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Innovating for growth: Ensuring an efficient, sustainable future
Production of HF from $\text{H}_2\text{SiF}_6$

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Catalytic Gas-Liquid Reaction Technology
Dynamic Phosgene Production

Green Anode Plants
Fluorine Technology
Why use (FSA) to produce HF?

- Processing costs and investment costs of fluorspar processing plants will increase with decreasing fluorspar quality (Particle size and impurities are linked to each other)
- Lower fluorspar exports from China
- Producers with own high quality fluorspar sources and written off plants can continue to operate economically
- Investors in new plants should seriously consider the route from FSA
Fluorosilicic Acid – Potential for Anhydrous HF (AHF) Production

- Waste from the production of Phosphoric Acid (PA)
- Available in large amounts in PA producing plants
- Cheap raw material for production of fluorochemicals (It’s a waste!)
- Theoretically, the current production of AHF worldwide (approx. 2 mio t/a, almost entirely from fluorspar) could be produced with FSA as raw material
Fluorosilicic Acid (FSA) – Current Use

- Aluminium Fluoride (AlF₃), LBD
- Metal Fluorosilicates
- Drinking Water Fluorination
- Preservation of Timber
- Disinfection of brewery equipment
- Concrete Hardening (Magnesium Salt)
- Insecticide
Typical F Distribution in the Dihydrate Phosphoric Acid Process

**RAW MATERIALS**
- **P-Rock**
- Sulfuric Acid
- Water
- Off Gas
- Fluorosilicic Acid (FSA)

**REACTION**
- Gypsum
- $\text{CaSO}_4 \times 2\text{H}_2\text{O}$

**SCRUBBER**
- Fluorosilicic Acid (FSA)
- Off Gas and Fluorosilicic Acid (FSA)

**CONDENSER**
- Waste Water

**EVAPORATOR**

**FILTRATION**

**PRODUCT**
- **P-Acid** ca. 54%-wt
  - **Scrubbers** 55%
  - **Gypsum** 31.6%
  - **P-Acid** 3%
  - **Waste Water** 10%
  - **Off Gas** 0.4%
Two ways have been researched within the last six decades and have led to numerous patents.

- **DIRECT REACTION WITH SULPHURIC ACID**
- **REACTION WITH INTERMEDIATE SALT PRECIPITATION**
Reactions with Salt Precipitation

1. **Precipitation**
   - FSA
   - Salt, e.g. Sodium (Na), Ammonia

2. **Filtration**
   - Byproduct to disposal

3. **Drying**

4. **Reaction**
   - $\text{H}_2\text{SO}_4$ Concentration
   - $\text{H}_2\text{SO}_4$

5. **HF/SiF$_4$ Separation**
6. **HF to Liquefaction**

7. **HF Product**
• BCT cooperation with Polish company: small production plant with a capacity of 800 t/a
• Direct scale-up and process improvement lead to the first full scale industrial plant in China with 20,000 t/a HF production, Startup in 2008
• Two more industrial plants operating in China at capacities of 12,000 t/a and 20,000 t/a
• More plants in project status (worldwide incl. China)
BCT process – block diagram

- **FSA, 18%-wt**
- **H₂SO₄, 98%-wt**

**FSA Reaction**
(Split to HF and SiF₄)

- **Conc. FSA**
- **SiF₄**

**FSA concentration**

- **SiO₂**
- **SiO₂ Purification**
- **SiF₄ Purification**

**HF**

**H₂SO₄, 74%-wt**

**Recycle to P-Plant**

**Added value for P-Producer**

**Added value for P-Producer**

**SiO₂**

**SiO₂ Purification**
The BCT process – specs

- Simple and robust process
- Gas/Liquid reaction and process allows a very efficient purification section and thus high acid quality
  - Silica quality not as good as with intermediate salt process.
  - Usage: quality improvement for food grade phosphoric acid
  - Quality can be improved by production of waterglass

± Has to be erected adjacent to a phosphoric acid plant
± Diluted sulphuric acid pumped back to phosphoric acid plant
Scaling up from 800 to 20,000 t/a

- Mass balance of existing small plant by BCT
- Identification of bottlenecks in the existing plant

Results:
- Fluorine recovery found to be 60% of entire F
- SiF$_4$ losses were found to be too high and were reduced
- Absorption columns were optimised

Requirements for new design:
- H$_2$SO$_4$ flows re-routed to achieve better absorption
- Absorption columns interconnected differently, design changed
- Fluorine recovery 90%, SiF$_4$ losses 0.5% of SiF$_4$ produced
BCT Operating Full Scale Plants

- WengFu Lantian (Poland): 800 t/a capacity
- Fujian WengFu Lantian (Fujian): 12,000 t/a capacity
- Hubei WengFu Lantian (Hubei): 20,000 t/a capacity
# Product Quality – AHF from FSA

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<thead>
<tr>
<th>Mass Fraction, %-wt</th>
<th>Reference, %-wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHF ex FSA (BCT Reference Plant)</td>
<td>AHF from Fluorspar&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>HF</td>
<td>99.96</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.001 max.</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.005 max.</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SiF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.001 max.</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.001 max.</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.001 max.</td>
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<tr>
<td>As</td>
<td>0.0005 max.</td>
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<sup>1</sup>From Website of International Manufacturer
Summary

- BCT has successfully scaled up a process to manufacture Anhydrous Hydrogen Fluoride from FSA
- Process efficiency has been improved with regards to the highest possible fluorine recovery
- Plants in industrial scale operate successfully since 2008
- Quality of AHF is equal to that manufactured from fluorspar
- The process is cheaper in operation (Raw material costs) compared to the traditional process using fluorspar
- Make money with your waste
THANK YOU!

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