Transforming phosphogypsum waste into products with market value

Ron Zevenhoven¹
& Victor Morales-Flórez²,³, Alberto Santos⁴, Luis Esquivias²,³

¹ Åbo Akademi University, Åbo/Turku, Finland
² University of Seville, Seville, Spain
³ Institute of Materials Science, ICMS (CSIC/US), Seville, Spain
⁴ University of Cádiz, Puerto Real, Spain
Production of phosphoric acid from apatite or fluorapatite rock, main reactions:

\[
\begin{align*}
Ca_3(PO_4)_2(s) + 3H_2SO_4(l) + 6H_2O(l) & \rightarrow 2H_3PO_4(l) + 3CaSO_4 \cdot 2H_2O(l) \\
Ca_5(PO_4)_3F(s) + 5H_2SO_4(l) + 10H_2O(l) & \rightarrow 3H_3PO_4(l) + 5CaSO_4 \cdot 2H_2O(l) + HF(l)
\end{align*}
\]

Worldwide 100 - 280 Mt phosphogypsum are produced annually

Only \sim 15\% finds use in e.g. construction or agriculture due to often too high levels of contaminants and possible radioactivity

May also contain rare earth elements and other valuable materials

Annual worldwide production amount of phosphogypsum can bind 26 - 72 Mt CO\textsubscript{2}, producing materials with market value
Phosphogypsum in Spain and Finland

Huelva ~ 120 Mt pile after depositing during 1968 - 2010

Siilinjärvi ~ 55 Mt pile, adding ~ 1.5 Mt/year currently, operating since 1979

~ 1200 ha

~ 60 ha
PG processing using ammonium

1. CaSO₄·2H₂O(s) + CO₂(g) + 2NH₃(aq) → CaCO₃(s) + 2NH₄⁺(aq) + SO₄²⁻(aq) + H₂O(l)

2. 2NH₄⁺(aq) + SO₄²⁻(aq) → (NH₄)₂SO₄ (s) + H₂O(l)

1.3 kg CO₂ + 1 kg NH₃ + 5.1 kg PG → 3.9 kg AS + 2.9 kg PCC + 0.6 kg H₂O

3. Removal of radionuclides from CaCO₃ PCC (not yet)
Process concepts work in Spain

**PG processing using alkaline soda**

1. **NaOH**
   - Phosphogypsum + Water
     - Solid
     - Liquid
     - Water vapor
   - Filter
2. **Ca(OH)₂**
   - Solid
   - Dissolution
3. **CaCO₃**
4. **Na₂SO₄**

**PG processing with aluminium-rich alkaline waste**

1. Aluminium-rich liquid waste
   - Filter
   - Liquid
2. **Water + CO₂**
   - Weathering
   - Solid
   - Bubbling
   - Solid
3. **CaCO₃ + Al(OH)₃** (primarily)

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Conclusions and outlook

- Phosphogypsum can be processed using routes that bind CO$_2$
- Calcium carbonate with a chosen size, quality and morphology can be produced with several process routes, while:
  - Valuable sulphate salts are produced as by-products
  - Levels of impurities must be reduced and controlled
  - Rare earth metals separation must be studied in more detail

- An overall evaluation of process carbon footprint and other environmental impacts must be performed: LCA
- The future: an HORIZON 2020 application & a demonstration plant