Phosphate Rock Beneficiation through Production of DCP “Super-Rock” as a Raw Material for Phosphoric Acid Plants

Sébastien Havelange

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Phosphate Beneficiation IX

Phosphate Rock Beneficiation through Production of DCP “Super-Rock” as a Raw Material for Phosphoric Acid Plants

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Prayon Technologies - Licensing Division of Prayon S.A.

June 8th, 2022
Agenda

1. Prayon Technologies as part of Prayon Group
2. Processes
3. DCP super-rock VS Standard Rock in traditional plants
4. Conclusion
Prayon Technologies
The licensing division of Prayon S.A.
Prayon Group – World Map

4 Production Sites and 3 R&D Centers

- ENGIS (BELGIUM)
- PUURS (BELGIUM)
- AUGUSTA (USA)
- ROCHELLES (FRANCE)
- VARNA (BULGARIA)

- 4 production sites
- 3 R&D centers (test facilities)
- 6 regional sales offices
- 7 commercial subsidiaries
- more than 100 local representative offices

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2 Core Activities in the Phosphates Chemistry

PHOSPHATES APPLICATIONS

- Technical application
  -prayphos
  -praybrite
  -polyplay
  - fluopray
  -fosping

- Food phosphates
  -karbopel
  - carlosel
  - fortipray
  - praylev
  -prayphos

- Agriculture & horticulture
  - hortipray

PHOSPHATES TECHNOLOGIES

Licensing Division of Prayon

Equipment Division of Prayon

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Processes

Sustainability of Phosphate Resources
Prayon Technologies - Process Portfolio

« Trusted Technologies for a Sustainable Future »

**Phosphoric Acid Production**
- Dihydrate (DH)
- Hemihydrate (HH)
- DH Attack / HH Filtration (DA-HF)
- Central-Prayon Process (CPP)
- Hemi – Dihydrate (HH-DH)

**Sustainability / Circular Economy**
- Low-grade rock – Ecophos
- Low-grade rock – GetMoreP
- Spent acids
- Secondary P-sources

**MCP/DCP Production**
- DCP – Ecophos
- DCP – GetMoreP
- MCP Process

**Gas Treatment**
- Fluorine Recovery
- Gas Scrubbing

**Purification**
- PUMA - Membrane Filtration
- Desulfation
- Heavy Metals (As, Cd...) removal

**Fertilizer grade**
**Feed grade**
**Food/Technical grade**

DCP Super-Rock

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Sustainability of Phosphate Resources – Rock Quality

Traditional Phosphoric Acid Process

“High-Grade” Rock

PHOSPHATE

OTHERS

M.E.*

SILICA

Prayon Technologies

DH
HH
DA-HF
CPP
HDH

* Minor Elements (M.E.) = Al, Fe, Mg

Traditional Phosphoric Acid Process

“Low-Grade” Rock

PHOSPHATE

OTHER IMPURITIES

MINOR ELEMENTS*

SILICA

Prayon Technologies

DH
HH
DA-HF
CPP
HDH

* Minor Elements = Al, Fe, Mg

Chemical Beneficiation Process

“Low-Grade” Rock

PHOSPHATE

OTHER IMPURITIES

MINOR ELEMENTS*

SILICA

Prayon Technologies

DH
HH
DA-HF
CPP
HDH

* Minor Elements = Al, Fe, Mg

Solution: Production of a DCP « Super-Rock »

Direct Phosphoric Acid Production from Low-Grade Rock meets the following challenges:

- Filtration affected by the high viscosity
- Formation of gel at the concentration stage
- Post precipitation and scaling

GetMoreP Ecophos

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Ecophos Process

Hydrochloric Acid-based technology:
- Use of low- to high-grade P-sources
- Loop process
- Each module: 1 reaction + 1 filtration
- Use of standard quality or spent HCl / H2SO4
- High quality DCP product up to 41% P2O5
- Low level of impurities in the DCP (MER, F, heavy metals...)
- Co-product Gypsum recoverable in the plaster/cement industry (down to 0.1% P2O5)
- Co-product Calcium Chloride recoverable in the market
- High recovery efficiency (up to 90% or more, depending on the phosphate rock)
Ecophos Process

Module 1A

- Solubilization of the phosphate rock with HCl:

\[
\begin{align*}
\text{Ca}_3(\text{PO}_4)_2 + 4 \text{HCl} & \rightarrow \text{Ca(H}_2\text{PO}_4)_2 + 2 \text{CaCl}_2 \\
\text{Ca(H}_2\text{PO}_4)_2 + 2 \text{HCl} & \rightarrow 2 \text{H}_3\text{PO}_4 + \text{CaCl}_2
\end{align*}
\]

- Ca(H$_2$PO$_4$)$_2$ is the MCP
- Impurities stay as undigested rock and/or precipitate after reaction
- Possibility to precipitate the fluorine (under CaF$_2$ form) by adding CaCO$_3$ (but impact on P$_2$O$_5$ yield)
- Typical P$_2$O$_5$ yield >80-90% even with preneutralization of fluorine
- Separation of liquid and solids using press filters
Ecophos Process

Module 1B
- Neutralization of liquid MCP with CaCO$_3$ to produce the DCP:
  \[ \text{Ca(H}_2\text{PO}_4\text{)}_2 + \text{CaCO}_3 + 3 \text{H}_2\text{O} \rightarrow 2 \text{CaHPO}_4\cdot2\text{H}_2\text{O} + \text{CO}_2 \]
  - DCP recovered by vacuum filtration
  - This wet DCP (CaHPO$_4\cdot2$H$_2$O) is the “super rock” phosphate
  - P$_2$O$_5$ yield >95% for Module 1B
Ecophos Process

Module CCP

- “Calcium Chlorine Purification”
- Fed with liquid fraction from Module 1B filtration
- Ca(OH)$_2$ is added for promoting the precipitation of any remaining P$_2$O$_5$ and precipitation of other metal contaminants by pH increase
- Solids are recovered by press filtration
Module 4

- Option depending on willingness to recycle HCl
- Back conversion of the purified CaCl₂ into HCl:

\[
\text{CaCl}_2 + \text{H}_2\text{SO}_4 (+ 2 \text{H}_2\text{O}) \rightarrow 2 \text{HCl} + \text{CaSO}_4.2\text{H}_2\text{O}
\]

- Gypsum and hydrochloric acid are separated by vacuum filtration
- Gypsum produced is very pure and suitable for usage in plaster or cement industry
DCP « Super-Rock » vs Sedimentary Rock

Through the chemical beneficiation (Ecophos), the MER goes down from 22% to < 1%

<table>
<thead>
<tr>
<th></th>
<th>Sedimentary Rock</th>
<th>DCP “Super-Rock”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al ppm</td>
<td>6404</td>
<td>73</td>
</tr>
<tr>
<td>C Total ppm</td>
<td>-</td>
<td>173</td>
</tr>
<tr>
<td>CaO %</td>
<td>40.9</td>
<td>32.3</td>
</tr>
<tr>
<td>Cd ppm</td>
<td>0.8</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Ce ppm</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>CO₂ %</td>
<td>-</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Cr ppm</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>D50 avec US µm</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>F ppm</td>
<td>26800</td>
<td>898</td>
</tr>
<tr>
<td>Fe ppm</td>
<td>6155</td>
<td>776</td>
</tr>
<tr>
<td>K ppm</td>
<td>2930</td>
<td>38</td>
</tr>
<tr>
<td>La ppm</td>
<td>-</td>
<td>&lt; 2.5</td>
</tr>
<tr>
<td>Mg ppm</td>
<td>32400</td>
<td>487</td>
</tr>
<tr>
<td>Na ppm</td>
<td>2137</td>
<td>364</td>
</tr>
<tr>
<td>Ni ppm</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>P₂O₅ %</td>
<td>24.6</td>
<td>41.2</td>
</tr>
<tr>
<td>SiO₂ %</td>
<td>16.70</td>
<td>0.06</td>
</tr>
<tr>
<td>SO₄²⁻ %</td>
<td>0.88</td>
<td>0.48</td>
</tr>
<tr>
<td>Ti ppm</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>U₃O₈ ppm</td>
<td>-</td>
<td>17</td>
</tr>
</tbody>
</table>
DCP “Super-Rock” vs Sedimentary Rock
Showcase
Note: DCP « Super-Rock » can be used as a raw material in all Phosphoric Acid processes (DH, HH, DA-HF, CPP, HDH)
Use of DCP « Super-Rock » - Sulfuric Acid Consumption

According to the analysis of our raw material, the ratio CaO / P₂O₅ is significantly lower for DCP super-rock compared to standard phosphate rocks:

- Ratio CaO / P₂O₅ = 0.78 (DCP super-rock)
- Ratio CaO / P₂O₅ = 1.30 (igneous Russian rock)
- Ratio CaO / P₂O₅ = 1.80 (sedimentary Algerian rock)

Using this DCP as phosphate source leads to a decrease of the Sulfuric Acid consumption:

- H₂SO₄ 100% = 1.45 t/t P₂O₅ (DCP super-rock)
- H₂SO₄ 100% = 2.90 t/t P₂O₅ (igneous Russian rock)
- H₂SO₄ 100% = 3.25 t/t P₂O₅ (sedimentary Algerian rock)
The quality of the Weak Phosphoric Acid (at the outlet of the filter) is significantly improved considering the use of DCP super-rock instead of the rock as is.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weak Acid from Rock</th>
<th>Weak Acid from DCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>kg/m³</td>
<td>1500</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>w/w%</td>
<td>37.9</td>
</tr>
<tr>
<td>CaO</td>
<td>w/w%</td>
<td>0.17</td>
</tr>
<tr>
<td>SO₂</td>
<td>w/w%</td>
<td>1.8</td>
</tr>
<tr>
<td>F</td>
<td>ppm</td>
<td>11700</td>
</tr>
<tr>
<td>K₂O</td>
<td>ppm</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td>ppm</td>
<td>200</td>
</tr>
<tr>
<td>SiO₂</td>
<td>ppm</td>
<td>6700</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>ppm</td>
<td>4600</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>ppm</td>
<td>6600</td>
</tr>
<tr>
<td>MgO</td>
<td>ppm</td>
<td>23700</td>
</tr>
<tr>
<td>Traces:</td>
<td>ppm</td>
<td>1.75</td>
</tr>
<tr>
<td>Cadmium</td>
<td>ppm</td>
<td>-</td>
</tr>
<tr>
<td>Cesium</td>
<td>ppm</td>
<td>-</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>ppm</td>
<td>-</td>
</tr>
<tr>
<td>Thorium</td>
<td>ppm</td>
<td>-</td>
</tr>
<tr>
<td>Strontium</td>
<td>ppm</td>
<td>-</td>
</tr>
<tr>
<td>U₂O₇</td>
<td>ppm</td>
<td>-</td>
</tr>
</tbody>
</table>

Post-precipitation is reduced and concentration stage is simplified.
Use of DCP « Super-Rock » - Concentration Stage

The strength of the Weak Phosphoric Acid is driven by its viscosity (amount of impurities) and impact on the filtration ratio:

- $\text{MER} < 0.01 \rightarrow 45.3\% \ P_2O_5$ (DCP super-rock)
- $\text{MER} = 0.09 \rightarrow 37.9\% \ P_2O_5$ (sedimentary rock)

For the same purpose (high viscosity), it might be impossible to reach the MGA (54\% \ P_2O_5).

Assuming that the concentration to 54\% is possible without formation of a gel, the Steam consumption at the concentration will be:

- LP Steam = 0.42 t/t \ P_2O_5 (DCP super-rock)
- LP Steam = 0.92 t/t \ P_2O_5 (sedimentary rock)

It means that the steam consumption is doubled if the plant is fed with sedimentary rock instead of DCP.
The quality of the co-product Gypsum (at the outlet of the filter) is significantly improved considering the use of DCP super-rock instead of the rock as is. It can be used in cement and plaster applications.

**Use of DCP « Super-Rock » - Co-Product Gypsum Quality**

**Figure 8 - Typical Gypsum Sample**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Gypsum from Rock</th>
<th>Gypsum from DCP</th>
<th>Spec. Plaster</th>
<th>Spec. Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total water (wet basis)</td>
<td>-</td>
<td>37.0</td>
<td>7 -14</td>
<td>6 - 12</td>
</tr>
<tr>
<td>Crystal water w/w%</td>
<td>-</td>
<td>19.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P$_2$O$_5$ w/w%</td>
<td>0.64</td>
<td>0.168</td>
<td>&lt;0.5</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>CaO w/w%</td>
<td>30.68</td>
<td>32.65</td>
<td>-</td>
<td>31 - 33</td>
</tr>
<tr>
<td>SO$_3$ w/w%</td>
<td>43.02</td>
<td>-</td>
<td>&lt;45.00</td>
<td>44 - 46</td>
</tr>
<tr>
<td>F ppm</td>
<td>800</td>
<td>47</td>
<td>-</td>
<td>&lt;7000</td>
</tr>
<tr>
<td>K$_2$O ppm</td>
<td>200</td>
<td>&lt;30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$O ppm</td>
<td>400</td>
<td>175</td>
<td>&lt;3200 Na salts &lt;0.06</td>
<td>-</td>
</tr>
<tr>
<td>SiO$_2$ ppm</td>
<td>50500</td>
<td>&lt;1000</td>
<td>-</td>
<td>&lt;10000</td>
</tr>
<tr>
<td>Al$_2$O$_3$ ppm</td>
<td>700</td>
<td>&lt;100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ ppm</td>
<td>200</td>
<td>43</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MgO ppm</td>
<td>100</td>
<td>&lt;40</td>
<td>Mg salts &lt;0.1</td>
<td>-</td>
</tr>
<tr>
<td>Traces:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium ppm</td>
<td>-</td>
<td>&lt;0.5</td>
<td>&lt;2</td>
<td>-</td>
</tr>
<tr>
<td>Cerium ppm</td>
<td>-</td>
<td>14.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lanthanum ppm</td>
<td>-</td>
<td>&lt;10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Thorium ppm</td>
<td>-</td>
<td>&lt;2.5</td>
<td>&lt;2.5</td>
<td>-</td>
</tr>
<tr>
<td>Strontium ppm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>U$_3$O$_8$ ppm</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Gypsum total quantity produced is also lowered (due to lower CaO/P$_2$O$_5$ ratio in the DCP)
Due to the low amount of impurities in the DCP, the amount of solids in the Concentrated Phosphoric Acid is significantly reduced:

- Solids CPA = 0.2% w/w (DCP super-rock)
- Solids CPA = 1.9% w/w (sedimentary rock)

The risk of post-precipitation in the CPA is also much lower.
Use of DCP « Super-Rock » - Other Advantages

Many other advantages:

- Residence time can be reduced by 2 thanks to higher reactivity
  - Smaller equipment for a same capacity
  - OR double capacity in a same equipment
- Filtration performance is significantly improved due to the shape of the calcium sulphate crystals
- Fluorine content in DCP super rock is reduced compared to standard rock:
  - Simplified attack, hydration & filtrations scrubbing systems
  - Higher quality of the cooling water
  - Simplified concentration unit (no need or simplified FSA recovery)
  - Reduction of the abrasion and corrosion in the vacuum circuit and in the plant in general
- Lower silica content in the DCP super rock compared to standard rock:
  - Fluorine & Silica precipitating in the process is negligible
  - Hard-scaling significantly reduced (no fluosilicates/ no silica deposit)
  - Reduction of the abrasion of rotating equipment (agitators / pumps)
  - Lower maintenance costs
Conclusions
Conclusions

The Ecophos process can be seen as a chemical beneficiation process for rocks with high $P_2O_5$ efficiency and valuable co-product

DCP produced through Ecophos process can be seen as a « Super-Rock » for feeding traditional phosphoric acid plants with lots of advantages:

- a lower sulfuric acid specific consumption (< 1.5 t/t $P_2O_5$ for HH/DH)
- a lower gypsum production (< 2.5 t/t dry DH)
- a higher-quality product acid (high $P_2O_5$, low MER, low solids, low heavy metals content)
- a higher process efficiency (> 99% vs > 97% $P_2O_5$ recovery for HH/DH)
- a higher-quality gypsum ($P_2O_5 < 0.2\%$, low radioactivity) valuable in the cement and plaster industry
- a lower steam consumption at the evaporation stage (< 0.5 t/t $P_2O_5$ for HH/DH)
- a significant reduction of the maintenance costs (low scaling, low abrasion /corrosion)
- an increase of design capacity (by almost +100%) considering the same equipment
THANK YOU FOR YOUR ATTENTION!

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