Innovation and sustainable engineering

Montviel Hydrometallurgy

Presented by
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SIGNIFICANT REDUCTION IN HYDROCHLORIC ACID CONSUMPTION IN RARE EARTH EXTRACTION FROM FERROCARBONATITE (MONTVIEL PROJECT)

• Introduction
• Montviel flotation concentrate
• Acid consumption
• Thermal treatment
• Weak-acid wash
• Weak-acid regeneration
• HCl leaching
• REE recoveries
• Energy and economy
Extractive metallurgy process of rare earth elements (REEs)

- Low-cost simple flowsheet
- Acid consumption: OPEX, CAPEX
- Low grade REE in ore
- Other reagents

The acid consumption in different projects

- Average: 500 kg/T ROM HCl 100% i

Minimizing the acid consumption is a critical priority

Table 1 – X-ray diffraction analysis of the head sample (Montviel)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>% Quantity</th>
<th>Mineral chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ankerite/Dolomite(Mn)</td>
<td>74.7</td>
<td>Ca(Mg,Fe,Mn)CO₃</td>
</tr>
<tr>
<td>Calcite</td>
<td>3.7</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Siderite</td>
<td>9.1</td>
<td>FeCO₃</td>
</tr>
<tr>
<td>Quartz</td>
<td>4.8</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Petersenite (Ce)</td>
<td>1.7</td>
<td>Na₄Ce₂(CO₃)₅</td>
</tr>
<tr>
<td>Allanite-(Ce)</td>
<td>1.1</td>
<td>Ca₁.₂₆Ce₀.₇₄Al₁.₈₃Fe₁.₁₇(SiO₄)₃(OH)</td>
</tr>
<tr>
<td>Burbankite</td>
<td>3.4</td>
<td>(Na;Ca)₃(Sr;Ba;Ce)₃(CO₃)₅</td>
</tr>
<tr>
<td>Celestine-Ba</td>
<td>0.2</td>
<td>SrSO₄</td>
</tr>
<tr>
<td>Biotite</td>
<td>0.9</td>
<td>K(Mg,Fe)₃<a href="OH,F">AlSi₃O₁₀</a>₂</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.4</td>
<td>(Mg,Fe)₅Al(Si₂Al)O₁₀(OH)₈</td>
</tr>
</tbody>
</table>

Table 2 – Montviel’s flotation concentrate elemental assay

<table>
<thead>
<tr>
<th>Element</th>
<th>% Elemental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>21.53</td>
</tr>
<tr>
<td>Ba</td>
<td>6.52</td>
</tr>
<tr>
<td>Sr</td>
<td>2.35</td>
</tr>
<tr>
<td>Ca</td>
<td>6.65</td>
</tr>
<tr>
<td>Mg</td>
<td>3.77</td>
</tr>
<tr>
<td>Mn</td>
<td>2.76</td>
</tr>
<tr>
<td>Si</td>
<td>1.12</td>
</tr>
<tr>
<td>Nb</td>
<td>0.21</td>
</tr>
<tr>
<td>TREE</td>
<td>3.99</td>
</tr>
</tbody>
</table>

How much acid required to extract +99% REE?
CONVENTIONAL LEACHING TECHNIQUES

- Direct leaching: **293 kg HCl (100%)/T ROM** to attain +99% REE

HCl Consumption distribution for +99% REE recovery,
Total Acid Consumption: 293 kg HCl (100%)/T ROM

How to save some acid value? 44% to Fe, 44% to AEM
Simplified set of reactions (Decomposition and oxidation)

- \((\text{AEM})\text{CO}_3 (s) \Rightarrow (\text{AEM})\text{O} (s) + \text{CO}_2 (g)\), AEM = Ca, Mg, Ba, Sr. \(\Delta H < 0\)
- \(2\text{FeCO}_3 (s) + 1/2\text{O}_2 (g) \Rightarrow \text{Fe}_2\text{O}_3 (s) + 2\text{CO}_2 (g)\) \(\Delta H > 0\)
- \(3\text{LnFCO}_3 (g) \Rightarrow \text{Ln}_2\text{O}_3 (s) + \text{LnF}_3 (s) + 3\text{CO}_2 (g)\)

Roasting (Calcination)

- Peak temperature: 900 °C
- Particle size: P80 = 53 mm
- LOI: 32%
- REO grade: 4.4% w/w
- Retention time
- Endothermic or exothermic
- Mild sintering!
- Multiple hearth roasting / Fluidized-bed

Less stable (active) CaO and MgO
More stable Ferric oxide
Remove active metals from the calcined concentrate

- \((\text{AEM})\text{O} (s) + 2 \text{ HA (aq)} \rightleftharpoons (\text{AEM})\text{A}_2 (aq) + \text{H}_2\text{O}\)  
  \text{AEM} = \text{Ca, Mg, Ba, Sr}

- Maximum AEM removal (water solubility)
- Minimum REE loss
- Regenerate
- Toxicity, handling, etc.

Weak acid regeneration reaction

- \((\text{AEM})\text{A}_2 (aq) + \text{CO}_2 (g) + \text{H}_2\text{O} \rightarrow (\text{AEM})\text{CO}_3 (s) + 2 \text{ HA(aq)}\)

A proper weak acid is chosen
WEAK ACID-WASH (RESULTS)

• Weak acid-wash elemental recoveries in filtrate:

<table>
<thead>
<tr>
<th>Element</th>
<th>% Elemental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>93.1</td>
</tr>
<tr>
<td>Mg</td>
<td>61.4</td>
</tr>
<tr>
<td>Ba</td>
<td>65.3</td>
</tr>
<tr>
<td>Sr</td>
<td>74.5</td>
</tr>
<tr>
<td>Mn</td>
<td>2.76</td>
</tr>
<tr>
<td>REE loss</td>
<td>0.98</td>
</tr>
</tbody>
</table>

• REO grade: 5.4% w/w
• MP: 55% of FC mass (Porous particles)
• Full HA recovery
• No pressurized vessel
• Energy source: Roasting
• CO\textsubscript{2} emotion mitigation
• HCl leaching of washed concentrate:
  191 kg HCl(100%)/T ROM
• 1% REE lost

35% HCl saved due to weak acid-wash

HCl Consumption distribution for +99% REE recovery,
Total Acid Consumption: 191 kg HCl(100%)/T ROM
REE LEACHING

- Particles average mass loss: 55%
- 67% of leachable is ferric iron oxide
- Pyrochlore and Silicate
- Regrinding and magnetic separation?
  - Yes: REO and Nb goes to non-mag
  - No: There are some REE loss
- Mild HCl Leaching
  - \[ 2y \text{HCl} + \text{Mi}_x\text{O}_y \rightarrow x\text{MiCl}_{2y/x} + y \text{H}_2\text{O} \]
  - \( \text{Mi} = \text{Fe, REE, Mn, Ca, Mg, Ba, Sr, Al, U, Th} \)
- \( \text{FeCl}_3 \) Leaching
  - \[ 2y/3 \text{FeCl}_3 + \text{Me}_x\text{O}_y + y \text{H}_2\text{O} \rightarrow x\text{MeCl}_{2y/x} + 2y/3 \text{Fe(OH)}_3 \]
  - \( \text{Me} = \text{REE, Ca, Mg, Ba, Sr} \)
  - Final pH = 1-2
  - Kinetics: T= 80°C - 90°C, atmospheric
  - Combination of two reactions
  - Bestowed to weak acid wash
    - HCl reacts with Fe in early stages
    - Leaching with \( \text{FeCl}_3 \) is dominant later

**Calcined and washed concentrate**

**PLS color: Low iron content**

**Black magnetic \( \text{Fe}_2\text{O}_3 \)**

**Reddish brown non-mag: \( \text{Fe(OH)}_3 \)**

**FeCl\textsubscript{3} leaches active metal oxides. How much Acid?**
HCl consumption (kg/T ROM) for +99% REE

• Direct leaching: 293 kg/T ROM
• Optimized leaching after weak acid wash: 63.2 kg/T ROM

Features

• 20% of HCl used for REE (5X of RECl₃)
• Less corrosivity in leaching reactor
• Less impurities in PLS simplifies downstream units

### Typical Acid leach recoveries based on FC

<table>
<thead>
<tr>
<th>Element</th>
<th>%Elemental</th>
</tr>
</thead>
<tbody>
<tr>
<td>REE</td>
<td>95.5</td>
</tr>
<tr>
<td>Ba</td>
<td>18.4</td>
</tr>
<tr>
<td>Sr</td>
<td>34.3</td>
</tr>
<tr>
<td>Ca</td>
<td>18.8</td>
</tr>
<tr>
<td>Mg</td>
<td>6.2</td>
</tr>
<tr>
<td>Mn</td>
<td>7.3</td>
</tr>
<tr>
<td>Al</td>
<td>99.3</td>
</tr>
<tr>
<td>Fe</td>
<td>1.5 – 5.5</td>
</tr>
</tbody>
</table>

### PLS I: Direct HCl leaching

<table>
<thead>
<tr>
<th>Element</th>
<th>PLS I gr/l</th>
<th>PLS II gr/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>REE</td>
<td>11.37</td>
<td>11.42</td>
</tr>
<tr>
<td>Fe</td>
<td>32.00</td>
<td>3.89</td>
</tr>
<tr>
<td>Mg</td>
<td>8.22</td>
<td>0.95</td>
</tr>
<tr>
<td>Ca</td>
<td>24.10</td>
<td>3.23</td>
</tr>
<tr>
<td>Ba</td>
<td>12.8</td>
<td>2.85</td>
</tr>
<tr>
<td>Sr</td>
<td>11.5</td>
<td>2.26</td>
</tr>
<tr>
<td>Other (ppm)</td>
<td>61.39</td>
<td>56.9</td>
</tr>
<tr>
<td>Sum (gr/l)</td>
<td>100.85</td>
<td>25.9</td>
</tr>
<tr>
<td>REE/Total</td>
<td>11.27%</td>
<td>45.5%</td>
</tr>
</tbody>
</table>

78.4% HCl saved compared to direct leaching
Mining: 2500 T/D ROM
Flotation: 92.6% REE in 45.5% MP
Chlor-Alkali is proposed to produce HCl and NaOH
Bases: NaOH, NaHCO₃, Na₂CO₃
Nb extraction with HCl in an autoclave reactor (No HF)
Solvent extraction for Nb recovery
Essential reagents are produced and regenerated on site
Potentially fully powered by electricity

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| Reagents for leaching and precipitation of REE, Montviel Hydrometallurgy, 2500 T/D ROM |
|----------------------------------------|----------------------------------------|
|                                       | Direct HCl leaching                     |
|                                       | Current process                         |
|                                        | Kg/T ROM                                | kg/T ROM |
| HCl (100%)                             | 293                                    | 63.2     |
| Base (NaOH)                            | 321                                    | 69.3     |
| Oxalic Acid                            | 17.3-86.5                              | -        |

Energy and economy estimation of leaching section, major units

<table>
<thead>
<tr>
<th></th>
<th>Direct HCl Leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Modified leaching process</td>
</tr>
<tr>
<td></td>
<td>M$</td>
</tr>
<tr>
<td></td>
<td>M$</td>
</tr>
<tr>
<td>Chlor-Alkali</td>
<td>150ii</td>
</tr>
<tr>
<td></td>
<td>40iii</td>
</tr>
<tr>
<td>Calciner</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>6iv</td>
</tr>
<tr>
<td>Ammoniation</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10iii</td>
</tr>
<tr>
<td>Total</td>
<td>150 M$</td>
</tr>
<tr>
<td></td>
<td>56 M$</td>
</tr>
<tr>
<td>Saving</td>
<td>94 M$</td>
</tr>
<tr>
<td>Saving %</td>
<td>62.6%</td>
</tr>
</tbody>
</table>
## Montviel Hydrometallurgy

### Montviel rare-earth elements and niobium recoveries

<table>
<thead>
<tr>
<th>Rare earth elements</th>
<th>Pre-concentrate</th>
<th>Hydrometallurgy</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum</td>
<td>92.7%</td>
<td>97.9%</td>
<td>90.7%</td>
</tr>
<tr>
<td>Cerium</td>
<td>92.9%</td>
<td>95.2%</td>
<td>88.4%</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>93.9%</td>
<td>98.3%</td>
<td>92.3%</td>
</tr>
<tr>
<td>Neodymium</td>
<td>93.0%</td>
<td>97.9%</td>
<td>91.0%</td>
</tr>
<tr>
<td>Samarium</td>
<td>91.0%</td>
<td>95.6%</td>
<td>87.0%</td>
</tr>
<tr>
<td>Europium</td>
<td>89.9%</td>
<td>96.0%</td>
<td>86.3%</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>88.6%</td>
<td>90.2%</td>
<td>79.9%</td>
</tr>
<tr>
<td>Terbium</td>
<td>83.8%</td>
<td>91.7%</td>
<td>76.8%</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>74.1%</td>
<td>84.8%</td>
<td>62.8%</td>
</tr>
<tr>
<td>Niobium</td>
<td>92.2%</td>
<td>71.7%</td>
<td>66.1%</td>
</tr>
</tbody>
</table>

### Montviel simplified process block diagram

- **Mine**
- **Pump**
- **Truck Ramp**
- **Waste Pad**
- **Ore Pad**
- **Crusher**
- **Silo**
- **FLOTATION**
- **CALCINATION**
- **MAGNETIC**
- **Leach**
- **Beneficiation**
- **Impurities precipitation**
- **Evaporation**
- **Regeneration**
- **Leach Solution**
- **REE Precipitation**
- **Paste Backfill**
- **50% +**
- **To Paste fill Plant**
- **To Storage Fill**
- **Leach Residue**
- **NIOBNIUM product**
- **REE CONCENTRATE**

### Note

58 kg HCl/Ton ROM
• Iron and alkaline earth metals consume 88% of HCl in direct leaching of Montviel ferrocarbonatite.

• Calcination:
  • activates AEM-carbonates to AEM-oxides.
  • converts Fe$^{II}$ to Fe$^{III}$.

• AEM-oxide is removable by a viable weak acid

• Mild HCl leaching extracts REE from ferric oxide rich concentrate

• FeCl$_3$ leaches REE and AEM-oxides effectively, leaving Fe(OH)$_3$ in residue.

• Energy consumption and CAPEX reduced.

• Downstream purification and precipitation is enhanced.

**Proper calcination is the key**
Question?

Please join us tomorrow for the next presentation on
REE Separation
15:40
SEPARATION AND PURIFICATION OF RARE-EARTH ELEMENTS BASED ON ELECTROPHORETIC MIGRATION

• Introduction to electrophoresis
• Capillary electrophoresis
• Free flow electrophoresis
• Separation results
• Concentration / Fractionation
• Remarks and conclusion
Electrophoresis: The differential movement or migration of ions relative to a fluid by attraction and repulsion in an electric field based on ion charge/size (electrophoresis mobility)

INTRODUCTION

What is ELECTROPHORESIS?

ELECTROPHORESIS SEPRATION: THE BASICS?

➤ Migration velocity:

\[ v = \mu_{ep} E = \mu_{ep} \frac{V}{L} \]

Where:
- \( v \) = migration velocity of charged particle (cm sec\(^{-1}\))
- \( \mu_{ep} \) = electrophoretic mobility (cm\(^2\) V\(^{-1}\) sec\(^{-1}\))
- \( E \) = field strength (V cm\(^{-1}\))
- \( V \) = applied voltage (V)
- \( L \) = length of capillary (cm)

➤ Electrophoretic mobility:

\[ \mu_{ep} = \frac{q}{6\pi \eta r} \]

Where:
- \( q \) = charge on ion
- \( \eta \) = viscosity
- \( r \) = ion radius

Frictional retarding forces
**ELETROPHORETIC MOBILITIES OF REE IONS**

Complex formation in the buffer:

- REE Electrophoretic mobilities without complexation \(\text{(Var: 0.07)}\)

- REE Electrophoretic mobilities with comp \(\text{(Var: 0.45)}\)

Chelate

Weak acids

Stronger retardation force

Solvation is more effective that hydration

<table>
<thead>
<tr>
<th>Ion</th>
<th>(\mu \times 10^8) (m²/Vs)</th>
<th>(\mu \times 10^8) (m²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La³⁺</td>
<td>7.23</td>
<td>4.77</td>
</tr>
<tr>
<td>Ce³⁺</td>
<td>4.52</td>
<td></td>
</tr>
<tr>
<td>Pr³⁺</td>
<td>4.35</td>
<td></td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>4.24</td>
<td></td>
</tr>
<tr>
<td>Sm³⁺</td>
<td>3.96</td>
<td></td>
</tr>
<tr>
<td>Eu³⁺</td>
<td>3.83</td>
<td></td>
</tr>
<tr>
<td>Gd³⁺</td>
<td>3.74</td>
<td></td>
</tr>
<tr>
<td>Tb³⁺</td>
<td>6.90</td>
<td>3.51</td>
</tr>
<tr>
<td>Dy³⁺</td>
<td>3.34</td>
<td></td>
</tr>
<tr>
<td>Ho³⁺</td>
<td>3.22</td>
<td></td>
</tr>
<tr>
<td>Er³⁺</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>Tm³⁺</td>
<td>2.93</td>
<td></td>
</tr>
<tr>
<td>Yb³⁺</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>Lu³⁺</td>
<td>6.70</td>
<td>2.67</td>
</tr>
</tbody>
</table>

CAPILLARY ELECTROPHORESIS (CE)

Molecules separate based on their size ($r$) and charge ($Q$):

$$
\mu = \frac{v}{E} = \frac{Q}{6\pi \eta r}
$$

Anion (-)
Neutral
Cation (+)

Light source
Electric field
Photocathode

Data in
Data out

Ab (280µm)
Time (min)
Migration time (min)

1.0  1.4  1.8  2.2  2.6  3.0  3.4

La (1.59 min)  Ce (1.68 min)  Pr (1.75 min)  Nd (1.79 min)  Sm (1.90 min)  Eu (1.97 min)  Gd (2.03 min)  Tb (2.15 min)  Dy (2.26 min)  Ho (2.35 min)  Er (2.47 min)  Tm (2.59 min)  Yb (2.78 min)  Lu (2.85 min)

Sensor at 310 mm
Temperature: 15 °C
Voltage >25 kV

Lanthanides simultaneous separation in 30 cm capillary

Free flow zone electrophoresis
FREE FLOW ELECTROPHORESIS

- Continuous laminar flow of buffer
- Electric field is perpendicular to the flow
- Different deflections of ions under EF due to their effective electrophoretic mobilities

http://www.igb.fraunhofer.de/
Free flow electrophoresis ("FFE") was developed in the 1960s by Kurt Hannig at the Max-Planck-Institute in Germany.
FFE developments focused on the separation of proteins and charged particles.

Source: www.ffeservice.com
SEPARATION TESTS 2014

- Mix REE solution
- Complexing agent
- Some op. condition
GéoMégA SEPARATION RESULTS

Demonstration series

Sample Composition
- Europium (33%)
- Lanthanum (33%)
- Ytterbium (33%)

Sample Composition
- Europium (17%)
- Lanthanum (66%)
- Ytterbium (17%)

Sample Composition
- Europium (17%)
- Lanthanum (17%)
- Ytterbium (66%)

Sample Composition
- Europium (33%)
- Lanthanum (33%)
- Ytterbium (33%)

lanthanides (rare earth metals)
Heavy REE tend to separate within a single-pass easily.
Concentration (C/C₀)

Mixture B (Eu, Nd, Pr and La)

Laminar flow

Neighbour series

Mixture B+
(Nd and Pr)

Laminar flow

Sample Composition
- Europium (10%)
- Neodymium (40%)
- Praseodymium (40%)
- Lanthanum (10%)

Sample Composition
- Neodymium (40%)
- Praseodymium (40%)

Sample Composition
- Neodymium (40%)
- Praseodymium (40%)

lanthanides (rare earth metals)
GéoMégA SEPARATION RESULTS

Neighbor series

**Neighbour series – Mixture C**

REE Concentration (%)
- Europium (10%)
- Praseodymium (40%)
- Cerium (40%)
- Lanthanum (10%)

**Mixture C** (Eu, Pr, Ce and La)

**Mixture C+** (Pr and Ce)

**Laminar flow**

**Mixed Pr/Ce**

**Mixed Pr/Ce**

**GéoMégA**

**SEPARATION RESULTS**

**Neighbour series**

**Separation channel**

**Concentration (C/C₀)**

**Concentration (C/C₀)**

**REE Concentration (%)**
- Praseodymium (40%)
- Cerium (40%)

**Separation channel**

**Concentration (C/C₀)**

**REE Concentration (%)**
- Europium (10%)
- Praseodymium (40%)
- Cerium (40%)
- Lanthanum (10%)

**La** (lanthanum) 138.9
**Ce** (cerium) 140.9
**Pr** (praseodymium) 144.2
**Nd** (neodymium) 144.2
**Pm** (promethium) 145
**Sm** (samarium) 150.4
**Eu** (europium) 152.0
**Gd** (gadolinium) 157.3
**Tb** (terbium) 158.9
**Dy** (dysprosium) 162.5
**Ho** (holmium) 164.9
**Er** (erbium) 167.3
**Tm** (thulium) 168.9
**Yb** (ytterbium) 173.0

† 4f
Figure 1 - REE Concentrate (All Elements)

Single pass
7 cm width channel
Figure 2 - REE Concentrate (Y Axis Scaled)

- Commercial concentrate
- Single pass
- 7 cm width channel

Concentration (%)
- Lanthanum (25.82%)
- Cerium (49.78%)
- Praseodymium (5.83%)
- Neodymium (16.22%)
- Samarium (1.23%)
- Europium (0.18%)
- Gadolinium (0.37%)
- Dysprosium (0.05%)
- Yttrium (0.05%)
- Ytterbium (0.01%)
- Calcium (0.14%)
- Strontium (0.07%)
Free Flow Electrophoresis (FFE)

Challenges regarding single pass FFE

- Multi-element channels
- Dilution

Focusing and Fractionation !!!

A single channel separation unit
BINARY IONINC FRACTIONATION OF REE USING FFE

Concentration electrodes

Separation electrodes
ELECTROPHORETIC REE SEPARATOR (EREES1)

Latest status in 2016

- Two working prototypes
- Higher throughput
- Cost of unit: one tenth of 2014
- 18 fold higher REE concentration
- Energy saving

Current activities

- Design: Electric field and flow
- Increasing the throughput per unit
- Chelate agent
- pH and temperature
- Energy
Continuous separation in solution

Preparative capacity, up to gram per hour

Low losses of material to be separated

Potentially high purity separation

Simultaneous separation of constituents and impurities

Easier on HREE

Powered by electricity
Question?
MULTICOMPONENT IONIC FRACTIONAL SEPARATION (FFE)

Diagrammatic view of a multistage reactor

Phase I

Phase II

Phase III

Step I

Step II