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Connecting matters

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University of Zagreb
FACULTY OF MINING, GEOLOGY AND PETROLEUM ENGINEERING

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Methods of extraction of Rare Earth Elements

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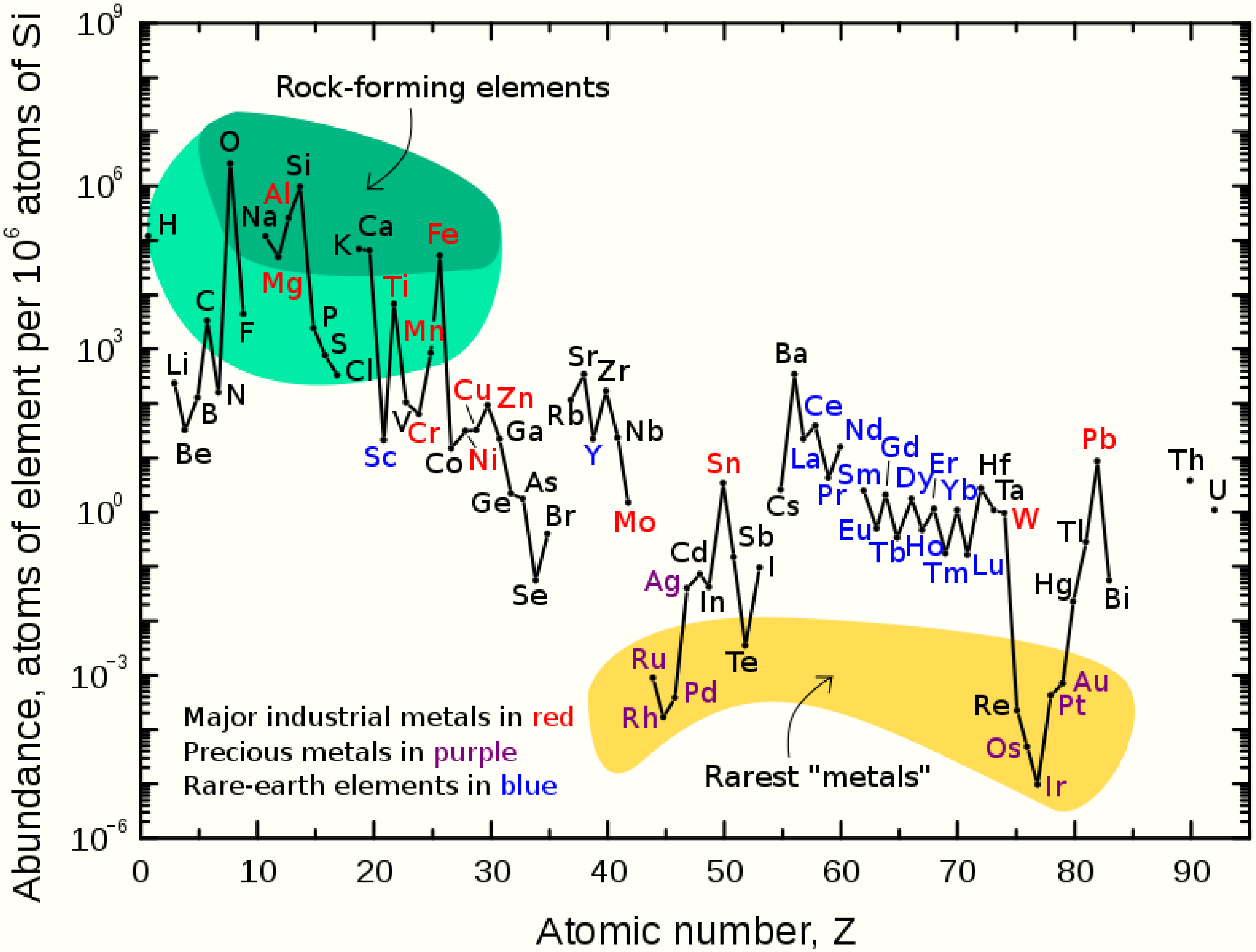
Terminology

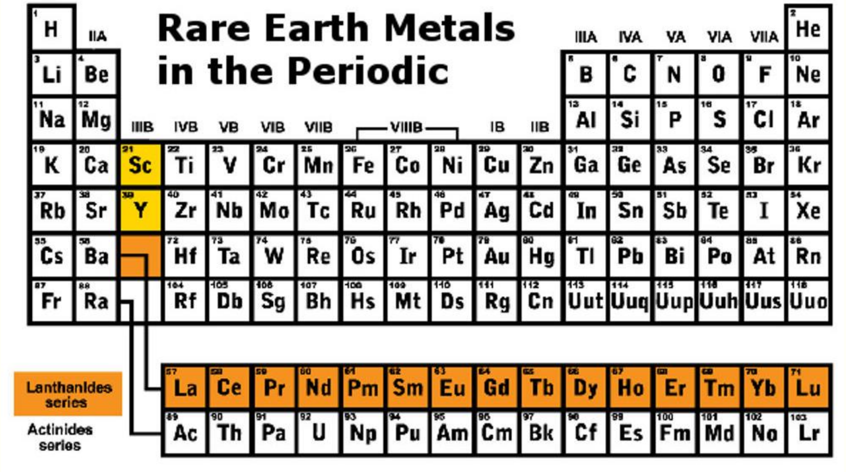
- RE – Rare Earth/s
- REE – Rare Earth Element/s
- REM – Rare Earth Metals
- REY – Rare-earth Elements and Yttrium
- REO – Rare Earth Oxide/s
- LREE – Light Rare Earth Element/s, aka cerium group (Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd)
- HREE – Heavy Rare Earth Element/s, aka the yttrium group (Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu)
- MREE – Middle Rare Earth Elements

Scandium (Sc)
Yttrium (Y)
Lanthanum (La)
Cerium (Ce)
Praseodymium (Pr)
Neodymium (Nd)
Promethium (Pm)
Samarium (Sm)
Europium (Eu)
Gadolinium (Gd)
Terbium (Tb)
Dysprosium (Dy)
Holmium (Ho)
Erbium (Er)
Thulium (Tm)
Ytterbium (Yb)
Lutetium (Lu)

Abundance of elements in Earth's crust per million Si atoms (USGS)



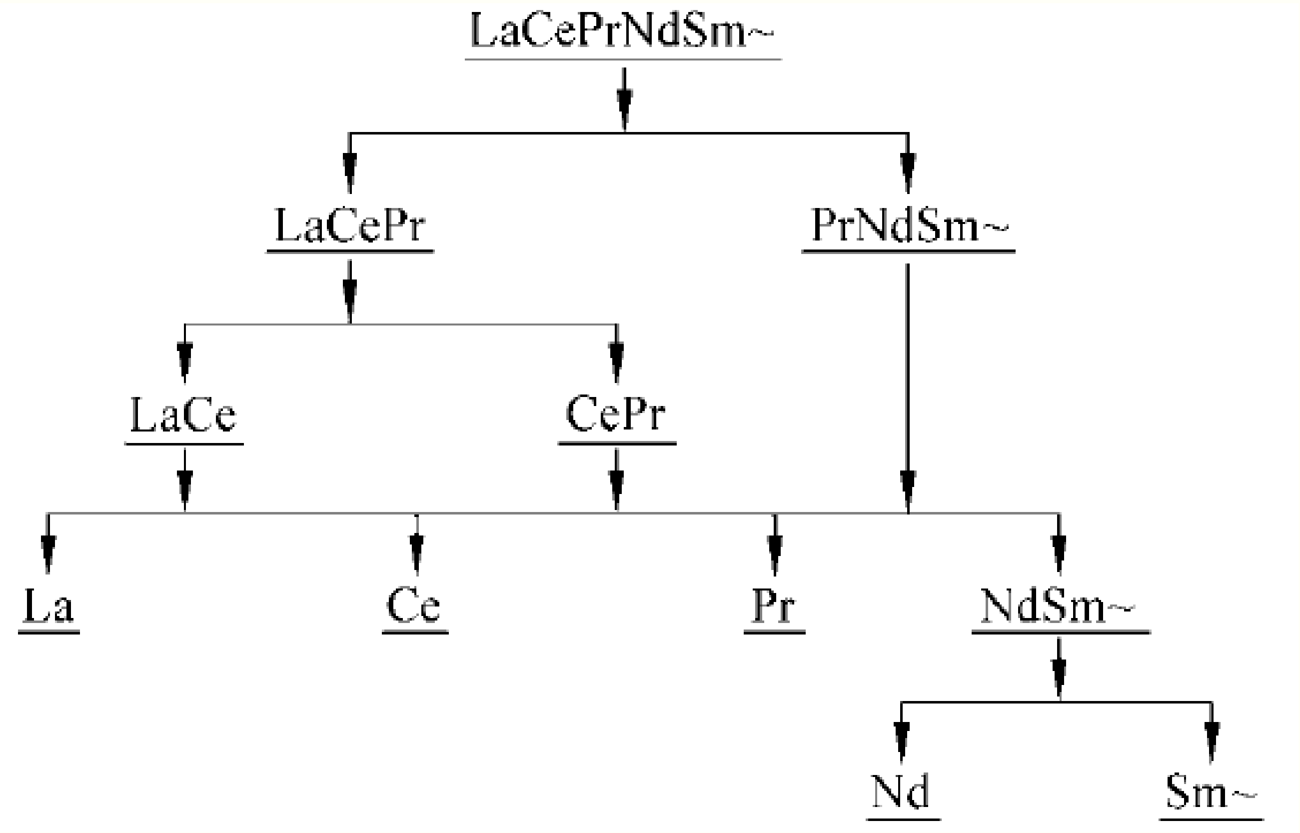
Why so rare?



- Occur in the same ore deposits
- Exhibit similar chemical properties
- Mineralogical, chemical, physical (electron shell configuration)
- Not especially rare, but they tend to occur together in nature
- Difficult to separate from one another

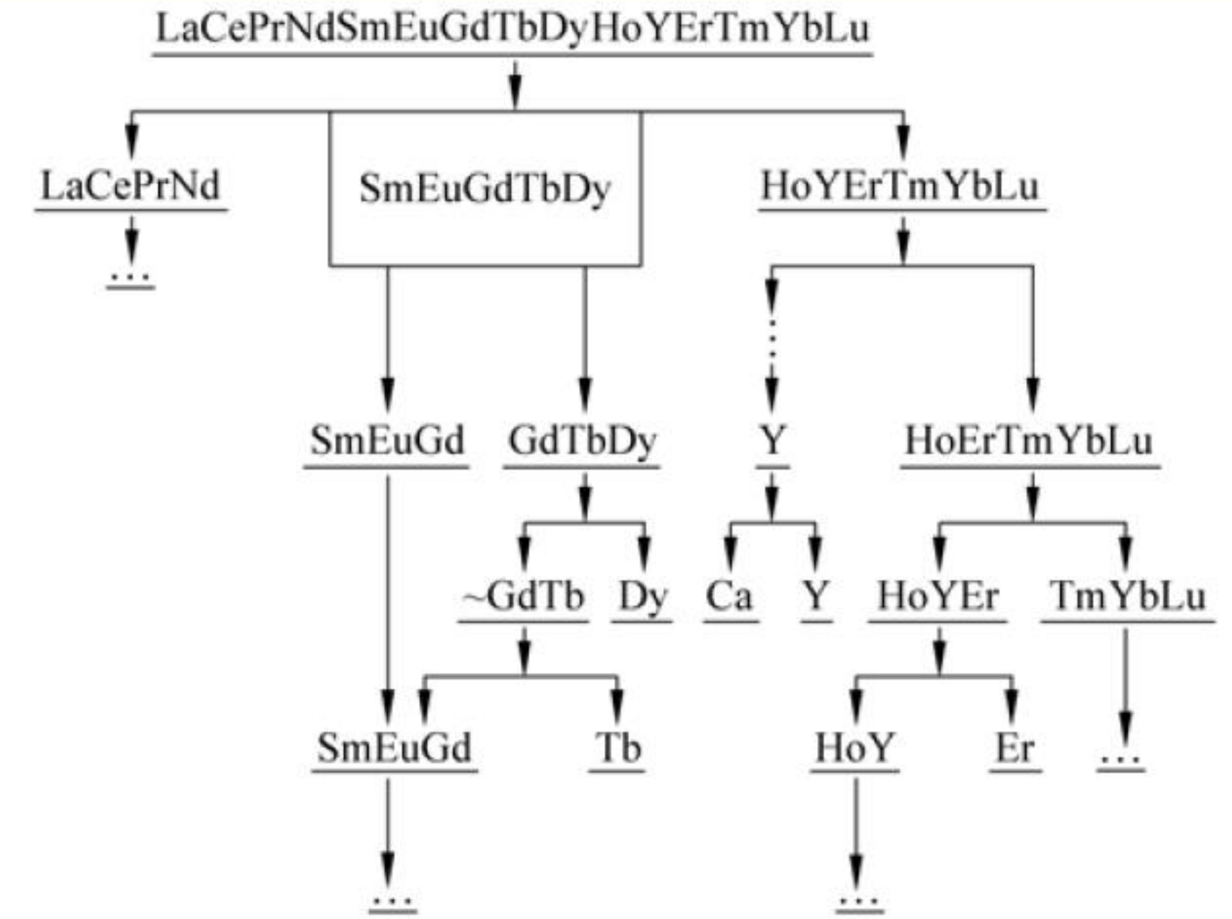
1. Alkaline magmas enriched with REE: carbonatites, peralkaline granites (pegmatites), nepheline syenite
2. Secondary alteration (hydrothermal fluids, meteoric water, erosion and transport of resistate REE-bearing minerals)
3. Sea-bed! one square patch of metal-rich mud 2.3 kilometers wide might contain enough rare earths to meet most of the global demand for a year (Yasuhiro Kato)

Typical separation flowsheet for REE from bastnäsite and monazite, from (Yan et al., 2006)



Royen and Fortkamp (2016)

Typical optimized separation flowsheet for REE from ion adsorption clay deposits, from (Yan et al., 2006)



Royen and Fortkamp (2016)

Mineral processing

1

Size reduction / liberation & classification

2

Concentration /separation

(physical properties: density, magnetic, electric, surface properties, …..)

3

Hydro/pyro metallurgy

(chemical and thermal)

REEproduction (extraction)

Ore mining → REE-containing material

Concentration (increasing the % content of REE from a very low level to about 60 – 70%)

Purification to produce a REE-containing mixture (usually an acidic solution) pure enough for separation

Separation of different REE or REE fractions present

Hundreds, thousands of repetitions

Refining into a sellable product (REE compounds or metals, either pure or in defined mixtures)

Royen and Fortkamp (2016)

Processing (in 90% of cases)

1. **Milling** of ore
2. Treatment with steam and **chemicals** to produce a slurry (only used in some installations)
3. Separation of gangue through **froth flotation.** Chemicals used include fatty acids, hydroxamates and dicarboxylic acids
4. Cleaning of the separated ore
5. Leaching of the ore with an ammonium- or salt-based chemical solution
6. Addition of oxalic acid to the leachate to precipitate REE oxalates.
7. Filtration
8. Roasting of filter cake to produce REO.

Royen and Fortkamp (2016)

Purification & Separation

- China, Japan, France→ property differences of REE

1. REE are III-valent ions / except
   - Ce,Pr,Tb (IV)
   - Eu, Sm, Yb (II)
   - used to separate Ce & Eu from mix

2. Ionic radius decreases with increasing atomic number (lanthanide contraction) - alkalinity

   → solubility, ionic hydrolysis, complexation

Scandium (Sc)
Yttrium (Y)
Lanthanum (La)
Cerium (Ce)
Praseodymium (Pr)
Neodymium (Nd)
Promethium (Pm)
Samarium (Sm)
Europium (Eu)
Gadolinium (Gd)
Terbium (Tb)
Dysprosium (Dy)
Holmium (Ho)
Erbium (Er)
Thulium (Tm)
Ytterbium (Yb)
Lutetium (Lu)

Royen and Fortkamp (2016)

Purification & separation

- Selective oxidation/reduction – electrochemical processes simpler, cheaper, and environmentally friendlier
- Fractional crystallization – historical
- Fractional precipitation – historical, original method for separating REE (small differences in solubility, large number of double salts, thousands of repetitions)
- Solvent extraction (liquid-liquid extraction) – large scale, continuous multi-stage batteries of mixer-settlers, stripping, scrubbing,…) – hundreds of repetitions, >>99.99% purity
- Ion exchange → very pure REE (> 99.9999%)

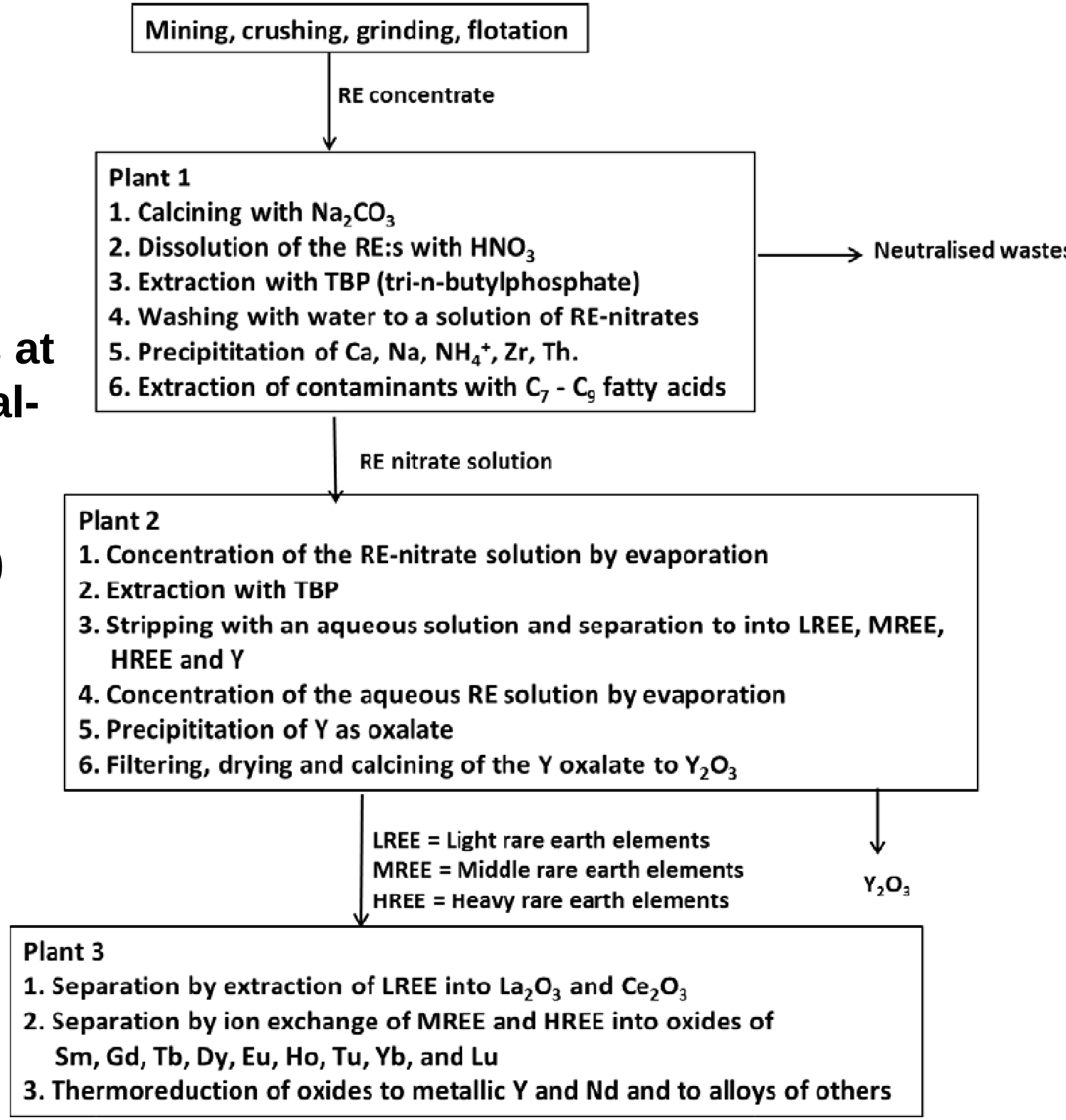
Royen and Fortkamp (2016)

Refining

- Molten salt electrolysis
- Metallothermic reduction
- 99.9999%
- Complicated, high consumption of electricity
- REO + HF → REF
- REF+Ca (redox) → RE + CaF (l)
- High temp. vacuum vaporization of CaF

Royen and Fortkamp (2016)

Overview of the historical REE production process at the Kyrgyz Chemical-Metallurgical Plant, based on (Stans Energy Corp., 2012)



Royen and Fortkamp (2016)

Methods to obtain REE concentrate from red mud

Processing

2

Size reduction / liberation & classification

Concentration /separation

(physical properties: density, magnetic, electric, surface properties, …..)

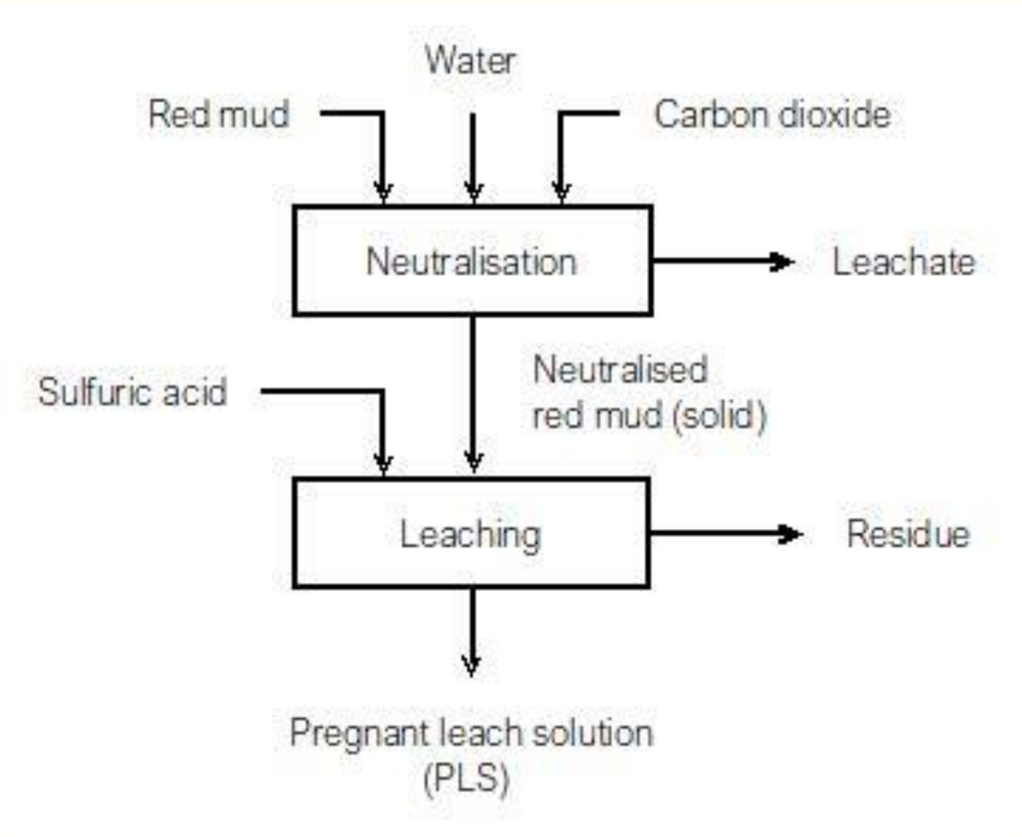
3

Hydro/pyro metallurgy

(chemical and thermal treatment)

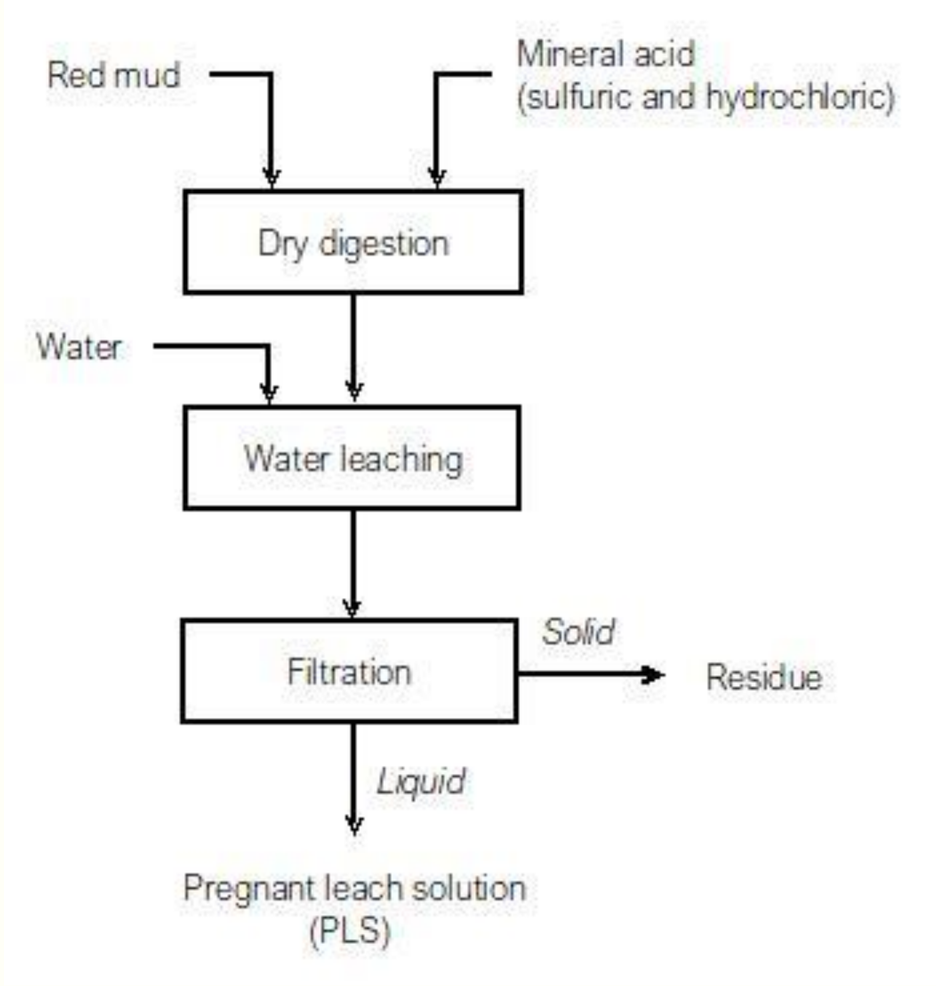
pH / neutralisation

Neutralization of red mud with CO_2 + acidic leaching of metals



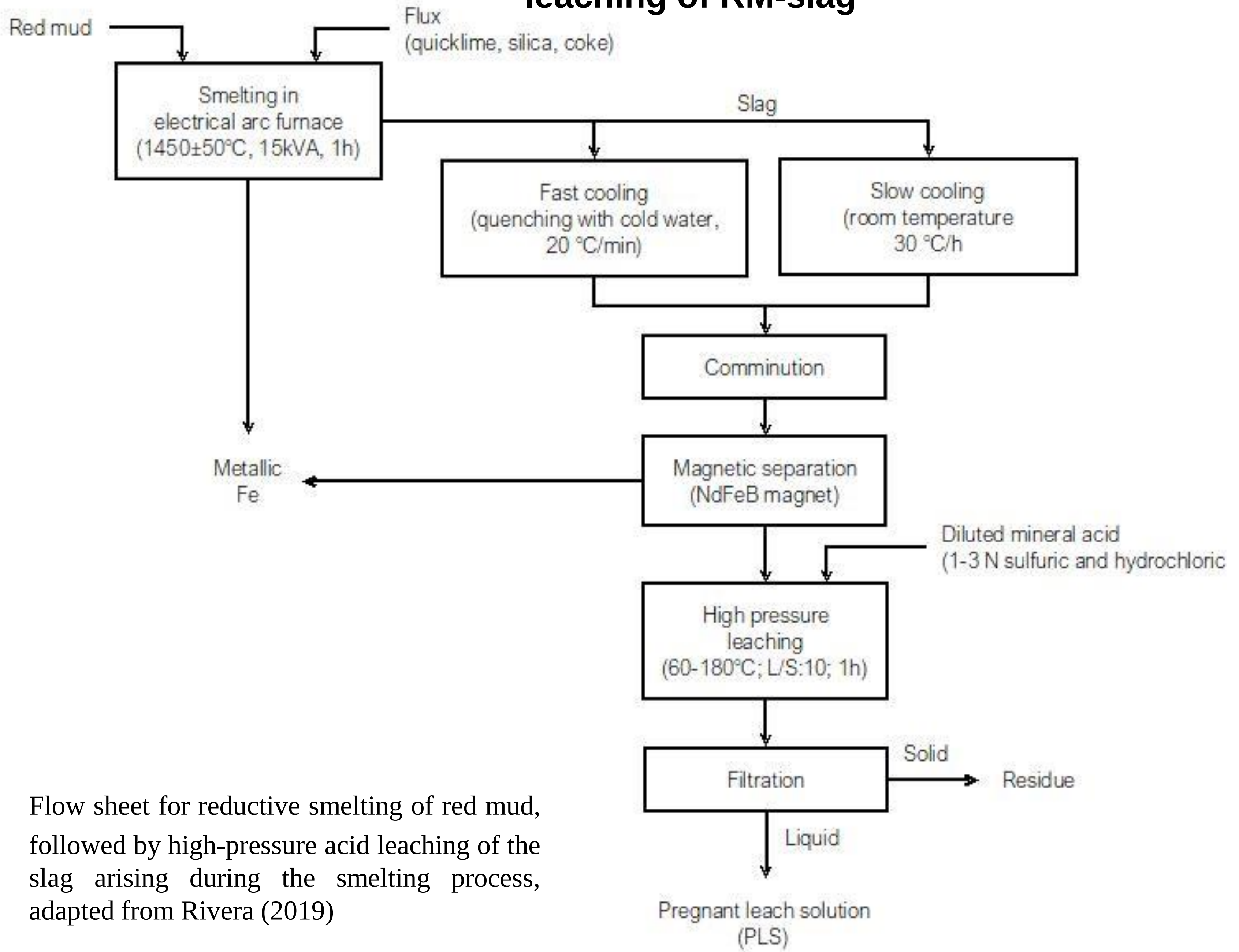
Flow sheet for neutralisation of red mud, followed by metal recovery from neutralised red mud by leaching with sulfuric acid, adapted from Rivera (2019)

Dry digestion of red mud + water leaching of REE



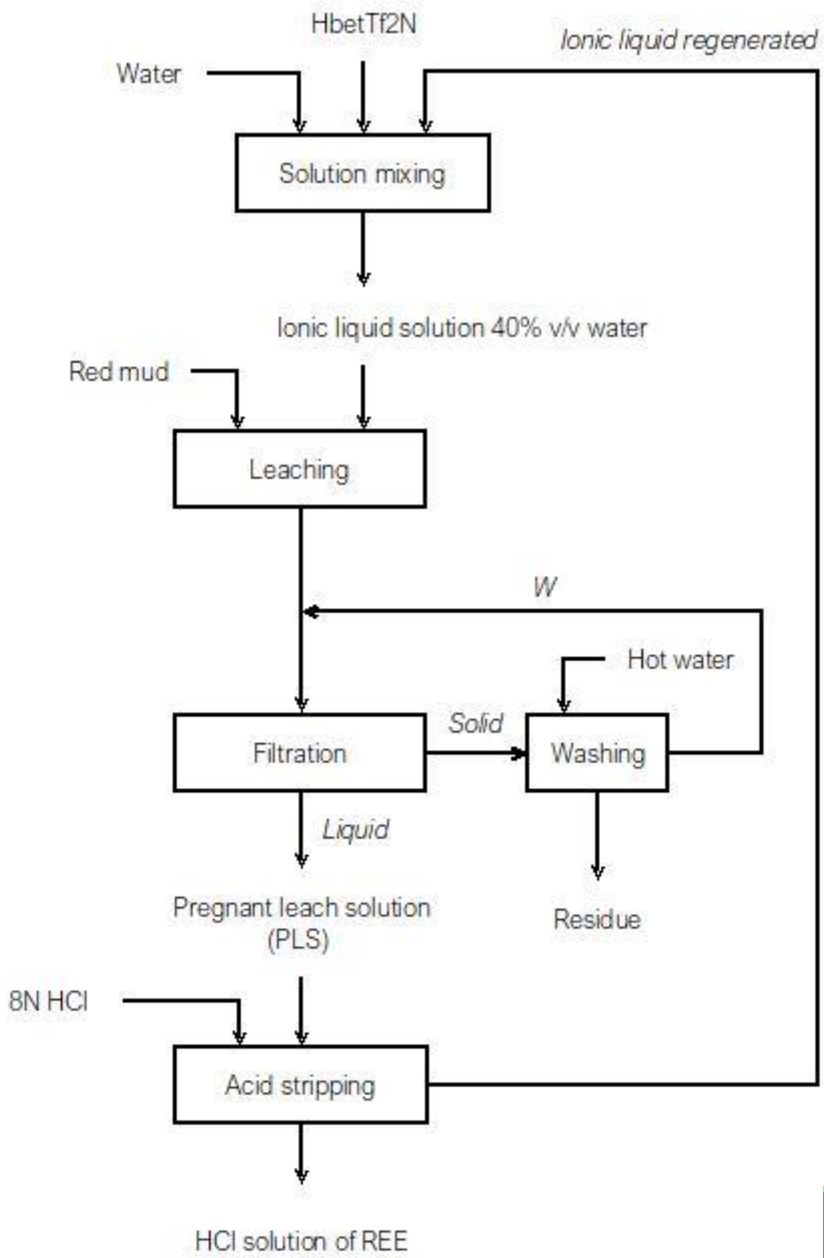
Flow sheet for dry digestion of red mud, followed by metal extraction from the digested red mud by water leaching, adapted from Rivera (2019)

Smelting of red mud and selective extraction of REE with high-pressure acid leaching of RM-slag



Flow sheet for reductive smelting of red mud, followed by high-pressure acid leaching of the slag arising during the smelting process, adapted from Rivera (2019)

Selective recovery of REE with functionalised ionic liquids



Flow sheet for selective REE recovery with ionic solution, adapted from Davris et al. (2018)

Biological recovery of REE from red mud

Biological recovery of rare earth elements from the solid phase:

1.Mobilization of REE to dissolved form in aqueous solution

1. redoxolysis,
2. acidolysis or
3. complexolysis.

2.Selective uptake

1. biosorption,
2. bioaccumulation or
3. bioprecipitation.

Physical and chemical factors that can affect the efficiency of the process:

1. aeration,
2. pulp density,
3. temperature,
4. pH, → *Penicillium tricolor* RM-10, *Aspergillus niger*
5. redox potential
6. metal toxicity

Chemical composition of red mud used for bioleaching of REE (Dev et al., 2018; Qu and Lian 2013; Li et al., 2015), pyro/hydrometallurgical methods (Rivera, 2019), by leaching with ionic liquids (Davris et al. 2018) and comparison with REEBAUX (2020) results

Assay→	**Fe_2O_3**	**Al_2O_3**	**CaO**	**SiO_2**	**TiO_2**	**Na_2O**	**LOI**	**Sc**	**Y**	**La**	**Nd**	**Total REE**	**Other**
	(Fe)	(Al)	(Ca)	(Si)	(Ti)	(Na)							
↓Source of data	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	
Bioleaching, Dev et al. (2018), Qu and Lian (2013) Li et al. (2015) Oxides in red mud Digestion XRF	12.04 (8.42) (8.41)	6.17 (3.27) (4.48)	16.58 (11.85 (23.8 5)	9.69 (4.53) (8.48)	n/a	7.14 (5.30) (4.63)	n/a	158 ±13 139 ±7	266 ±24 113 ±19	416 ±56 454 ±22	341 ±9 92± 5	2 647	
Hydro/pyrometallurgical methods, Rivera (2019)	46.7	18.1	8.5	7.3	5.8	2.8	8.5	121 ±10	76± 10	114 ±10	99± 10	n/a	
(with ionic solution) Davris et al. (2018), red mud	43	25	9	5	5	2	10	134	115	156	125	1 149	
REEBAUX (2020), red mud Min. Max. Avg.	12.3 42.1 36,0	11.3 31.1 18.1	1.9 22.9 8.0	8.5 25.2 12.2	1.7 6.9 4.2	2.1 9.3 6.6	n/a	35 224 101	58 224 148	83 408 236	66 283 182	0 1 782 1 202	

REE extraction yields of bioleaching (Dev et al., 2018; Qu and Lian 2013; Li et al., 2015), hydro/pyrometallurgical methods (Rivera, 2019) and by leaching with ionic liquids (Davris et al. 2018)

Assay→	Fe	Al	Ca	Si	Ti	Na	LOI	Sc	Y	La	Nd	Total REE	Other
↓Source of data	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	
Bioleaching, Dev et al. (2018), Qu and Lian (2013) Li et al. (2015) Extraction yield								30-45%		16-27%			Ga 31%, Ge 33%, V 19%, Eu 23-30%, Yb 44-62%
Hydro/pyrometallurgical methods, Rivera (2019) Extraction yield (with H2SO4; with HCl) **DLx** **CO2 N-Lx** **DD 1 Lx** **DD M Lx** **HPAL BR** **S-HPAL BRS**	3;3 2;0 4;4 5;4 40;74 82;84	26;30 21;0 30;23 22;24 50;40 70;91			28;30 29;0 23;2 21;3 5;7 0;0			39;45 36;0 24;30 20;32 68:88 91;79	58;70 56;0 15;47 13;50 34;99 16;99	23;38 20;0 13;30 12;32 12;77 9;98	21;50 23;0 12;33 10;34 11;99 9;98		
Hydrometal. with ionic solution, Davris et al. (2018) Extraction yield		100	100	0			-	45%	>70%				
In precipitate, % wt	1.35	23.33	0.27			1.06		0.04	0.05	0.05	0.05		Ce 0.21

Literature

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6. Grbeš, A. (2018): Methodology for extraction of Rare Earth Elements. ESEE Dialogue Conference Workshop Mineral potential of the ESEE region – focus on Montenegro. Podgorica, 6.11.2018. Presentation.

Thank you!