Hydrothermal Pre-Treatment Process of Phosphogypsum for Enhanced Rare Earths Recovery

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Hydrothermal pre-treatment process of phosphogypsum for enhanced rare earths recovery
Phosphogypsum (PG) and Rare Earths

Phosphate ore + $\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{PO}_4 + \text{CaSO}_4 \cdot n\text{H}_2\text{O}$

"Wet phosphoric acid process"

- $n = 2 : \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- $n = \frac{1}{2} : \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
- $n = 0 : \text{CaSO}_4$

- 70% to 90% of REEs originally in phosphate ore end up in PG;
Phosphogypsum (PG) as a source of REE

Phosphate ore + $H_2SO_4 \rightarrow H_3PO_4 + CaSO_4\cdot nH_2O$

“Wet phosphoric acid process”

- $n = 2 : CaSO_4\cdot 2H_2O$
- $n = \frac{1}{2} : CaSO_4\cdot \frac{1}{2}H_2O$
- $n = 0 : CaSO_4$

- 70% to 90% of REEs originally in phosphate ore end-up in PG;
- Average REEs content in PG between 0.27 wt.% and 0.8 wt.%;
- PG considered a secondary resource for REEs

<table>
<thead>
<tr>
<th></th>
<th>Worldwide</th>
<th>In South Africa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG dumps, t</td>
<td>&gt;7 billion</td>
<td>&gt;70 million</td>
</tr>
<tr>
<td>Current growth rate, t/a</td>
<td>150-200 million</td>
<td>13,000-20,000</td>
</tr>
</tbody>
</table>
Methods for REE recovery from PG

- Chemical conversion to CaCO$_3$, REE$_3$CO$_3$, (NH$_4$)$_2$SO$_4$

- Bio-technologies
  - Bio-enhanced leaching
  - Sulphate reduction

- Leaching
  - HNO$_3$
  - HCl
  - H$_2$SO$_4$

- Resin-in-Leach process developed and piloted at Mintek (2011-2012):
  @ a price of >$21/kg for mixed REE oxide @ an overall recovery of 15%
  economics may already be favourable; BUT implementation requires significant financial investment
Non-destructive methods most attractive BUT…

REE recovery varies from 5 to 80 % depending on:

- Origin of the raw material (apatite);
- Specifics of the wet-phosphoric process;
- Age of the sample and conditions of storage

“Recoverable REE”

“Locked REE”
Recovery of REE from PG: problem statement

The Problem
- PG is highly variable
- Low and variable REEs recovery

Research Question
How can REEs associated with PG be “unlocked” and lead to increased recovery?

Upfront limitations:
- minimum use of reagents & generation of as little waste as possible
- conversion of PG into a saleable product
Approach followed…

- Construction industry uses “dry” and “wet” methods for natural gypsum conversion into hemihydrate

- Apply two approaches to modify gypsum and then

- Recover REEs from the modified PG, and for comparison, from the as received (unmodified) PG

- If found to be successful => confirm efficiency on various samples

Sources of PG:

- Rustenburg (initial testwork)
- Richards Bay
- Phalaborwa
**PG modification and REE extraction**

**Phosphogypsum “as received”**

**“Dry” conversion:**
calcining @ 100°C for 24 hrs

**“Wet” conversion:**
autoclaving @ 120°C for 5 hrs
(10% m/m solids)

**REE recovery:**
20 % (m/m) solids,
ambient temperature,
100 g/L H₂SO₄,
24 hrs residence time
SEM: (a) PG “as is”, (b) after “dry” and (c) “wet”
REE leaching from PG “as is” and after conversion

Wet/hydrothermal way of PG modification =>

- distinct change of crystals structure,
- liberation of REE phases and
- noticeable increase in recovery of REE in subsequent leach
Recovery of REE from variability samples

- Rustenburg
- Richards Bay
- Phalaborwa I
- Phalaborwa II

REE recovery
- as-received
- converted

Before modification
Encapsulated REE

After modification
Liberated REE phase
To address economics of REE recovery

Parameters/options to be optimized/tested:

- Temperature
- Solids content
- Residence time
- Slow cooling/flash cooling
- Subsequent REE phases upgrade via magnetic separation or flotation
- Hydrothermal treatment of PG => α-hemihydrate – better product for construction industry

Autoclaving @ 120°C
Hydrothermal conversion and construction industry

**Giulini process** (2 plants in Western Germany & 1 in Ireland):

- Feed - PG;
- Operating temperature - 120°C;
- Residence time – 1.5-2 hrs;
- pH 1-3
- Seeding
- Additives to control size and shape of α-hemihydrate (sulfite waste liquor or surface active substances)
- Filtration, drying and grounding

<table>
<thead>
<tr>
<th>Material and process requirements per ton of α-hemihydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam LP (tons)</td>
</tr>
<tr>
<td>0.4-0.6</td>
</tr>
</tbody>
</table>
Hydrothermal conversion and construction industry

**Imperial Chemical Industries, Inc. (ICI) α-hemihydrate process** (semi-industrial process):

- Operating temperature - 150°C;
- 50 %(m/m) solids;
- Residence time – 3 minutes;
- 2 autoclaves;
- Crystal modifiers;
- Centrifuge for crystals separation at 100°C

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**Material and process requirements per ton of α-hemihydrate**

<table>
<thead>
<tr>
<th>PG  (tons)</th>
<th>HP Steam (tons)</th>
<th>Electric power (KWh)</th>
<th>Water (tons)</th>
<th>Effluent (tons)</th>
<th>Extent of conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.22</td>
<td>0.35</td>
<td>45</td>
<td>1.5</td>
<td>1.7</td>
<td>70-80</td>
</tr>
</tbody>
</table>
Flowsheets under consideration

PG → Hydrothermal pre-treatment, pH 1 → S/L → IX → REE liquor

H$_2$SO$_4$

α-hemihydrate

PG → Hydrothermal pre-treatment, water → Centrifuging → Physical separation (S/S) → REE concentrate

water

REE concentrate

α-hemihydrate
Conclusions

• During formation of phosphogypsum REE are partially locked in the gypsum structure => high REE recoveries require either complete dissolution of gypsum matrix or its recrystallization

• Hydrothermal modification process used in construction industry to produce α-hemihydrate releases up to 80% of REE associated with PG

• Further optimization testwork and evaluation of economics of the optimum flowsheet is required to confirm viability of simultaneous recovery of REE and production of high quality alpha-hemihydrate for construction industry
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Title of paper: Hydrothermal modification of phosphogypsum to improve subsequent recovery of rare earth elements