21st Century Phosphoric Acid Plant Designs

(Bigger is Better)

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Raytheon’s presentation at last year’s AIChE’s conference showed a conceptual single-train design for a 1,000 tons per day P$_2$O$_5$ Phosphoric Acid Plant in three dimensional CAD. This design concept features a single reactor vessel converting the phosphate rock slurry to gypsum and phosphoric acid. This year we can announce that the largest single reactor vessel constructed by Raytheon can process 2,000 tons per day of P$_2$O$_5$. This single reactor vessel is 40 feet in diameter with a working volume of 46,000 cubic feet (1,300 cubic meters).

**Basic Operating and Design Features**

This paper reviews the basic operating and design features that allow this single vessel to replace the multistage conventional units so common throughout this industry. In order to understand the Phosphoric Acid System described in this paper, experienced operators and owners must break free from their old paradigms.

**Crystal Size and Shape**

In a conventional plant for the manufacture of phosphoric acid by the wet process, there are one or more reactor and crystallizer tanks all of which are equipped with agitators. The purpose of these tanks is to react or dissolve the phosphate rock and produce phosphoric acid. Unfortunately, most commercial phosphoric acid processes also produce byproduct gypsum or some form of calcium sulfate. This is where life gets interesting for the Chemical Engineer and the Plant Operating Staff. Fortunes, and, more importantly, reputations are made or lost on this very point. Phosphoric acid product losses are related to the filterability and washability of the calcium sulfate crystals produced. In this regard, it is known that recoveries of the phosphoric acid product are inversely proportional to the number of crystals produced and directly proportional to the size of such crystals. Accordingly, it is desirable to produce gypsum crystals which are few in number and large in size. In this regard, Raytheon’s Isothermal Reactor Process, when properly operated, forms byproduct gypsum crystals that are easily filtered, washed, and dewatered. The Isothermal Reactor should be renamed the **Isothermal Crystallizer**.
Circulation, Cooling and Temperature Control

This process and crystallizer provide for large crystal growth by cooperatively employing a high rate of circulation of the body of reaction slurry in combination with a controlled rate of evaporative cooling. In particular, this crystallizer involves an apparatus for circulating the vessel contents in a combination Reactor, Crystallizer and Cooler unit to expose the entire body of the vessel contents to subatmospheric pressures for affecting evaporative cooling that is maintained in balance with the heat generated through exothermic reactions that occur in the body of reaction slurry. Localized differentials in temperature and concentration are thereby effectively minimized to provide a uniform level of calcium sulfate supersaturation throughout the mass of reaction slurry which reduces the number of nuclei being formed. This factor becomes particularly significant when it is noted that the rate of nucleation increases exponentially, rather than directly, with an increase in supersaturation.

The combined use of vacuum cooling and high circulation rate of the reaction slurry in a predetermined flow pattern accomplishes a new result which, for purposes of explanation, may be characterized as an “extended surface.” For example, the largest reactor vessel designed to date by Raytheon used for producing approximately 2,000 tons per day of $\text{P}_2\text{O}_5$ would have a diameter of approximately 40 feet and an equivalent surface area of approximately 1,257 square feet. The combined effect of the high circulation rate and vacuum cooling of the reaction slurry in accordance with the present design creates a highly turbulent and greatly increased “extended surface” equivalent to a surface area many times the 1,257 square feet provided by the geometry of the reactor. One important advantage of this “extended surface” is that it significantly enhances uniformity of temperature throughout the body of reaction slurry.

Sulfuric Acid Addition and Distribution

The Reactor/Crystallizer involves the mixing and distribution of sulfuric acid into the circulating mixture of phosphoric acid, calcium phosphate, and the slurry of gypsum crystals. To distribute the sulfuric acid uniformly, the sulfuric acid is injected through multiple nozzles into the circulating mixture of phosphoric acid, calcium phosphate, and the slurry of gypsum crystals. This distribution system provides for heretofore unobtainable uniformity of sulfuric acid distribution into the reaction mixture, thereby substantially reducing and preventing excessive nucleation in localized areas.
**Saturation Level Uniformity**

The Reactor/Crystallizer enables the production of large and uniform calcium sulfate crystals. This occurs during the wet process production of phosphoric acid where the product losses are inherently minimized during filtration and washing of the calcium sulfate crystal cake resulting in both lower operating costs and improved recoveries. In this regard, advantage is taken of the highly important principle of crystal growth, which is the control and maintenance of the proper supersaturation level throughout the entire vessel. The conditions within the vessel lie within the stable zone for the formation of the dihydrate gypsum crystals, and these conditions favor the deposition of calcium sulfate upon existing dihydrate crystals rather than the formation of new nuclei.

**Reactor Design**

The Reactor/Crystallizer is designed to provide a combination reactor/crystallizer and slurry cooler unit by utilizing vacuum. The power used for agitation is also used for circulation of the vessel contents. Power requirements are reduced by as much as two thirds of the power demand for conventional wet process installations. The constant circulating mass within this single vessel provides a continuously renewed surface for evaporation. The high rate of circulation of the vessel contents through the internal circulator is equal to 133% of the working volume of the Reactor/Crystallizer per minute. The complete recirculation of the vessel contents will occur at least once every 45 seconds.

The agitation system employs a draft tube equipped with a propeller which provides a positive direction and path for high internal circulation. This creates and maintains a controlled flow of the entire slurry contents throughout the Reactor/Crystallizer. Rapid and uniform dispersion is achieved with close control of supersaturation levels. In addition, this agitation system eliminates costly recirculation pumps and piping to transfer the reaction slurry to a separate vacuum cooler which is required by other processes.

The circulator described above causes a rapid turnover of the vessel contents in conjunction with a vacuum system which allows this vessel to operate at a constant temperature. Isothermal temperature conditions exist within the vessel, and the average bulk temperature of the circulating fluid rarely exceeds temperature differences by more than 0.5⁰ C. In this manner, a favorable environment for dispersion, reaction, and crystal growth is created. The net result is appreciably less nucleation in the reactor. Therefore, this causes larger and more suitable calcium
sulfate crystal formation and growth giving a slurry with substantially improved filtration and working characteristics resulting in increased filter capacity and correspondingly reduced phosphoric acid losses.

The vacuum cooling at high circulation rates provides a substantially uniform level of calcium sulfate supersaturation and temperature throughout the entire body of vessel, providing evaporative cooling at a rate which is substantially equal to the heat evolved in the exothermic reactions that occur in the vessel.

The manufacture of phosphoric acid involves the reaction of calcium phosphate/phosphate rock and sulfuric acid. The sulfuric acid is injected into the draft tube unit through one or more nozzles to provide distribution of the sulfuric acid into the circulating vessel contents. This results in uniform distribution of the sulfuric acid throughout vessel contents, thus preventing excessive nucleation in the circulating fluid caused by uneven concentrations of sulfuric acid.

**Lower Environmental Emissions**

This system is simpler to operate and control than conventional installations. Obnoxious fluorine gases produced in the reactions of the wet process are condensed by, and removed with, the condenser water. The usual fluorine scrubber system with its ductwork, dampers and fans, normally required to prevent atmospheric pollution, are unnecessary.

**Reduced Number of Operating Equipment**

All the reactants are introduced into a single vessel combining the function of a reactor, crystallizer and slurry cooler. This eliminates the usual pre-mix tanks found in many conventional installations.

This single vessel, reactor, crystallizer and cooler, occupies less space, and requires fewer moving parts.

**Process Advantages of the Isothermal Reactor Process**

- Simplicity of Isothermal Reactor Crystallizer Cooler Operation
- Higher $P_2O_5$ Recovery Efficiency
- Superior Sulfate Control
- High Operating Factor
Economic Advantages of the Isothermal Reactor Process

- Lower Capital Investment
- Significantly Lower Power Costs
- Lower Maintenance Costs

Process Flow Diagram and Description

A process flow schematic for the Isothermal Reactor Process is shown in Figure 1. Phosphate rock slurry containing approximately 68 wt. % solids is pumped to the bottom inlet of the Isothermal Reactor and into the recirculating mass of reactor slurry. The Reactor Circulator pumps reactor slurry up through the draft tube and around the annular space in the reactor to maintain the necessary velocity for suspension of gypsum solids. Sulfuric acid (93 to 98 wt. % H₂SO₄) is injected into the recirculating mass of reactor slurry through feed nozzles located above the Reactor Circulator blades. Phosphate rock slurry and sulfuric acid are fed under flow control to the reactor. The operator has precise control over the free sulfate levels in the reactor. Sulfate corrections are calculated based on the fixed volume of the reactor and physical properties of the reactor slurry. The Isothermal Reactor produces reactor slurry containing 28 to 29 wt. % P₂O₅ phosphoric acid (solids free basis) and 35 to 40 wt. % gypsum solids.

Reactor slurry is maintained in the Isothermal Reactor by a fixed point overflow and reactor product line which is sealed below the liquid level in the Filter Feed Tank. A horizontal centrifugal slurry pump, with variable frequency drive, is utilized to transfer reactor slurry to the filter for separation of phosphoric acid product from dihydrate gypsum.

Reactor Design

The single train Isothermal Reactor is 40 feet (12.32 m) in diameter and is equipped with a single 400 hp (300 kw) Reactor Circulator. The Reactor Circulator is designed to circulate 480,000 gpm (109,000 m³/hr) of reactor slurry in order to maintain a reactor slurry differential temperature of less than 0.5°C in the reactor. This high slurry circulation rate turns over the entire volume of the Isothermal Reactor in less than 45 seconds, producing homogenous concentrations and isothermal conditions for the reactor slurry.
The high circulation rate allows excellent control of sulfates in the reactor and promotes the formation of large gypsum crystals, which results in high \( P_2O_5 \) recovery efficiencies from the filter cake.

The reactor is maintained at constant temperature by controlling the absolute pressure (vacuum) in the reactor. Water vapor, which is flashed from the surface of the reactor slurry, is condensed in a Reactor Barometric Condenser. Non-condensable gases, air leaks and carbon dioxide, produced from the reaction of phosphate rock and sulfuric acid, are removed from the reaction system by a liquid ring vacuum pump and are discharged to the atmosphere.

**SF Phosphates Isothermal Reactor Performance**

SF Phosphates operating experience with the Isothermal Reactor has been quite good if not remarkable. SF has been able to operate the 34-foot internal diameter version of the Isothermal Reactor at sustained rates in excess of 1,100 tons per day. Residence times in Raytheon’s Isothermal Reactor vessel are approaching the 100 minute mark. Through the use of rock blending, the SF facility has achieved excellent sulfate control. The standard deviation for sulfate control is often below the 0.15% level on a monthly basis. The SF facility benefits from having a blended three day rock supply on site. Four 2,500-ton rock slurry tanks, which are agitated and equalized, provide a consistent rock feed to Raytheon’s Isothermal Reactor. Rock quality is further enhanced by being mined from a single hard rock mine face and ground to a very fine particle size. The rock slurry feed to the reactor contains less than 2%+65 mesh and approximately 20-25% -325 mesh. Density compensation on the rock feed to the reactor provides the final effect leading to excellent sulfate control.

SF is currently expanding its complex with the addition of another #11 Ucego filter and additional evaporation capacity. After the expansion is completed, the SF complex plans to produce 26% \( P_2O_5 \) at an instantaneous rate exceeding 1,200 tons per day with a single 34-foot internal diameter Isothermal Reactor. While the \( P_2O_5 \) efficiency factors at SF are confidential, they easily exceed those experienced by most Florida phosphate producers. The SF Phosphates site, a Raytheon designed facility, is a low-cost producer and is cost competitive with any of the much larger facilities in Florida.
Conclusion

Based on scale-up, Raytheon’s 40-foot Isothermal Reaction System would achieve production rates of 2,000 tons per day $\text{P}_2\text{O}_5$ in addition to achieving 96% $\text{P}_2\text{O}_5$ recovery through the primary gypsum filter. The Reaction System, which includes Rock Slurry Feed Pump, Rock Slurry Tank Agitator, Reactor Circulator, Reactor Vacuum Pump and Filter Feed Tank and Agitator, consumes less than 9 kw/hr of electric power per ton of $\text{P}_2\text{O}_5$ produced.

**In this case, Bigger is Better with the following advantages:**

- Higher reactor circulation rate increases digestion rate.
- Optimum conditions for crystal growth.
- Higher reactor circulation rate maintains uniform concentration and ensures high $\text{P}_2\text{O}_5$ recoveries.
- Lower environmental risks.
- More efficient and less maintenance required than multi-compartment reactors.
- Easier operation and control.

This single vessel, reactor, crystallizer and cooler, occupies less space, requires fewer moving parts and is substantially less expensive to build, operate, clean and maintain than conventional installations, thereby substantially reducing capital and operating costs.

References:
Becker, Phosphates & Phosphoric acid Chapter 2, section 2.2.3, figure 2.21
Phosphorus & Potassium No. 210 July-August, pages 30, 31
Phosphorus & Potassium No. 211 September-October, pages 45, 50
AIChE 21st Annual Clearwater Conference, Phosphoric Acid Plant Design for the 21st Century
Isothermal Reactor Flow Diagram

- **Rock Slurry Storage Tanks**
- **Rock Slurry Pumps**
- **Concentrated Sulfuric Acid Feed**
- **Recycle Acid From Filter**
- **Vapor**
- **Barometric Condenser**
- **Cooling Water**
- **Vapors to Vacuum System**
- **To Seal Tank**
- **Reactor Product**
- **Filter Feed Tank**
- **Filter Feed Pumps**

**SF Phosphates Limited Company**
Figure 2

Crystallization Diagram - Wet Process Phosphoric Acid

Weight %CaO

Weight %SO₄

Isothermal reactor maximum, operating point
2.1% SO₄
0.46% CaO
2.0% SO₄ (control point)

spontaneous nucleation zone
supersaturation curve
saturation curve

1 1.4 1.8 2.2 2.6 3 3.2 3.8 4.2 4.6 5 5.4
### Comparison of Phos Acid Technologies

<table>
<thead>
<tr>
<th></th>
<th>Competitive Reactor Technology</th>
<th>Raytheon’s Isothermal Reactor/Crystallizer</th>
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<tbody>
<tr>
<td><strong>Reaction Volume (M³/MTPD P₂O₅)</strong></td>
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<td></td>
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<tr>
<td>Attack Tank/Tanks</td>
<td>1.35</td>
<td>0.65</td>
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<tr>
<td>Digestion/Filter Feed Tank</td>
<td>0.65</td>
<td>0.35</td>
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<tr>
<td><strong>Total</strong></td>
<td>2.00</td>
<td>1.00</td>
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<td><strong>Slurry Cooling</strong></td>
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<tr>
<td>Slurry Recirculation (M³/Hr/MTPD P₂O₅)</td>
<td>15</td>
<td>54.5</td>
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<tr>
<td>Delta T, °C</td>
<td>1.8</td>
<td>0.5</td>
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<tr>
<td><strong>Power-Consumption Section (KWH/MT P₂O₅)</strong></td>
<td>27</td>
<td>9</td>
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<tr>
<td><strong>Equipment</strong></td>
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<tr>
<td>Total Equipment including Spares</td>
<td>30</td>
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<td>Operating Motors</td>
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</table>

**Figure 3**

Raytheon

Engineers & Constructors

SF Phosphates Limited Company
Raytheon Experience in Wet Processes
Phosphoric Acid - Isothermal Reactor

Client

Rotem, Israel 1050
Chevron, Wyoming (SF Phosphates) 1100
Fertimex, Mexico (Fertinal) 1500
US Agrichemical, Florida (Sinochem) 1600
Farmland, Florida (Farmland Hydro) 1000

NOTE: Luzhai, China - 440 STPD $P_2O_5$ to be started up in 1999.
Figure 5

Isothermal Reactor Performance Summary

<table>
<thead>
<tr>
<th>Rock Source</th>
<th>Farmland Farmland Hydro L.P.</th>
<th>USSAC (Sincochem)</th>
<th>Fertilmer (Fertinal)</th>
<th>SF Phosphates</th>
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<tbody>
<tr>
<td>% P205 Gypsum</td>
<td>0.8</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
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<tr>
<td>% P205 Phos Acid from Filter</td>
<td>28</td>
<td>29</td>
<td>28</td>
<td>28</td>
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<tr>
<td>Design Capacity STPD P205</td>
<td>600</td>
<td>1400</td>
<td>1320</td>
<td>1320</td>
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<tr>
<td>Demonstrated Operating Capacity STPD P205</td>
<td>1000</td>
<td>1600</td>
<td>1500</td>
<td>1500</td>
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</tbody>
</table>
Advantages of Isothermal Reactor Process

Process Advantages

• Simplicity of Isothermal Reactor Crystallizer
• Cooler Operation
• Higher P2O5 Recovery Efficiency
• Superior Sulfate Control
• High Operating Factor

Economic Advantages

• Lower Capital Investment
• Significantly Lower Power Costs
• Lower Maintenance Costs