y…
Typical process flow sheets

- Molycorp process for Europium (1965)
- Megon process for yttrium from xenotime (1975)
- Typical chinese process for all purified Rare Earths
- Rhone-Poulenc/Solvay process for all purified Rare Earths
**Molycorp for Eu from bastnaesite**

**Years ‘70**

- **Bastnaesite Concentrate**: REO 70%
- **Calcination**
- **HCl Leaching**: RECl₃ solution
- **Ce concentrate**: REO 75% (Ce 92%)
- **HCl**
- **LRE concentrations**
- **HDEHP-kerosene**
- **5 stages**
- **4 stages**
- **HDEHP-kerosene**
- **2 stages**
- **4 stages**
- **Sm, Eu, Gd, ... HRE**
- **Jones Zn reduction**
- **La, Pr, Nd**
- **Eu₂O₃**
- **Eu²⁺SO₄**
- **Sm, Gd, HRE concentrate**

**Extraction and separation of Rare Earths**

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Megon for Y from Xenotime

Years ‘70

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Rare Earths separation in China
Typical process flow sheet

LRE separations

- La / Ce, Pr / Nd
- La / Ce / Pr
- recycling

HRE separations

- Y / Ho ... Lu
- Ho, Er / Tm, Yb, Lu
- Ho / Er
- Tm, Yb / Lu

MRE separations

- Sm, Eu, Gd / Tb, Dy / Ho, Y ... Lu
- εSmEu, Gd / Tb / Dy
- Gd, Tb / εDy
- Gd / Tb

Solvent used

- P 507 (HEHEHP)
- Naphtenic acid

Mix RE concentrate

Mix RECl₃

La..Nd / Sm..Dy / Ho, Y ... Lu

La
Ce
Pr
Nd

La / Ce / Pr

Sm / Eu / Gd

Sm, Eu / Gd

Sm / Eu

recycling

Sm
Eu

Gd
εEu / Gd

Gd / εTb

εEu / Gd

recycling

NH₄ or Na chloride

Liquid effluents

60
Extraction and separation of Rare Earths
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Solvay separation scheme
capacity 9,000 TREO/year

Ore processing until 1994

monazite bastnaesite xenotime

Alcali attack Mix RE-Th-U hydroxide Acid HNO₃ solubilization

RE/Th/U Th/U U Th

All Solvent types are used in 18 batteries and #1200 MS

Ammonium nitrate
valorization

All Solvent
concentrates

Mix RE nitrates

LRE/HRE separation

La, Ce / Pr, Nd

La / Ce

Pr / Nd

Sm, Eu / HRE, ...

Sm/Eu

HRE separ

La, Ce, Pr, Nd

La, Ce

Pr, Nd

Sm, Eu

Gd, Tb, Dy, Y

Ho, Er, Tm, Yb, Lu

Extraction and separation of Rare Earths
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The SX technology for RE separation is mature. It has largely demonstrated its efficiency since 50 years. Improvements are made continuously and experience is a key factor for performance.

For the RE industry major weaknesses are pointed out and need to be addressed:
- gaseous emissions during sulfuric ore treatment,
- radioactive wastes and more widely radioactivity management,
and some others which are more specifically linked to separation technology:
- large amount of salt containing liquid effluents,
- high costs for reagents and water use,
- high capital investment.

In the recent plants improvements are dedicated to environmental concerns:
- limitation of solid wastes, air emission reduction, controlled management of radioactivity,
- better power generation and use.
- recycling of reagents (i.e. NaCl electrolysis) and process water.

- but no real improvement has been made on separation technology:
- use of the classical solvent (phosphonic acid ester) and quite classical mixer-settler.
For RE recycling and new raw materials, existing technologies for separations are efficient enough but the flexibility of the processes vs. various sources is a key factor to handle.

New solvents would help in some specific aspects
- better separation properties (selectivity)
- reduction of salt effluent generation
- more friendly solvents (limitation of use of petroleum derivative solvents)
  
- **New molecules**
- **New synergistic formulations**
- **Ionic Liquids** is a new approach but still at the very beginning of R&D stage.

The development of new technologies others than solvent extraction is certainly a real challenge.
Thanks for your attention