The Improved Hard Process: Technological Innovations Necessary for the Commercialization of the Kiln Phosphoric Acid Process

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A patented, transformational technology for phosphoric acid production

- 12,000 ton per year facility built in 2013 near Fort Meade
- Key aspects of technology have been demonstrated

IHP provides advantages across the value chain

- Uses low grade, higher impurity rock that expands reserves
- Lower Capex and Opex per ton of product than existing technology
- Produces higher quality super phosphoric acid
- IHP co-product is a useful aggregate (no phosphogypsum)
IHP as Originally Envisioned

- Low Grade Phosphate Rock
- Petroleum Coke
- Silica Sand
- Dryer
- Ball Mill
- Balling Drum
- Ported Kiln
- \( \text{P}_4\text{O}_{10} \) Gas
- J•ROX Commercial Aggregate
- High-Grade Phosphoric Acid

JDC Phosphate
Key Technological Innovations that Make IHP Commercial

• Silica control to avoid melting of feed stock in kiln and to lower reduction reaction temperatures

• Grind size control to improve reaction kinetics

• Heat treatment process that produces a low dust and higher purity feed agglomerate to the reduction kiln

• A ported rotary kiln designed to achieve high phosphorus yields with a high temperature reduction zone and a controlled oxidation zone
**Carbothermal Reduction of Phosphate**

\[
\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 9z\text{SiO}_2 + 15\text{C} \longrightarrow 9\text{CaO} \cdot (\text{SiO}_2)_z + 3\text{P}_2 + 15\text{CO} + \text{CaF}_2
\]

<table>
<thead>
<tr>
<th>Reaction, z</th>
<th>Silica Reaction Product</th>
<th>Temperature where Off-gas Partial Pressure &gt;1 Atm</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>CaSiO_3</td>
<td>1,252°C</td>
</tr>
<tr>
<td>0.5</td>
<td>Ca_2SiO_4</td>
<td>1,377°C</td>
</tr>
<tr>
<td>0</td>
<td>CaO</td>
<td>1,510°C</td>
</tr>
</tbody>
</table>

Silica Control - Thermodynamic Basis for IHP

- Changing calcia-silica composition of spent feed pellets during P reduction
- Colored boxes, required reduction temperature with formation of various end products
- Phase diagram of minerals formed at equilibrium
- Demo plant scale operations without melting

Grind Size Control – Reaction Kinetics

- Minimum of ~200 mesh required for reasonable kinetics
- Allows for proximity of carbon to phosphate particles
- Achieved and demonstrated at demo plant scale
- Recent data indicates a finer grind improves lower temperature kinetics and yield
Yield versus Residence Time at Various Reduction Temperatures

Fine Grind (80%-325) vs. Coarse Grind (80%-200)

- 325 at 1200 °C
- 200 at 1200 °C
Heat Treatment to Reduce Dust Potential in Kiln

- 5-10X hardening of agglomerates
- Occurs at temperatures below reduction
- Finer grind size improves strength
- Impurities are removed during the heat treatment
- Achieved at demo plant scale
Heat Treatment

\[ \text{CaCO}_3 + (1 + x) \text{SiO}_2 \rightarrow \text{CaSiO}_3 \cdot (\text{SiO}_2)_x + \text{CO}_2 \]

\[ T = 930 - 1,125 \, ^\circ\text{C} \]
\[ t > 30 \, \text{minutes} \]
Demo Plant Data: After Tumble Dust Generated

- **Indurated Pellets Fines 0.12% Average**
- **Non-Indurated Feed Pellets 1-3% Fines, 2% Average**

Graph showing After Tumble % dust generated over hours.
## Demo Plant Data: Induration Impurity Removal

<table>
<thead>
<tr>
<th></th>
<th>Pre-Induration*</th>
<th>Post-Induration*</th>
<th>% Reduction</th>
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</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>7,053</td>
<td>2,800</td>
<td>60</td>
</tr>
<tr>
<td>Arsenic</td>
<td>6.1</td>
<td>2.3</td>
<td>62</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2.2</td>
<td>0.2</td>
<td>91</td>
</tr>
<tr>
<td>Lead</td>
<td>6.0</td>
<td>0.2</td>
<td>97</td>
</tr>
<tr>
<td>Chloride</td>
<td>7,192</td>
<td>345</td>
<td>95</td>
</tr>
<tr>
<td>Fluoride (%)</td>
<td>1.5</td>
<td>1.2</td>
<td>20</td>
</tr>
</tbody>
</table>

*(Outside Lab Results - PPM except for %)*
Ported Rotary Kiln – Dual Zone System

- Kiln Phosphate Reduction Yields averaged < 50% with a max. of 80%
- Oxidation zone via porting system was proven and controlled
- Reduction zone burner not able to achieve 0% oxygen reduction conditions
  - Root cause of lower yields
  - High carbon burnout thus minimizing availability for phosphate reduction
Summary of Last Production Run

- Produced 6,000 gallons of ~20% $P_2O_5$ Acid
- Demonstrated dust free operation with stockpiled heat treated pellets
- Demonstrated impurity removal during heat treatment
- Max Kiln Yield 72%
  - Carbon burn out
  - Non-reducing burner
- Demo plant modifications identified to achieve high yields
IHP Flowsheet with Induration Heat Treatment

LOW GRADE PHOSPHATE ROCK
PETROLEUM COKE
SILICA SAND

DRYER
GRINDING
AGGLOMERATION

INDURATION GRATE-KILN
PORTED KILN
P_4O_10 GAS

J•ROX COMMERCIAL AGGREGATE
HIGH-GRAD PHOSPHORIC ACID
HYDRATOR
JDC has demonstrated most of the key technological innovations at a multi-ton scale required for full-scale commercialization of IHP

Notable innovations include:

- High silica/calcium ratio to avoid melting of the feed material in the kilns and significantly lower the temperature of the phosphate reduction reaction

- Two processes to produce feed agglomerates: balling drum and extrusion - provides design flexibility for different phosphate and silica characteristics

- Heat treatment process for producing hardened feed agglomerates to achieve high plant availability:
  - Produces little dust in the reduction kiln reducing kiln deposits and erosion damage in the acid plant
  - Removes impurities before phosphate reduction improving product acid quality

- Production of phosphoric acid with improved commercial-grade qualities
Future work at JDC is to modify the existing Demonstration Plant to obtain data for commercial scale-up.

The remaining technologies to be demonstrated are:

- Low oxygen reducing burner to heat rotary kilns that minimize carbon burnout
- A ported rotary kiln to achieve high yield and production rates via control of the temperature and oxygen distribution across the phosphate reduction kiln
- Multi-month demonstration of the two-kiln system to produce high quality acid
The authors wish to dedicate this work to the memory of the Founder of JDCPhosphate, Inc., Dr. Joseph A. Megy. Without his creativity, vision and determination, the progress made toward commercialization of the Improved Hard Progress would not have been possible.