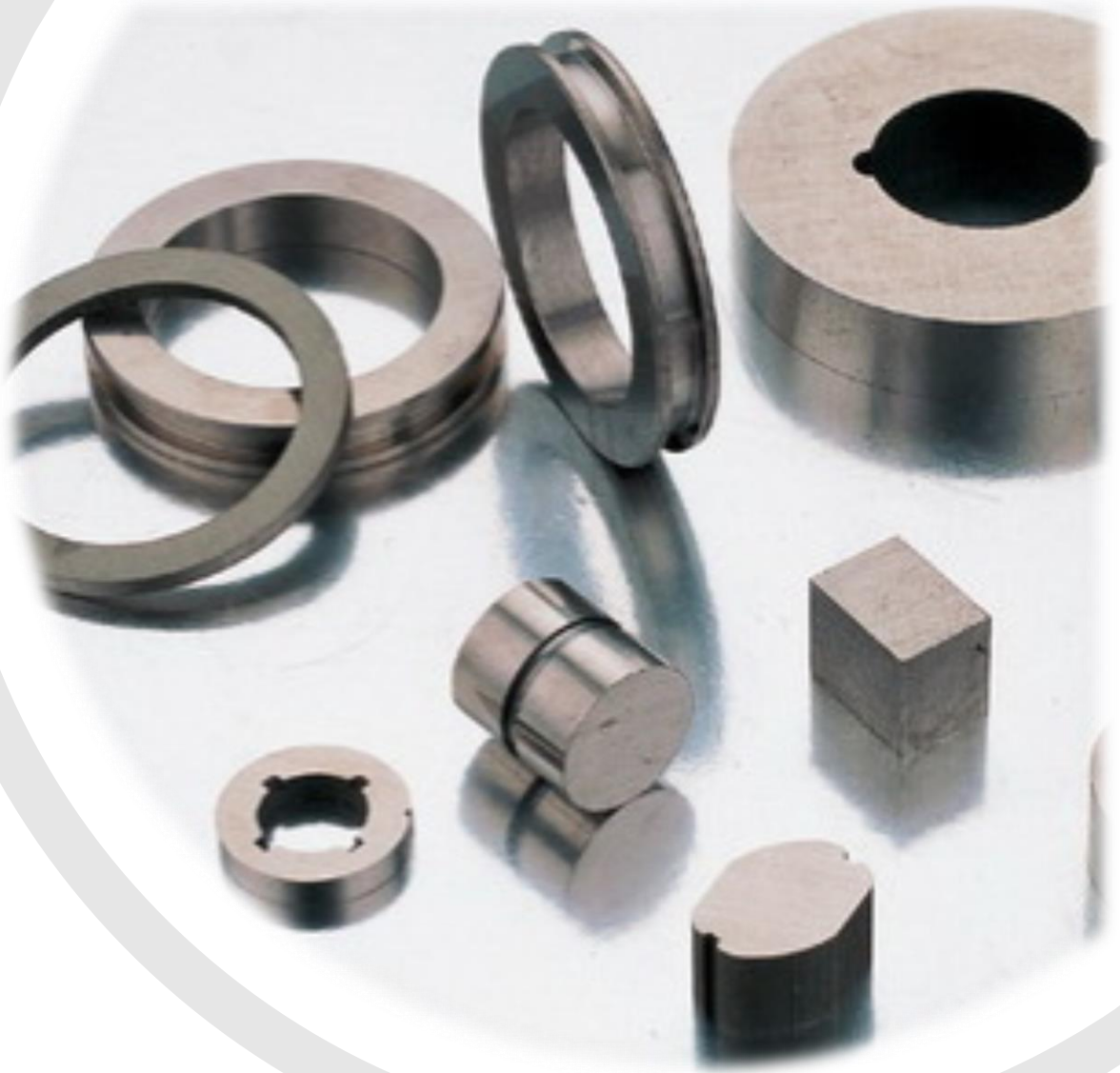
eit RawMaterials
Connecting matters

VALOMAG

Transformation to the production of REE oxides through hydrometallurgical routes

Sahar Belfqueh I Online I 03/12/21



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La Région Occitanie Pyrénées - Méditerranée

Géosciences pour une Terre durable brgm

ICSM

cnrs

AGENDA

1. Context
2. The process
3. Characterization of the HDD NdFeB magnets
4. Leaching of NdFeB powder using organic acids
5. Selective leaching using organic acids
6. Conclusions and perspectives

CONTEXT

Rare earth permanent magnets:

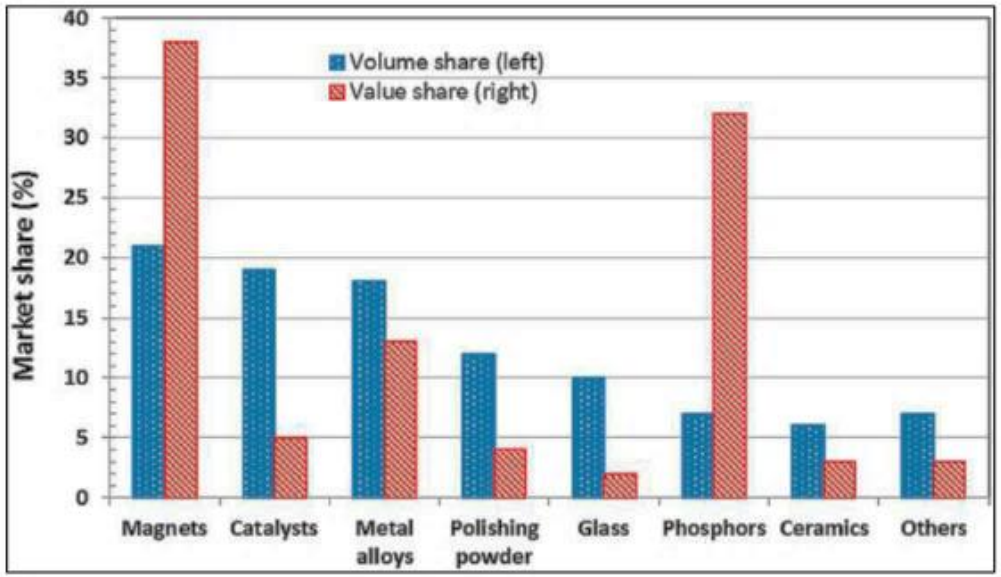
- One of the most important applications of REEs

Neodymium magnets (NdFeB) :

- Has the highest energy density
- Used in several high-tech products, wind power turbines and electric vehicles
- Contains: Nd, Pr, Dy, Tb, Gd

Recycling potential of NdFeB magnets:

- Contains metals identified as critical by the European Commission (2011): Nd, Dy, Co, Tb
- Importance of current stocks of spent NdFeB magnets
- Continuous increase in stocks due to growth in the wind power and electric transportation sectors



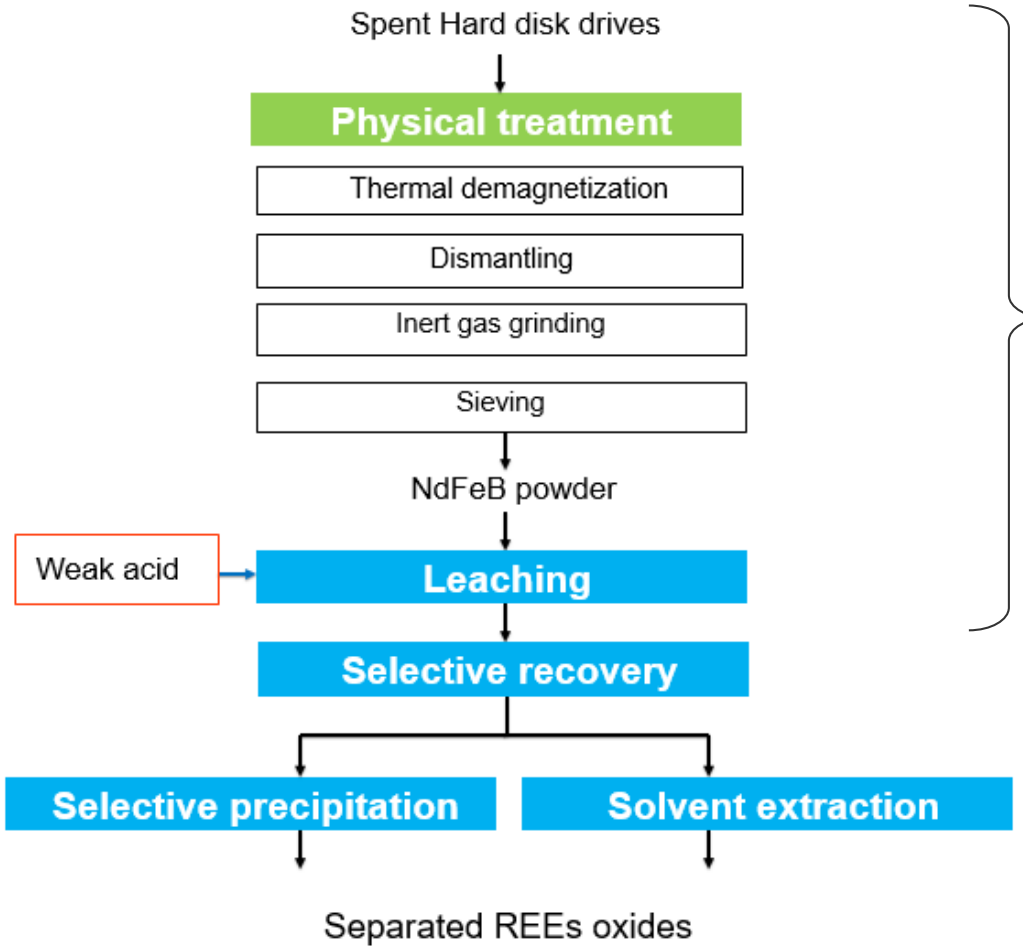
Market share of REEs applications.

CONTEXT

- Direct reuse
- Hydrogen decrepitation
- Hydrometallurgy
- Pyrometallurgy
- Resintering…

- Applicable to all types of waste.
- Can handle large variations in composition/impurities
- Similar to virgin mining of REEs

THE PROCESS



ANR EXTRADE project

FR 3 052 171 - A1

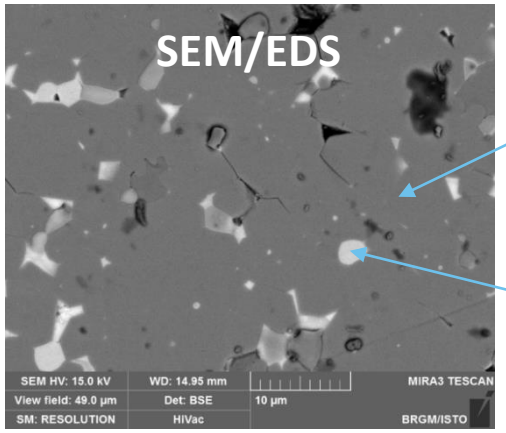
Results patented by BRGM

High-scale physical treatment of spent NdFeB magnets

PhD's scope

CHARACTERIZATION OF THE HDD NDFEB MAGNETS

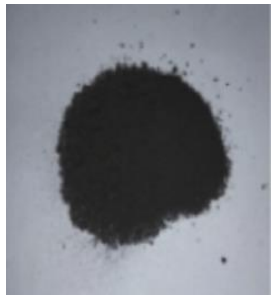
Sample study: HDD's NdFeB magnet.

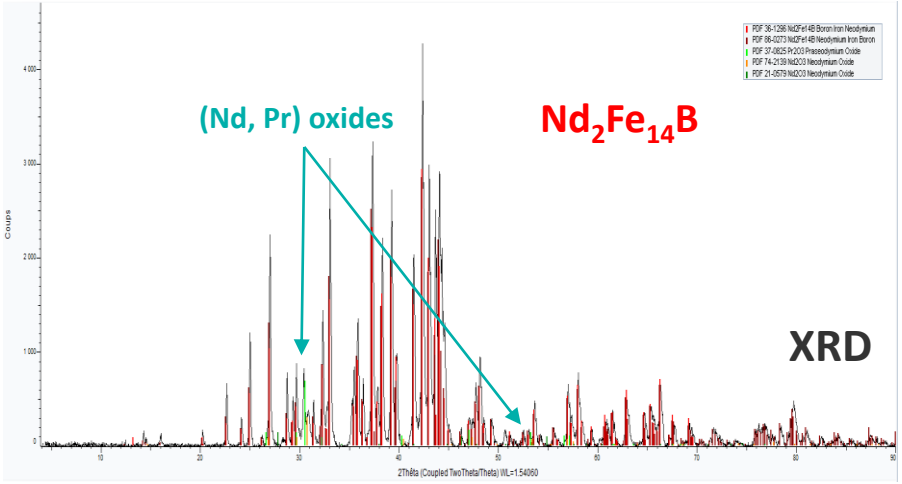


$Nd_2Fe_{14}B$

REE-rich intergranular phase

Ball milled in inert gas to avoid pyrophoric character and minimize oxidation.





Element	B	Co	Dy	Fe	Nd	Ni	Pr
% wt	0.9	1.5	1.2	62.6	22.8	0.6	3.3

LEACHING OF NDFEB POWDER USING ORGANIC ACIDS

In a hydrometallurgical process, leaching is the process of dissolving certain metals from the ore or waste.

Mineral acid, such as: H_2SO_4, HCl, HNO_3

$TR_{(s)} + 6H^+_{(aq)} \leftrightarrows TR^{3+}_{(aq)} + 6H_{2(g)}$

$TR_2O_{3(s)} + 6H^+_{(aq)} \leftrightarrows 2TR^{3+}_{(aq)} + 3H_2O_{(g)}$

$TR(OH)_{3(s)} + 3H^+_{(aq)} \leftrightarrows TR^{3+}_{(aq)} + 3H_2O_{(l)}$

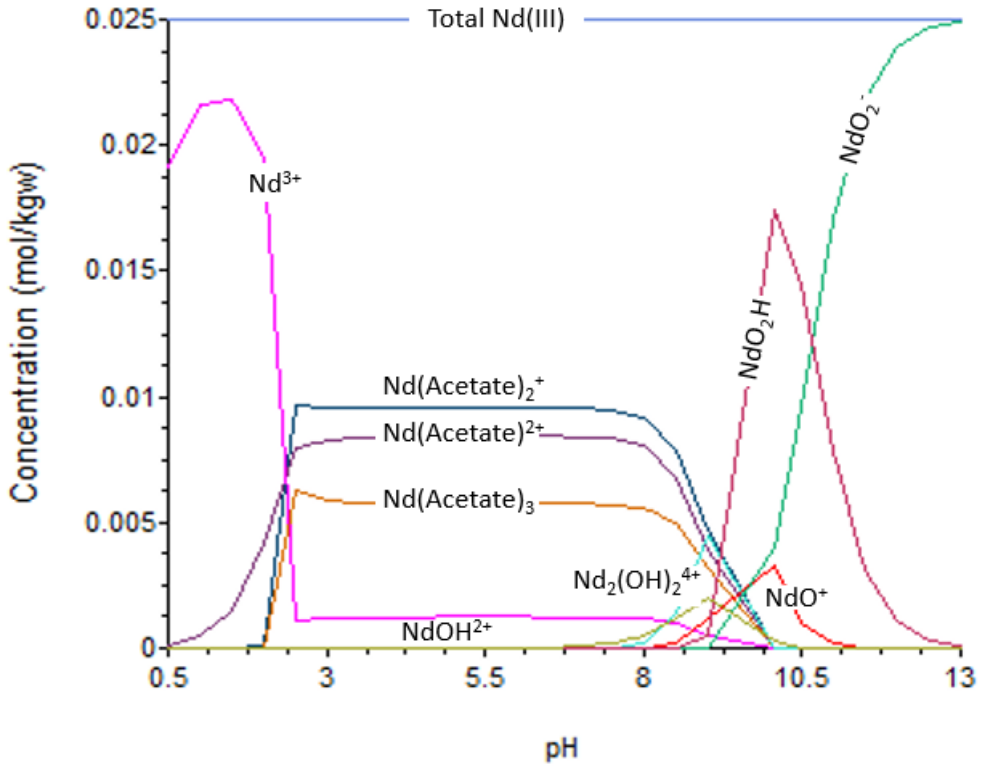
Eco-friendly alternatives: organic weak acids

Acetic acid : $Nd^{3+} + jCH_3COO^- \leftrightarrows Nd(CH_3COO)_j^{(3-j)+}$, j = 1, 2, 3

Citric acid : $nNd^{3+} + jH^+ + kCit^{3-} \leftrightarrows Nd_kH_jCit_k^{(3n+j-3k)}$

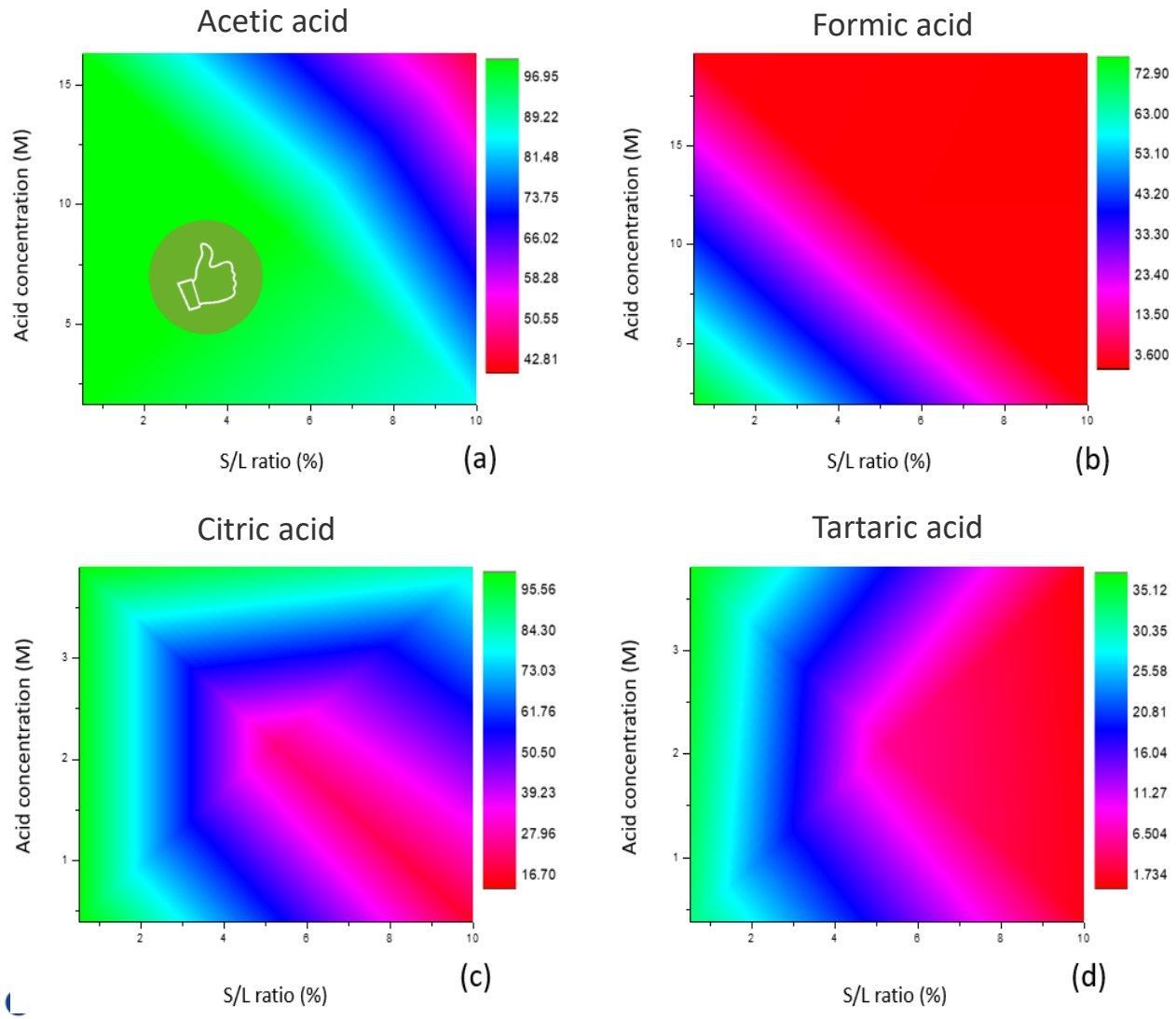
Presence of NdCit, NdHCit, $NdHCit_2$, $NdCit_2$ in a pH range of [2-5].

Easier to handle, form less toxic gases, easier biodegradability, possible production from agro-industrial waste…



Aqueous speciation of Nd(III) as a function of pH in diluted acetic acid using pHreeqC (Database: LLNL).

LEACHING OF NDFEB POWDER USING ORGANIC ACIDS



Nd, Pr and Dy have the same leaching behavior in all tested acids

Acetic acid: Best candidate for leaching REEs under industrially favorable conditions; high S/L ratios and low acid concentrations

> 90% of REEs leached:
S/L ratio (%) [0.5 - 5]
Acetic acid concentration (M) [1.6-10]

Partial/ total co-leaching of Fe, Co and B

Formic acid: Precipitation of REEs in formates
Tartaric acid: Precipitation of REEs in hydroxides

SELECTIVE LEACHING USING ORGANIC ACIDS

Patented results

Oxidative roasting of NdFeB powder

$2NdO + ½\ O_2 \rightarrow c\text{-}Nd_2O_3$

$Nd_2Fe_{14}B + 3/2\ O_2 \rightarrow 14\ \alpha\text{-}Fe + h\text{-}Nd_2O_3 + B$

$2\alpha\text{-}Fe + 3/2\ O_2 \rightarrow \alpha\text{-}Fe_2O_3$

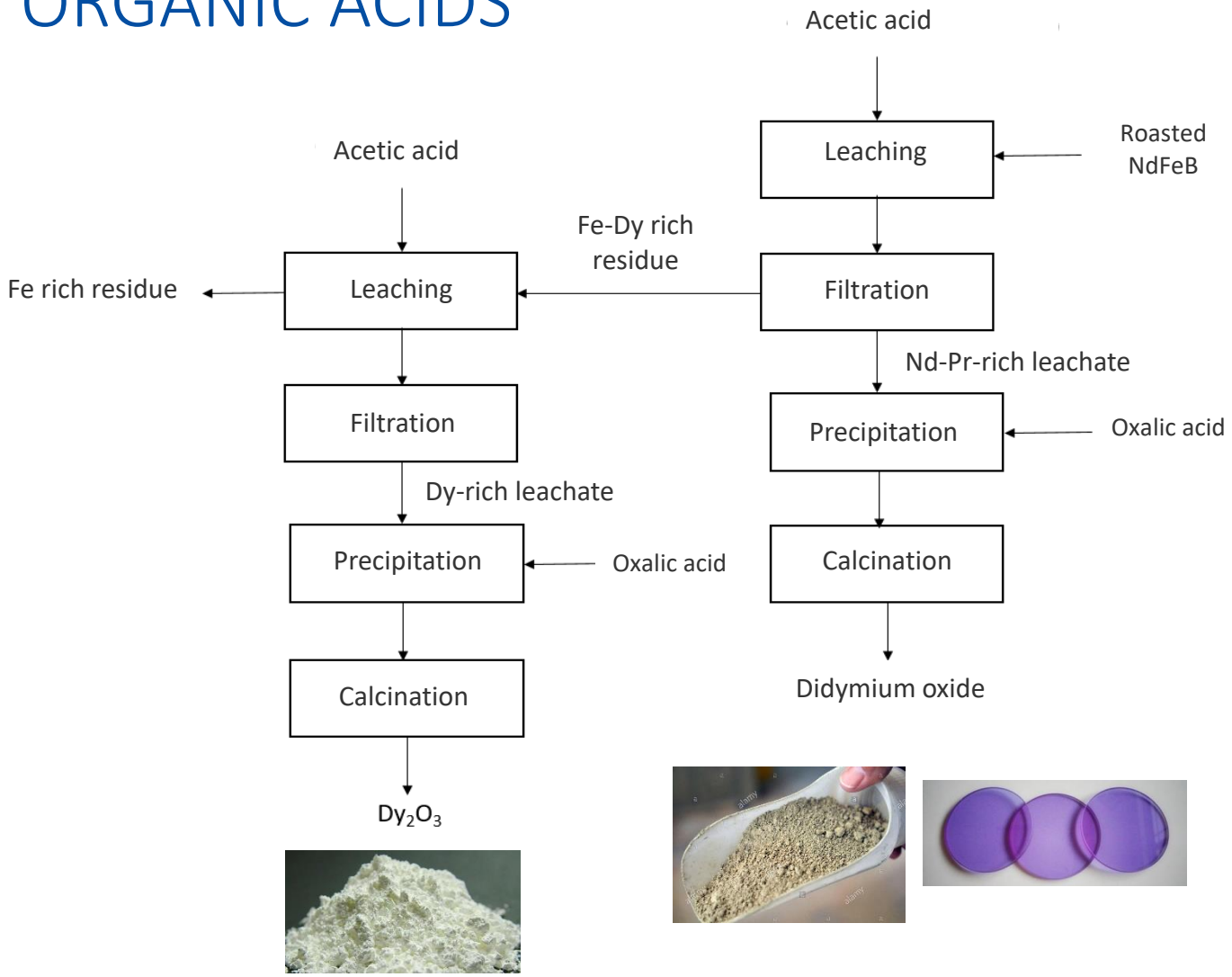
From 500°C:

$\alpha\text{-}Fe_2O_3 + h\text{-}Nd_2O_3 \rightarrow 2NdFeO_3$

Nd, Pr, Dy > 95%
Pureté > 99.9%

Feasibility verified from oxides

Ongoing studies on NdFeB magnets

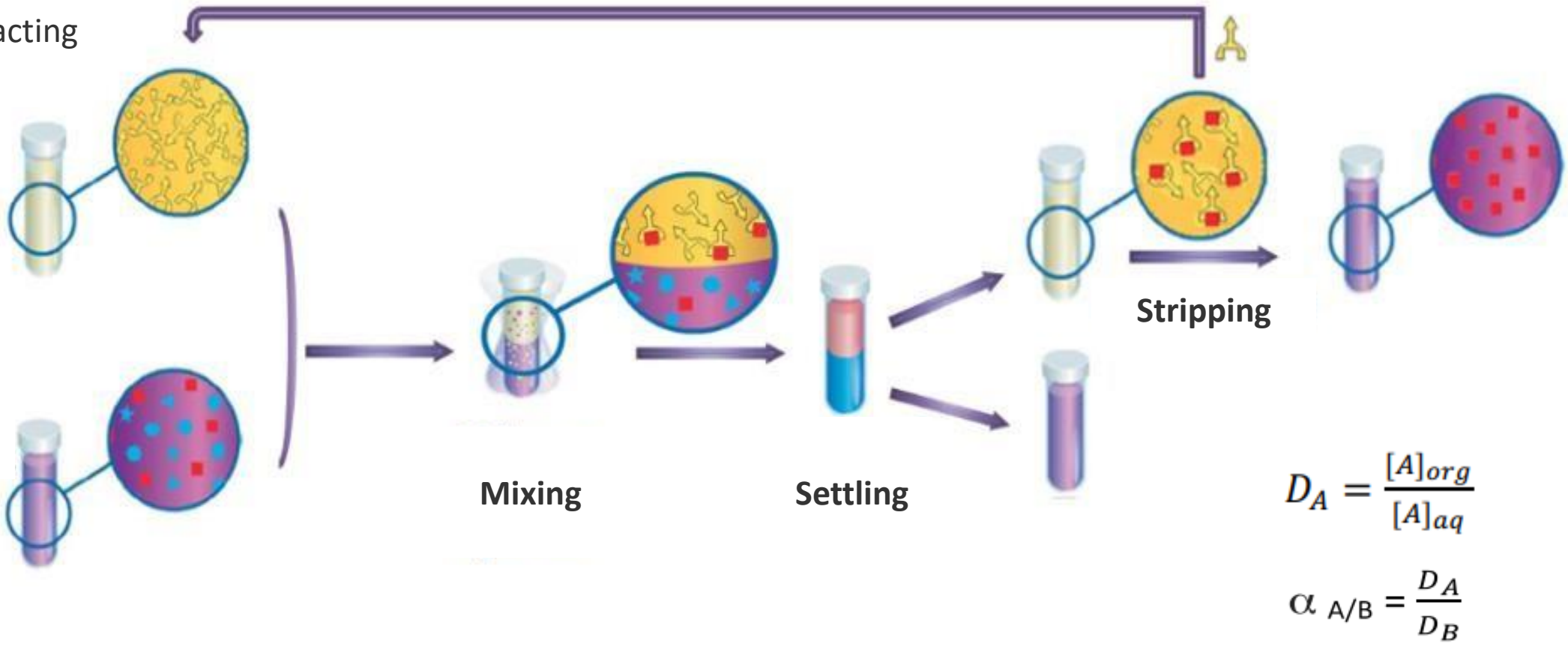


SOLVENT EXTRACTION ON ORGANIC ACID LEACHATES

Organic phase
Containing extracting molecules

Aqueous phase
Containing metallic cations

Metallic cations of interest



$$D_A = \frac{[A]_{org}}{[A]_{aq}}$$

$$\alpha_{A/B} = \frac{D_A}{D_B}$$

CONCLUSIONS AND PERSPECTIVES

Characterization

- Microstructure: Matrix phase ($Nd_2Fe_{14}B$), intergranular phase (REEs oxides)
- Chemical composition: 63% Fe, 23% Nd, 1% Dy, 3% Pr, 1% B

Leaching

- Acetic acid: Efficient weak acid to leach REEs in favorable conditions
- Feasible intra-REEs selective leaching on oxidized NdFeB powder

Thank you for your attention

Questions?