

The Rare-Earths refinery: Is there an alternative industrial solution to Solvent Extraction?

Hydrometallurgy Seminar Lillestrom
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The importance of RE separation

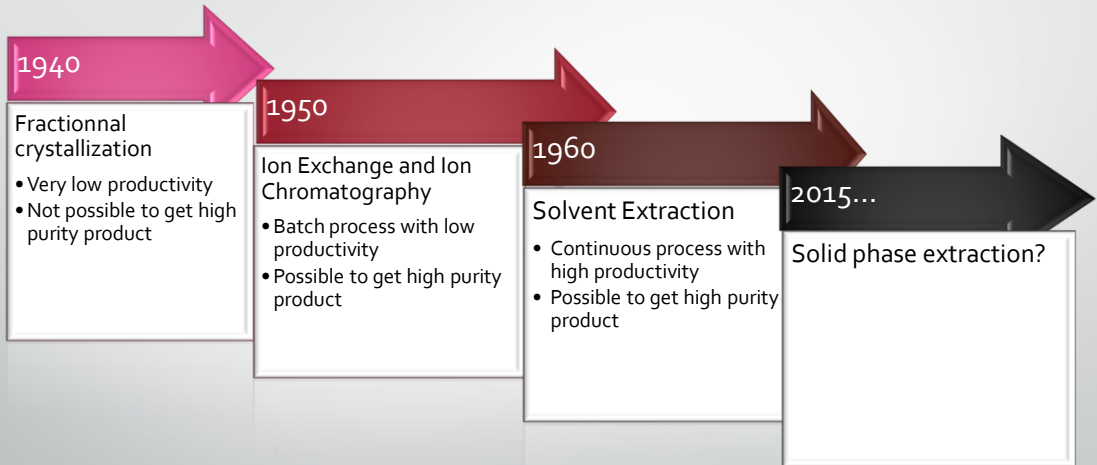
The RE separation process is important for 2 main reasons:

- The quality of the final application is mainly related to the purity of the REs used in the application
- The RE separation technology is a large part of the CAPEX and the OPEX of the RE industry

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2

The history of RE separation



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3

What are the new Solid Phase Extraction proposed as industrial processes ?

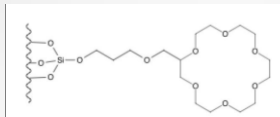
- A process based on columns containing a solid phase with complexing groups. The RE being separated during the elution.
- Among the various solid phase extraction processes, 2 of them have been proposed as industrial solutions:
 - Molecular Recognition Technology (MRT), proposed by IBC
 - Continuous Ion Exchange (CIE) or Continuous Ion Chromatography (CIC) proposed by K Tech

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4

What is MRT?

- MRT is a solid phase extraction process developed by IBC and based on grafted macrocycles called Superlig



- The scientific articles about MRT are related to:

- Base metals: Cu, Ni, Co,
- Alkaline and alkaline earths metals,
- Heavy metals (Pb, Cd)
- Platinum Group Metals

But no scientific data about RE separation (litterature and patent survey):
RE Stability constants, separation factors...

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5

What do we know about RE separation by MRT?

- An american RE junior mining company, UCORE, has chosen MRT for their RE separation technology, but due to confidentiality policy of IBC, Ucore did not answer to our questions about RE separation technology
- UCORE and IBC made a lot of commercial advertisements about RE separation using Superlig,
- A Pilot plant based on Ucore raw materials has been built. UCORE claims being able to separate RE, but still no scientific data.

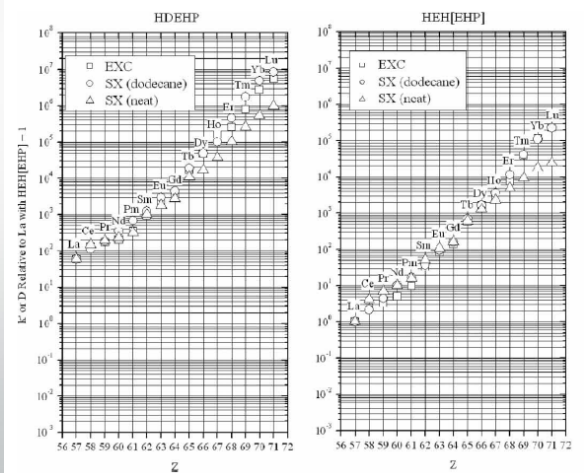


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6

Impregnated resin, the alternative SPE process

- Since we don't have any data allowing us to assess MRT, we will assess Impregnated Resin process with known selective ligands. Several authors have worked on RE separation by impregnated or grafted resins or silica materials grafted with HDEHP
- Horwitz has compared the selectivities of HDEHP and H(EH)EHP both in solvent extraction conditions and in impregnated resin conditions. The results show a very similar behaviour.
- Horwitz gave also the basic data aiming to calculate a separation column (thermodynamic and kinetic data of fixation and elution).



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EP Horwitz Separation Science and Technology 41: 2163-2182, 2006

7

What is Continuous Ion Exchange?

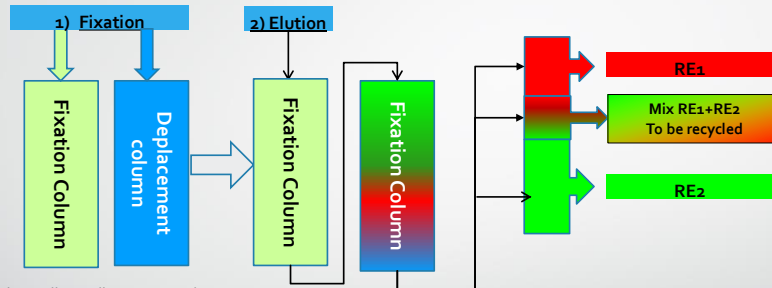
A classical Ion Exchange process from a chemical point of view ... working in a semi continuous way by using a carousel



8

What is the chemistry used by K Tech?

The chemical principles used by K Tech are the same as the old Ion Exchange process used in the 50_s and 60_s:



- Non selective strong acidic resin,
- Elution with a selective complexing agent (EDTA or DTPA)
- Displacement of the RE band along a series of columns initially loaded with a retaining ion (Fe^{3+} , Cu^{2+})

9

What are the drawbacks of SX and how to assess the new technologies?

- Main drawbacks of Solvent Extraction (as seen by RE producers)
 - High CAPEX
 - High working capital (RE stored in the SX batteries = hold up)
 - High chemicals consumption (depending on the type of solvent used)
- How to assess the new technologies for RE separation?
 - ⇒ Back to the basic:
 - What chemistry is used for RE separation and how it works?
 - How this chemistry and the process used (SX or Solid phase extraction) will impact on CAPEX, OPEX and waste water?

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10

Chemistry of RE separation: All the processes use organic ligands

- Both Solid Phase Extraction (SPE= IEx - or MRT) and Solvent Extraction (SX) use organic molecules (ligands) in order to get selectivity along the lanthanide series,
- The choice of the ligand will be of 1st importance in term of CAPEX, OPEX and waste water for both Solvent Extraction and Solid phase Extraction,
- The 3 criteria to assess a ligand:

	OPEX	CAPEX	Waste water
Chemical reaction involved	◆		◆
Selectivity between REEs	◆	◆	
Loading capacity		◆	

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11

1- Chemical reaction between aqueous phase and organic phase

Acidic ligands	Neutral ligands	Anionic ligands
$\text{RE}^{3+}_{\text{aq}} + 3\text{HL}_{\text{org}} \rightleftharpoons [\text{RE}(\text{L})_3]_{\text{org}} + 3\text{H}^+_{\text{aq}}$ <p>Where HL is an acidic molecule</p>	$\text{RE}^{3+}_{\text{aq}} + 3\text{NO}_3^-_{\text{aq}} + n\text{S}_{\text{org}} \rightleftharpoons [\text{RE}(\text{NO}_3)_3 \cdot n\text{S}]_{\text{org}}$ <p>Where S is a neutral molecule</p>	$\text{RE}^{3+}_{\text{aq}} + 3\text{NO}_3^-_{\text{aq}} + (\text{R}^+, \text{NO}_3^-)_{\text{org}} \rightleftharpoons [\text{R}^+, \text{RE}(\text{NO}_3)_4]_{\text{org}}$ <p>Where $\text{R}^+, \text{NO}_3^-$ is an anionic molecule</p>
<p>Extraction step</p> $\text{RE}^{3+}_{\text{aq}} + 3\text{HL}_{\text{org}} \rightarrow [\text{RE}(\text{L})_3]_{\text{org}} + 3\text{H}^+_{\text{aq}} + 3\text{OH}^-_{\text{aq}}$ <p>Consumption of alkaline solution (caustic or ammonia)</p>	<p>Extraction step</p> $\text{RE}^{3+}_{\text{aq}} + 3\text{NO}_3^-_{\text{aq}} + n\text{S}_{\text{org}} \rightarrow [\text{RE}(\text{NO}_3)_3 \cdot n\text{S}]_{\text{org}}$ <p>High concentration in nitrate \Rightarrow Consumption of energy (steam)</p>	<p>Extraction step</p> $\text{RE}^{3+}_{\text{aq}} + 3\text{NO}_3^-_{\text{aq}} + (\text{R}^+, \text{NO}_3^-)_{\text{org}} \rightarrow [\text{R}^+, \text{RE}(\text{NO}_3)_4]_{\text{org}}$ <p>High concentration in nitrate \Rightarrow Consumption of energy (steam)</p>
<p>Stripping step</p> $[\text{RE}(\text{L})_3]_{\text{org}} + 3\text{H}^+_{\text{aq}} \rightarrow \text{RE}^{3+}_{\text{aq}} + 3\text{HL}_{\text{org}}$ <p>Consumption of acid (hydrochloric or nitric)</p>	<p>Stripping step</p> $[\text{RE}(\text{NO}_3)_3 \cdot n\text{S}]_{\text{org}} + \text{H}_2\text{O} \rightarrow \text{RE}^{3+}_{\text{aq}} + 3\text{NO}_3^-_{\text{aq}} + n\text{S}_{\text{org}}$ <p>Consumption of water</p>	<p>Stripping step</p> $[\text{R}^+, \text{RE}(\text{NO}_3)_4]_{\text{org}} + \text{H}_2\text{O} \rightarrow \text{RE}^{3+}_{\text{aq}} + 3\text{NO}_3^-_{\text{aq}} + (\text{R}^+, \text{NO}_3^-)_{\text{org}}$ <p>Consumption of water</p>

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12

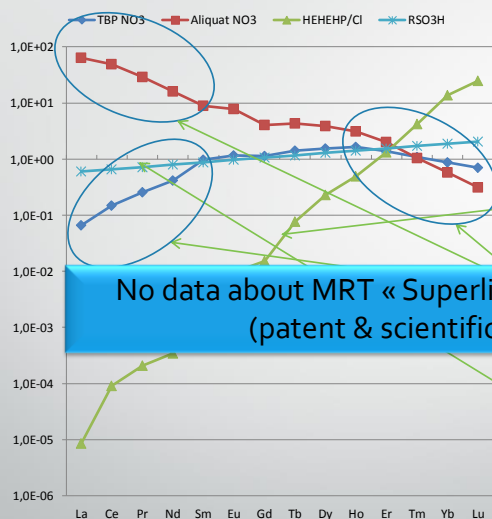
1- Chemical reaction between aqueous phase and organic phase

	Acidic molecules	Neutral molecules	Anionic molecules
Route	Chloride or Nitrate	Nitrate	Nitrate or Thiocyanate
Typical molecules	H(EH)EHP (P507/ PC88A) Strong acidic resins	TBP Crown Ether (MRT?)	Aliquat 336 Ionic liquids
Main consumption	Loading: NaOH (NH ₄ OH) Stripping: HCl (HNO ₃)	Loading: Steam Stripping: Water	Loading: Steam Stripping: Water
Variable costs	High	Low	Low
Waste water	NaCl or NH ₄ NO ₃	No	No

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13

2- Selectivity of RE separation with solvents or solid phase extractants



The selectivity of the organic molecules among RE is a key parameter.

H(EH)EHP is selective all along the RE series and thus can be used for all separations

No data about MRT « Superlig » selectivity among the RE (patent & scientific literature survey)

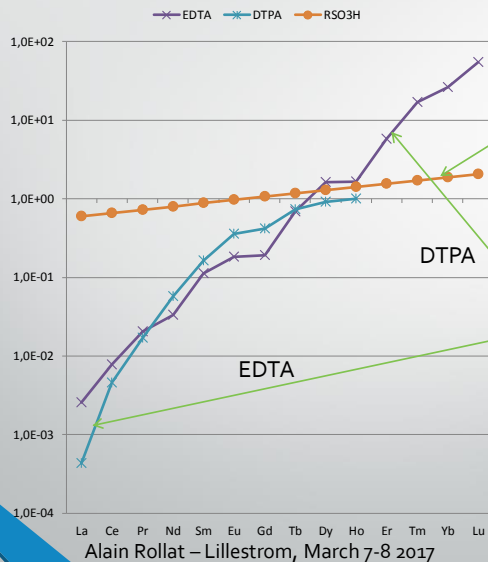
solution

The Strong Acidic Resins (K Tech) have almost no selectivity

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14

2- Selectivity of RE separation with the strong acidic resins (Texas RE - K Tech technology)



The Strong Acidic Resins have almost no selectivity along the RE series

The RE separation will be obtained by addition of selective organic molecules in the aqueous phase during the elution step

15

2- Selectivity of RE separation: consequences on the CAPEX & OPEX

- The selectivity of the organic molecules among RE will impact both OPEX and CAPEX for both Solvent Extraction batteries and Solid Phase Extraction columns

	Solvent extraction		Solid Phase Extraction	
	OPEX	CAPEX	OPEX	CAPEX
Increase selectivity	Lower scrubbing = lower chemical or energy	Lower number of stages	Lower quantity of RE to be recycled	Lower number of columns

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16

3- REO concentration in the aqueous phase and organic solvent or solid phase

		Aqueous phase	Organic phase	Productivity
Solvent extraction	Cationic	50g/l to 150g/l	10g/l to 40g/l	Medium
	Neutral	250g/l to 450g/l	50g/l to 150g/l	High
	Anionic	150g/l to 350g/l	20g/l to 50g/l	Medium
Solid phase extraction	Selective organic molecule onto the solid phase (MRT?)	25g/l to 50g/l <small>H(EH)EHP Horwitz 2006</small>	40g/l to 50g/l <small>H(EH)EHP Horwitz 2006</small>	Medium
	Selective organic molecule in the aqueous phase (K Tech)	2g/l to 15g/l	50g/l to 150g/l	Low

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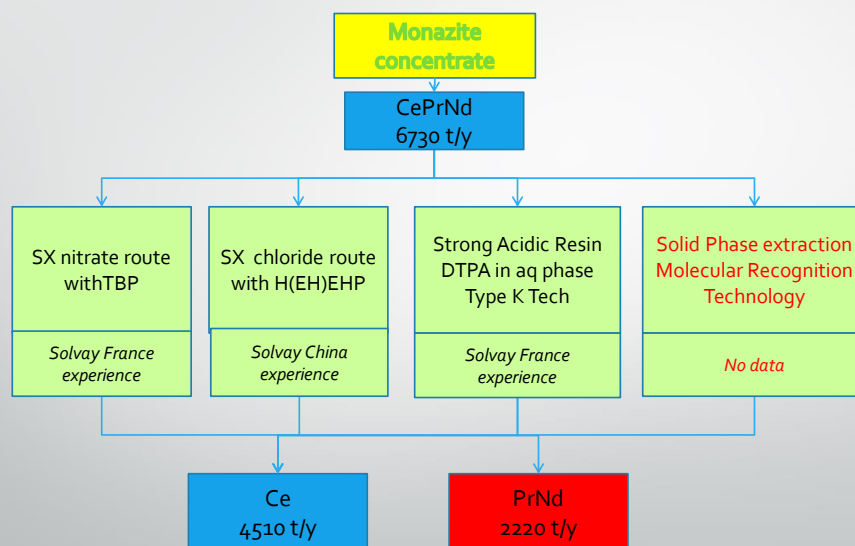
17

The Example of didymium production The comparison between SX and Solid Phase Extraction

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18

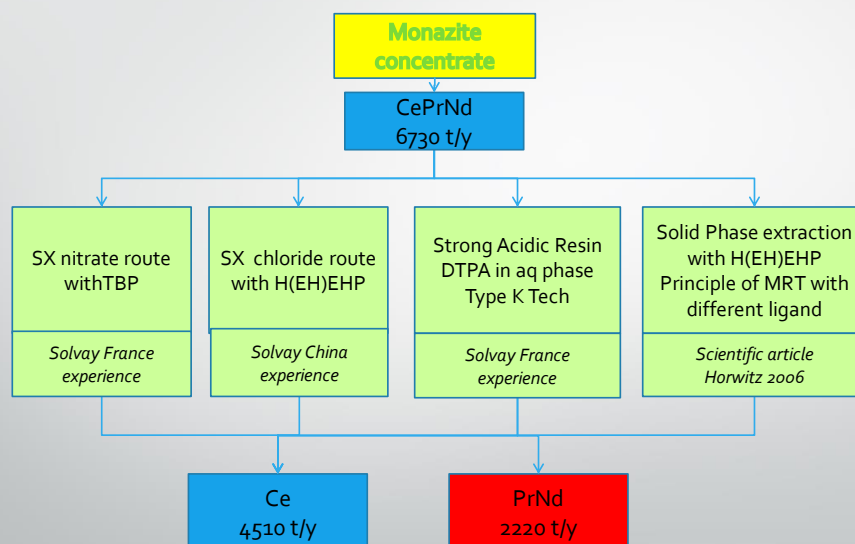
Didymium production from a monazite concentrate: Comparison between SX and Solid Phase Extraction



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19

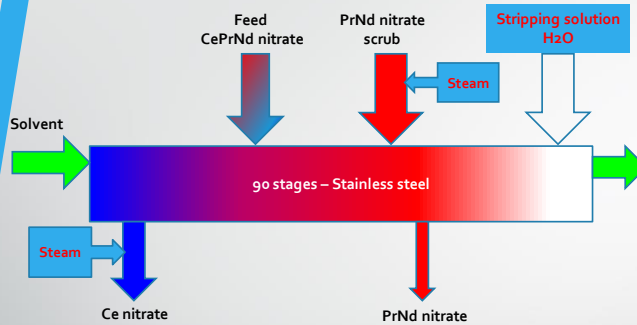
Didymium production from a monazite concentrate: Comparison between SX and Solid Phase Extraction



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20

Ce/PrNd separation by SX with TBP in nitrate route



Solvay La Rochelle (France)

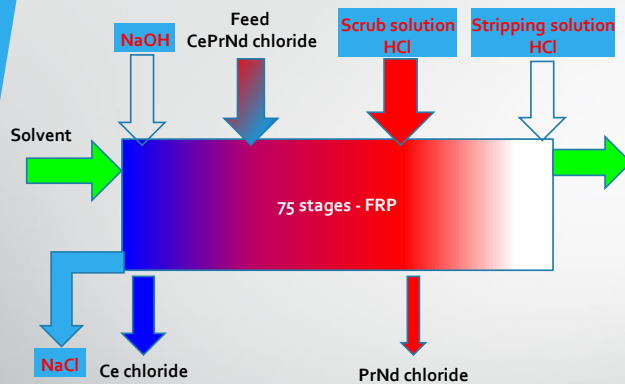


Continuous process – Highly concentrated solutions – Consumption of steam and water

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21

Ce/PrNd separation by SX with H(EH)EHP in chloride route

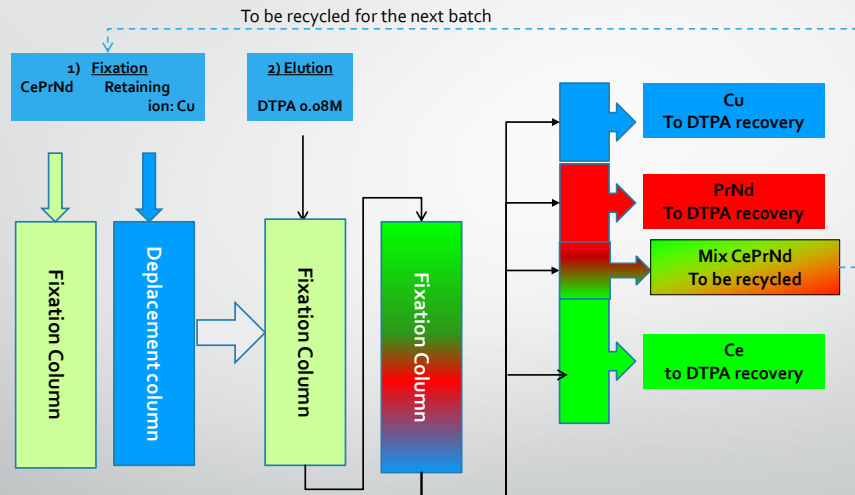


Continuous process – Moderately concentrated solutions – Consumption of Alkali and acid

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22

Ce/PrNd separation by Solid Phase Separation with a non selective resin & a selective eluent: DTPA



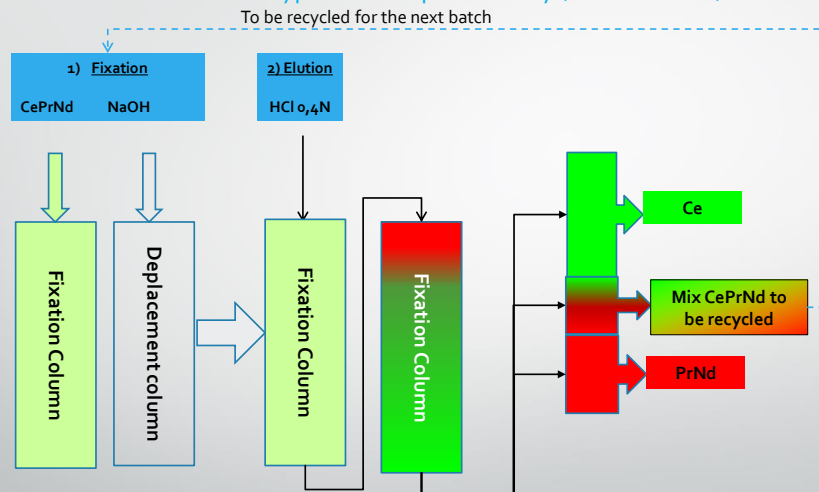
Very low productivity due to low solubility of the EDTA complexes (very low concentration)
Additional and costly process for Cu and EDTA recovery

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23

Ce/PrNd separation by Solid Phase Separation with a resin impregnated with H(EH)EHP

Hypothesis of productivity (Horwitz 2006)



Better productivity than with the non selective resin (higher concentration).
No problem of Cu and EDTA recovery

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24

SX and Solid phase separation comparison for Didymium production (CAPEX estimate done in 2015)

	SX / TBP	SX / H(EH)EHP	Strong cationic resin with DTPA	Resin impregnated with H(EH)EHP
Aqueous solution	Nitrate	Chloride or nitrate	Chloride or nitrate	Chloride or nitrate
Process	Continuous	Continuous	Batch (Continuous ?)	Batch (Continuous?)
Variable costs	0.2 \$/kg REO	0.7 \$/kg REO	3.8 \$/kg REO	0.7 \$/kg REO
RE Hold up or RE to be recycled	Ce 51t PrNd 36t	Ce 20t PrNd 15t	17% of the RE for each batch	22% of the RE for each batch
C A P E X	Equipment	7.8 M\$	12.7 M\$	2.3 M\$
	Solvent / resin	800 k\$	15600 k\$ Lanxess prices for strong acid resin*	8900 k\$ Lanxess data for impregnated resin**
Waste water NaCl	None	930 kg/t REO	1180 kg/t REO	1260 kg/t REO
Other	Need to have a NH_4NO_3 valorization loop		Need Cu as retaining ion	Process studied only at lab scale

* Lewatit MDS 1268/290μ (RSO₃H)

** Lewatit TP272; contains bis(2,4,4 trimethyl pentyl) phosphinic acid
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25

Can Solid Phase Extraction compete with Solvent Extraction

- Continuous Ion Exchange using strong acidic resins:

Even if CIC can decrease the CAPEX compare to the batch Ion Exchange, this process cannot be competitive due to the use of complexing agents

- Resins impregnated with H(EH)EHP:

There is an interest in term of CAPEX (depending on the cost of the Solid Phase), but the OPEX cannot compete with a neutral extractant (TBP).

The losses of the ligand and the breakage of the resin have not been assessed,

- We have not been able to assess MRT. What should we know to really assess this technology?

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26

What should we know to assess MRT?

- Chemistry of RE separation:
 - aqueous solution = nitrate?
 - Chemical reaction = neutral?
- Selectivity along the REE series:
 - The highest selectivity currently known is obtained with H(EH)EHP/P507 ($F_{Lu/La} > 10^6$).
 - What is the selectivity of MRT ligands compared to the classical ligands (H(EH)EHP, TBP and Aliquat 336)?
- Loading capacity:
 - Typical loading capacity of impregnated resin is 40g/l to 50g/l
- Kinetics of complexation:
 - This will impact the productivity and thus the height and number of columns.
- Price of the solid phase
 - Private information: 1000\$/l ! For Superlig used in PGM separation

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27

Conclusions

- From the data we have Solid Phase Extraction technology cannot compete with Solvent Extraction for Rare Earths separation
- K Tech technology uses complexing agents in the liquid phase (EDTA, DTPA...) and will lead to low productivity and high chemical consumption. The improvement proposed by K Tech (continuous process) should decrease the CAPEX, but should not modify significantly the variable costs
- The published technologies based on selective ligands impregnated or grafted onto the solid phase are still non competitive due to the high price of the Solid Phase itself.
- The lack of data about the materials using grafted crown ethers (IBC) cannot allow the positioning of this technology. But the information about the price of this type of solid phase indicates that whatever the process, the CAPEX related to the material itself should be uneconomical as such.
- However, Solid Phase Extraction should allow to decrease the RE inventory (hold up).
- A Solid Phase Extraction process based on non acidic molecules would be interesting for the production of a limited quantity of high price REs.

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28

Thank you for your attention

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