Recovery of REE from an apatite concentrate in the nitrophosphate process of fertilizer production

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RECOVERY OF REE FROM AN APATITE CONCENTRATE IN THE NITROPHOSPHATE PROCESS OF FERTILIZER PRODUCTION

Mahmood Alemrajabi, Kerstin Forsberg, Åke Rasmuson
Outline

• Introduction
• Process description
• Digestion
• Cooling Crystallization
• Partial Neutralization
• Selective Precipitation
• Conclusion
Introduction

✓ Nitrophosphate process

✓ Integrated recovery of REE

✓ Governing parameters on concentration of REE in precipitates

✓ CaO: P2O5 ratio (0.25 - 1) and final pH

✓ More environmental friendly process and new source for REE
REE Recovery Unit

Digestion

Conversion of CNTH

Nitric acid

Cooling Crystallization

Partial Neutralization

NH3 gas

REE

NP- acid Solution

NP solution at higher pH

Neutralization

K salts

Evaporation & Particulation

NPK Fertilizer

Apatite
Apatite concentrate from LKAB

Apatite (Ca$_5$(PO$_4$)$_3$(F,Cl,OH)) is one of the REE rich minerals ending up in the tailings pond when Luossarvaaara-Kiirunavaara AB (LKAB) in Sweden processes Malmberget and Kirunas iron ore deposits.

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<th>Element or Ratio</th>
<th>Unit</th>
<th>Amount</th>
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<tr>
<td>Fe</td>
<td>mass%</td>
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<tr>
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</tr>
<tr>
<td>Ce</td>
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<tr>
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<td>As</td>
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Particle sizes: < 500 µm
Previous study (Forsberg K.M., 2014)

- Leaching parameters (Temperature, Particle size, Acid concentration and residence time)

Fig. 1 – Leaching in HNO$_3$ at 60°C
- Residues: 3 wt. % HREE, 97 wt. % LREE
- Concentrate: 29 wt. % HREE, 71 wt. % LREE

Fig. 2 – Leaching in 5 mol/L HNO$_3$
Ca$_5$(PO$_4$)$_3$F + 10 HNO$_3$ → 5 Ca(NO$_3$)$_2$ + 3 H$_3$PO$_4$ + HF

Elements recovery in 10 mol/L nitric acid (20% excess)

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<tr>
<th>Element</th>
<th>Ce</th>
<th>Y</th>
<th>Nd</th>
<th>La</th>
<th>Ca</th>
<th>P</th>
<th>Fe</th>
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<td>99</td>
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Different tests

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<th>Test No.</th>
<th>Initial acid Con. (mol/L)</th>
<th>Liquid/Solid ml/g</th>
<th>Temp °C</th>
<th>CNTH Elimination %</th>
<th>Seeding</th>
<th>CNTH particle size µm</th>
<th>CaO:P2O5</th>
<th>Final pH</th>
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<td>2.4</td>
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<td>2.1</td>
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Seeded cooling crystallization of Ca(NO₃)₂·4H₂O (CNTH)

CNTH concentration in NP acid solution during the cooling Crystallization

CNTH Crystallization and dissolution in HNO₃-H₃PO₄ medium
CaO : P2O5 ratio during the elimination of Ca

Less than 1 % by mass of total REE coprecipitated with CNTH crystals in both quick cooling and low cooling rare test
Partial Neutralization

Ammonium hydroxide 25% as precipitation agent

- By the pH 1.8 more than 95% of the REEs has recovered
- Different trend can be seen for HREE and LREE
  Solubility products study and Powder XRD analysis The REE are precipitated as Phosphates
✓ Early coprecipitation of REE with CaHPO4 in test 4
✓ The precipitates contain 0.04 mass% in test 4 at pH 1.2 and 2.07 mass% in test 1 at pH 2.18

✓ Ce elimination trend is almost the same in test 1 & 2
✓ Late precipitation of REE in test 3 and Forsberg results
✓ Precipitates contain 2.07 and 1.63 mass% REE in Test 1 and 2 in CaO:P2O5 ratio of 1.15 and 1.54
✓ In test 3 at pH 1.8 the precipitates contain 9.94 mass% REE
Effect of pH and Ca concentration on REE precipitates

In test 3 the precipitates in pH 1.8 contain 9.8 mass% of REE and 1 mass% in pH 2.1

REE mass % in precipitates versus CaO:P₂O₅ ratio in pre-neutralization solution in test 1

99.9 mass% of REE has been recovered in each point
Conclusions

✓ Less than 1% of REEs coprecipitated with CNTH crystals during cooling crystallization.

✓ CNTH Crystallization process reach the equilibrium after 2hr in NP-acid solution.

✓ The REE could be effectively separated from the leach solution by precipitation with ammonium hydroxide.

✓ The final pH where the partial neutralization is stopped and Ca elimination both play an important role in determining the content of REE in the precipitates.

✓ pH 1.8 is the optimum pH for stopping the partial neutralization.
Our research group

Crystallization

Supported liquid membrane extraction

Chromatography

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