New Development in Dihydrate -Hemihydrate processes: The new Prayon DA-HF process

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Prayon

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New Development in Dihydrate - Hemihydrate processes: The new Prayon DA-HF process
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5. Conclusion
**Introduction**

\[
[\text{Ca}_3(\text{PO}_4)_2] + 3 \text{H}_2\text{SO}_4 + x \text{H}_2\text{O}
\]

3 \(\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} + 2 \text{H}_3\text{PO}_4 + \text{heat}\)

or

3 \(\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O} + 2 \text{H}_3\text{PO}_4 + \text{heat}\)

<table>
<thead>
<tr>
<th>Single Crystal</th>
<th>Double crystal Single filter</th>
<th>Double crystal Double filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydrate (DH)</td>
<td>Di attack – Hemi Filtration (DA-HF)</td>
<td>Dihydrate-Hemihydrate (CPP)</td>
</tr>
<tr>
<td>Hemihydrate (HH)</td>
<td>Hemi Re-Crystalisation (HRC)</td>
<td>Hemihydrate-Dihydrate (HH-DH)</td>
</tr>
</tbody>
</table>

From P. Becker, Phosphates and phosphoric acid
Introduction

• Plant revamping
  • Double crystal processes considered
  • Profitability limited by investment level
    • Extra filtration;
    • Extra conversion / crystallisation
• Prayon invests in R&D to improve plant efficiency and profitability
• One high newcomer: DA-HF process
From DH to CPP process

• 40 years ago
• Double crystal process
• Gypsum sealable
• Stacking issue solved
• 90% of gypsum sold
Dihydrate Process

Typical P$_2$O$_5$ Yield : 95%

- Phosphate
- H$_2$SO$_4$ 98%
- Recycled acid
- Attack
- Digestion
- Phos acid 28% P$_2$O$_5$
- Water
- Filter
- Dihydrate

- Typical
- 28% P$_2$O$_5$
- 2,5% SO$_3$
Dihydrate Process

H₂SO₄ 98%

Phosphate

Recycled acid

Attack
Digestion

Phos acid

Filter

Water

Dihydrate
Stability regions of CaSO$_4$ hydrates

From P. Becker, Phosphates and phosphoric acid
Central-Prayon Process

Typical $\text{P}_2\text{O}_5$ Yield: 98%

- $\text{H}_2\text{SO}_4$ 98%
- Phosphate
- Recycled acid
- Attack
- Digestion
- Phos acid 32% $\text{P}_2\text{O}_5$
- Conversion
- DIHYDRATE
- Typical 32-35% $\text{P}_2\text{O}_5$
- 1% $\text{SO}_3$
- HEMIHYDRATE
- Typical 28% $\text{P}_2\text{O}_5$
- 8% $\text{SO}_3$

Steam

Filter

Water

Hemi
• Advantages with respect to DH
  - P2O5 Recovery higher than 98%
  - Acid strength 32% \( P_2O_5 \) or higher
  - Dry gypsum obtained after rehydration

• Disadvantages with respect to DH
  - Higher capital cost (extra filter and conversion tank)
  - More complex operation
  - Somewhat higher maintenance costs
Looking for a New Process route:

Di Attack – Hemi Filtration

- **Phosphate**
  - **H$_2$SO$_4$ 98%**
  - **Recycled acid**

- **Conversion**
  - **Steam**

- **Filter**
  - **Water**
  - **Hemihydrate**

- **Hemi Filtration**
  - **28% P$_2$O$_5$$\rightarrow$ 32-36% P$_2$O$_5$$\rightarrow$ 8% SO$_3$$\rightarrow$ 3% SO$_3$
The DH – HH conversion limits
The DH –HH conversion limits

At very low sulfate content (0.2-0.4% sulphate)
Looking for a New Process route:

Di Attack – Hemi Filtration

- **Phosphate**
  - $\text{H}_2\text{SO}_4$ 98%

- **Recycled acid**

- **Conversion**

- **Steam**

- **Filter**

- **Hemihydrate**

- **Hemi Filtration**
  - 28% $\text{P}_2\text{O}_5$
  - 8% $\text{SO}_3$
  - 32-36% $\text{P}_2\text{O}_5$
  - 3% $\text{SO}_3$
Pilot tests

Several rocks tested successfully
- Morocco, Syrian, Jordan, Kola, Egypt...

e.g. Syrian rock

Rock analyses

- 28.3 % P$_2$O$_5$,
- 47.9 % CaO,
- 3 % F,
- 6.8 % CO$_2$, 
## Pilot test with Syrian rock

<table>
<thead>
<tr>
<th>Elements</th>
<th>Unit</th>
<th>Phosphate Rock</th>
<th>Gypsum (250°C basis)</th>
<th>Acid C2</th>
<th>Hémihydrate (250°C basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2O5T</td>
<td>% w/w</td>
<td>28,3</td>
<td></td>
<td>36,08</td>
<td>0,2</td>
</tr>
<tr>
<td>P2O5UN</td>
<td>% w/w</td>
<td>0,07</td>
<td></td>
<td>0,11</td>
<td></td>
</tr>
<tr>
<td>P2O5 CO</td>
<td>% w/w</td>
<td>1,57</td>
<td></td>
<td>0,09</td>
<td></td>
</tr>
<tr>
<td>% SO3</td>
<td>% w/w</td>
<td></td>
<td>3,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal water</td>
<td>% w/w</td>
<td>19,60</td>
<td></td>
<td>6,23</td>
<td></td>
</tr>
<tr>
<td>Efficiency</td>
<td>%</td>
<td></td>
<td></td>
<td>99%</td>
<td></td>
</tr>
<tr>
<td>Filtrability</td>
<td>tpdP2O5/m² (cycle 180s)</td>
<td></td>
<td></td>
<td>5,99</td>
<td></td>
</tr>
</tbody>
</table>
For these conditions:

the P$_2$O$_5$ process recovery is > 2% higher than DH
the filtration rate is about 20% - 30% better than DH
• Nominal capacity: 150 tpd \( \text{P}_2\text{O}_5 \)
• 4 compartments 225 m³
• Slurry cooled by flash cooler
• Filter: 40 m² useful – dry discharge
Industrial Test Design

Plant design – DA-HF
Test Results

- Quality of acid and gypsum
- Calcium sulphate filterability
- Efficiency
- Plant operation
**Test Results - Analyses with Moroccan Rock**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Unit</th>
<th>Rock Morocco</th>
<th>Acid DH</th>
<th>Gypsum (250°C basis)</th>
<th>Acid HH</th>
<th>Hemihydrate (250°C basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_2O_5$ WS</td>
<td>% w/w</td>
<td>30.7</td>
<td>37.4</td>
<td>32.85</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>$P_2O_5$ UN</td>
<td>% w/w</td>
<td></td>
<td></td>
<td>1.42</td>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>$P_2O_5$ CO</td>
<td>% w/w</td>
<td></td>
<td></td>
<td>0.59</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>Crystal water</td>
<td>% w/w</td>
<td></td>
<td></td>
<td>19.60</td>
<td></td>
<td>6.3</td>
</tr>
</tbody>
</table>
# Test Results - Filterability

<table>
<thead>
<tr>
<th></th>
<th>DH operation first test</th>
<th>DA-HF operation Morocco rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slurry temperature</td>
<td>°C</td>
<td>76</td>
</tr>
<tr>
<td>Filtrate Density</td>
<td>20°C</td>
<td>1.308</td>
</tr>
<tr>
<td>Filtration rate :</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atm. Pressure (local)</td>
<td>(mmHg)</td>
<td>760</td>
</tr>
<tr>
<td>Filter Vacuum</td>
<td>(mmHg)</td>
<td>500</td>
</tr>
<tr>
<td>Filtration cycle</td>
<td>(s)</td>
<td>180</td>
</tr>
<tr>
<td>Filtration rate</td>
<td>(TPD P$_2$O$_5$/m$^2$)</td>
<td>3.8</td>
</tr>
</tbody>
</table>
Test Results – DH Crystals

- Small individual crystals
- No clusters
- Slurry easy to pump
Test Results – HH Crystals

- Clusters
- Ball shape
- Aggregates easy to filter
Test Results – Efficiency

- Industrial values observed: 97 – 98%
- To be compared with a DH process results: 94-95%
Test Results – Plant Operations

- Some difficulties due to filter hopper not designed for HH operation (solids accumulation)
- Operators could easily operate the plant
- Start-up and shut downs are as easy as for DH process
- Flash cooler to be operated at lower pressure
Lessons learned for conversion of existing DH plant

<table>
<thead>
<tr>
<th></th>
<th>Check</th>
<th>Modify</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attack tank</td>
<td>Agitators,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cooling</td>
<td></td>
</tr>
<tr>
<td>Digestion tank</td>
<td>Agitator,</td>
<td>Steam injector</td>
</tr>
<tr>
<td></td>
<td>lining SA pipe</td>
<td>New tank</td>
</tr>
<tr>
<td>Filter</td>
<td>Barometric</td>
<td>prewash</td>
</tr>
<tr>
<td></td>
<td>legs</td>
<td>Sectors</td>
</tr>
<tr>
<td>Cake discharge</td>
<td>Hopper</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Conveying</td>
<td></td>
</tr>
<tr>
<td>Gas scrubber</td>
<td>capacity</td>
<td></td>
</tr>
</tbody>
</table>

Most DH plants can be converted to DA-HF technology
Profitability – preliminary study

- Profitability highly linked to local condition
  - Energy cost;
  - Utility cost;
  - Usage of gypsum;
  - Raw material cost.

- For a new plant producing MGA (500 tpd $P_2O_5$)
  - Investment cost similar
  - Lower steam, $P_2O_5$ consumption
  - Profitability 7 to 25% higher

- For a revamping (500 tpd $P_2O_5$)
  - Without capacity increase: 2 to 5 years depending local conditions (Raw mat and reagents prices; selling of gypsum...);
  - With capacity increase: payback of less than 2 years.
Concluding remarks

With the all the challenges ahead (raw materials, energy, environment) phosphoric acid production remains an exciting field for process developments
Thank you for your attention!