International
Fertilizer Industry
Association

IFA Technical Conference

Marrakech, Morocco
28 September-1 October 1998

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

Date of Receipt: 16 September 1998

PHOSPHATE TECHNOLOGY FOR THE NEXT MILLENNIUM[1]

R.L. Hemmings, C.J. Felice and M.W. Huang
Raytheon Engineers & Constructors Inc, United States

SUMMARY

Raytheon's presentation at the 1997 AIChE conference in Clearwater, Florida, featured a conceptual single-train design for a 1,000 tons per day P_2O_5 phosphoric acid plant. This design concept featured a single Raytheon Isothermal Reactor vessel converting the phosphate rock slurry to gypsum and phosphoric acid. Now, in 1998, Raytheon can announce that this same reactor, the largest single reactor vessel designed by Raytheon, can be operated in such a way as to process up to 2,000 tons per day of P_2O_5. This much higher rate is the result of application of new information and technology. An AspenPlus® simulation of the Isothermal Reactor System that confirms the production rate of the design. The model was developed in-house by one of Raytheon’s simulation experts, using the powerful AspenPlus® process simulation software, Release 9-3.2. This software contains the electrolyte simulation capability to simulate all the complex chemistry taking place in the Raytheon Isothermal Reactor/Crystallizer.

RESUME

La présentation de Raytheon à la conférence de AIChE en 1997 à Clearwater, en Floride concernait le plan conceptuel d'un atelier d'acide phosphorique de 1000 t/j P_2O_5 en une seule ligne. Il comportait une cuve d'attaque unique isotherme Raytheon transformant la bouillie de phosphate en gypse et en acide phosphorique. Actuellement, en 1998, Raytheon peut annoncer que le même réacteur, la plus grande cuve d'attaque conçue par Raytheon, peut fonctionner de telle façon qu'elle produit 2000 t/j P_2O_5. Ce rendement accru résulte de l'application d'informations et de technologies nouvelles. Une simulation AspenPlus® du système de réacteur isotherme confirme la capacité de production du modèle. Le modèle a été développé par nos moyens internes par un des experts de simulation de Raytheon, utilisant le puissant logiciel de procédé de simulation AspenPlus®, Version 9-3.2. Ce logiciel possède la faculté de simulation de l'électrolyte pour simuler toute la chimie complexe qui se passe dans le réacteur isotherme/cristalliseur Raytheon.

✦ ✦ ✦

Background

Raytheon has developed a new Isothermal Reactor/Crystallizer of a size that will produce up to 2,000 MT/d of P_2O_5, is 40 feet (12+ meters) in diameter with a working volume of 46,000 cu ft (1,300 cubic meters). This reactor was described in previous papers[i, ii] and demonstrates the flexibility and the stretch capability of the Isothermal Reactor/Crystallizer operating parameters.

The Isothermal Process for converting phosphate rock into gypsum crystals and phosphoric acid consists of a simple train of equipment: a conveyer from the feed pile; a rock slurry storage tank or tanks; rock slurry pumps; the Isothermal Reactor vessel; a condenser for cooling; filter feed tanks and associated pumps; and the final filters. The heart of the process is the Isothermal Reactor which, if operated carefully as described in the 2nd reference, and with a detailed understanding of the chemical reactions taking place inside the reactor, can be used to double the previously identified “maximum” throughputs.

Under careful control, this reactor and crystallizer provide the environment for growth of large and easily filtered crystals by employing a high rate of recirculation to maintain the desired supersaturation level of the slurry contents of the vessel, but not at too high a rate to physically break the crystals, in combination with a controlled rate of evaporative cooling. In the Isothermal reactor/crystallizer, the recirculating slurry contents are exposed to vacuum conditions for enhancing the evaporative cooling from the exposed surface, to balance the heat generated by the exothermic reactions that occur in the body of the reactor vessel.

---

[1] *Technologie du phosphate pour le prochain millénaire*

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 P_2O_5 has 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 that 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 to the point that temperatures vary less than 0.5°C throughout the reactor.

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 central area of the reactor, where there is maximum circulating of the 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. Further, it provides for maintenance of an even concentration of sulfate in the recirculating liquid.

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. These large, uniform crystals are more readily washed, requiring less wash water and leaving behind less P_2O_5 in the gypsum. This effect both increases recovery of P_2O_5 as well as offsets the additional water introduced with the wet rock feed system.

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 about 110% of the working volume of the Reactor/Crystallizer per minute. The complete recirculation of the vessel contents will occur at least once every 54 seconds. Note that this recirculation rate is somewhat less than that indicated in the previous paper, as we have determined a balance between heat rejection, slurry suspension, and particle size.

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.

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 0.5°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.

This system is simple to operate and control. Obnoxious fluorine gases produced in the reactions of the wet process are condensed by, and removed with, the condenser water. This does not need a special and extensive fluorine scrubber system with its ductwork, dampers and fans, normally required to prevent atmospheric pollution.

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/Crystallizer

- 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/Crystallizer

- 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. % H_2SO_4) 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. % P_2O_5 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 Summary

The single train Isothermal Reactor is 40 feet (12.32 m) in diameter and is equipped with a single 250 hp (180 kw) Reactor Circulator. The Reactor Circulator is designed to circulate 400,000 gpm (90,000 m^3/hr) of reactor slurry in order to maintain a reactor slurry differential temperature of less than 0.5°C in the reactor. As indicated before, the recirculation rate has been balanced against heat removal, slurry suspension, and crystal size, leading to a reduction of the recirculation rate, with a considerable savings in power consumption. Yet, the circulation rate remains sufficiently high to turn over the entire volume of the Isothermal Reactor/Circulator in less than a minute, producing a homogenous concentration 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 using less wash water, and producing higher P_2O_5 recovery efficiencies from the filter cake. The reactor is maintained at constant temperature by controlling the 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.

Developing a Process Simulation Model for this Technology

With our extensive knowledge and experience in the area of process modeling, and encouraged by a paper presented in the recent Clearwater Conference[iii], Raytheon determined to develop a model of the Isothermal Reactor/Crystallizer, using the powerful and versatile AspenPlus® Simulation technology. There are several reasons for using AspenPlus® for the P_2O_5 reactor modeling in preference to other simulators.

1. One reason is that AspenPlus® already contains an extensive library of the various ionic species involved in the aqueous phase inorganic chemistry, complete with the appropriate data for these separate species.
2. Another reason is that the "electrolyte" option in AspenPlus® includes customized thermodynamics for handling these ionic species and can operate concurrently with the "standard" thermodynamic options for dealing with conventional components and dissolved gases acting as Henry's Law components. These all work together to reliably produce stream properties and Vapor/Liquid Equilibrium information.
3. In addition to the above reasons, the AspenPlus® reactor modules can accommodate the ionic reactions in addition to the molecular reactions more commonly found in simulation reactor modeling, and can handle solid materials at the same time.

All these factors combine to cover the aspects needed to simulate the aqueous inorganic and ionic properties and reactions. Once the model is benchmarked against a specific configuration of installation, it is readily used to evaluate alternatives of operating conditions, etc. This is all done within the same AspenPlus® simulator program; a separate package for the electrolyte processes is not required.

However, there is a significant challenge in setting up a rigorous process simulation model that deals with all the ionic reactions that take place within the wet phosphoric acid process, at the operating conditions of the Isothermal Reactor/Crystallizer. This is further complicated by the conventional reporting of the composition of phosphate ore, which does not really provide for a true ionic balance of the species that take part in the reaction. And, further, dealing with the non-reactive portion of the ore requires an approach that “fools” the AspenPlus® program into handling these species correctly. All of the species usually identified in an ore analysis break down into a much larger number of ionic species when hydrolyzed, and the rigorous AspenPlus® model is able to handle this very large number of components and their reactions. A typical assay, as shown in Table 1, has only about 15 major species listed, and some of them may not show any values. There may be as many as another 15 species identified in the parts per million range (some also with zero values). This would lead to perhaps 15 significant species in an assay. However, these 15 break down into many more species during reaction. Our AspenPlus® model currently deals with about 30 different ionic species, and their combined reactions. These species are shown in Table 2.

Table 1
Conventional Ore Assay

Component	**%** (Dry Rock Basis)[iv]
P_2O_5	32.04
SO_3	1.88
F	4.07
SiO_2	4.16
CO_2	4.73
Cl	0.02
CaO	50.68
Al_2O_3	0.54
Fe_2O_3	0.13
MgO	0.50
Na_2O	0.74
K_2O	0.26
C (org)	-
SrO	-
BaO	-

Also included, at times, are some parts per million components, such as the following in this case: As, 6; Cd, 10; Zn, 193; Pb, 3.3; Hg, 0.025; U_3O_8, -; Co, -; Cr, 304; Ni, 41; Ti, -; V, -; Mn, 21; Cu, 47.

Table 2
Constituents Analyzed in AspenPlus® Model

H_2O	SiF_6--	CO_2	Al_2O_3
H_3O+	F-	Gypsum	Fe_2O_3
OH-	Ca++	H_3PO_4(s)	MgO
H_3PO_4	AlOH++	Ca_3PH(s)	Na_2O
H_2PO_4-	FeOH++	CaF_2	K_2O
H_2SO_4	Mg++	$CaCO_3$	
HSO_4-	Na+	SiO_2(s)	
SO_4--	K+	Na_2SiF_6	

The typical assay is first broken down into a detailed and balanced chemical analysis, accounting for a molecular balance of the constituents. Running this complex model takes a significant amount of time on even a Pentium computer, as there are all the interactions between these constituents to be addressed. However, the results predict a complete and rigorous heat and material balances across the reactor and filtration stages of the process, including all the wash water stages. The input for the model includes: rock chemical assay; rock feed rate; inlet slurry concentration; reactor conditions (temperature, pressure, etc.), wash water flow and temperature, moisture in filter cake, and number of wash water stages. The model develops the optimum conditions for crystal formation rate, the optimum residence time, optimum recycle and wash conditions and stages, production rate, etc.

The AspenPlus® model developed by Raytheon is a tool with which can be used to optimally design new Isothermal Reactor systems, as well as use as to check on current plant operations, and to “tune” them towards their optimum operating conditions.

For new reactors, a range of ore concentrations can be input in the design stage, and the reactor system designed to handle the average rock, as well as the high and low extremes in variability of the rock. Thus, the model can not only predict the operation for the main body of the ore, but also identify the maximum and minimum conditions that suit the range of rock assays actually encountered, and could be used to predict the ranges of production and recovery that would be encountered over the complete exploitation of the ore body. Further, this tool can be used to identify the operational adjustments needed if the type and characteristics of the feed rock were to be changed, say from one rock supply to another.

The Raytheon AspenPlus® model is still under development, as it has yet to be completely validated. However, it has been run for two actual plant operation conditions, and compares favorably with actual results. It has also been compared to the benchmark comparison of phosphate rock behavior as presented by Becker[v] with excellent results. In fact, in a comparison against the specific heat and mass balance case developed by Becker[vi], the Raytheon AspenPlus® model shows considerable agreement, with the only significant difference being in the heat balance, where the Becker model does not account for all impurities, nor does it account for the heat of crystallization. Also, the Raytheon AspenPlus® model shows better closure, not having to arbitrarily account for acid losses. The comparison is shown in Table 3.

Table 3
Comparison of Raytheon AspenPlus® Model
And Becker Case Study

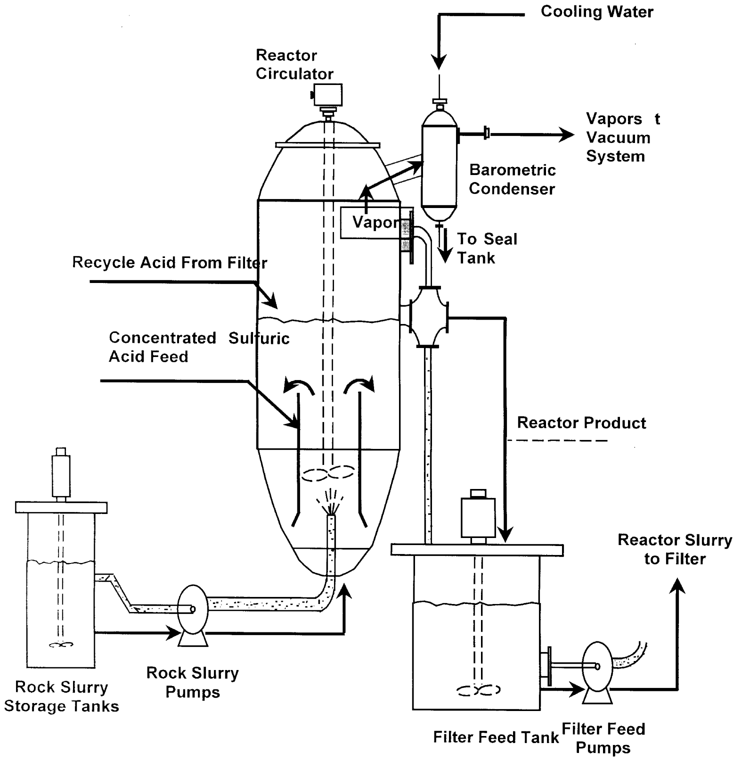
	Raytheon AspenPlus® Model		**Becker Case Study**	
Into Reactor	**Kg/hr**	**Kg/kg rock**	**Kg/hr**	**Kg/kg rock**
Phosphate rock	113,200	1.000	113,200	1.000
Rock moisture	1,724	0.015	1,724	0.015
Sulfuric Acid	104,099	0.920	98,597	0.871
Return acid	334,123	2.952	307,564	2.717
Total input	**553,145**	**4.886**	**521,086**	**4.603**
Out of Reactor	**Kg/hr**	**Kg/kg rock**	**Kg/hr**	**Kg/kg rock**
Cake (dry)	181,938	1.607	175,573	1.551
Mother liquor	309,785	2.737	298,508	2.637
Evaporation H_2O	57,592	0.509	38,148	0.337
CO_2	3,830	0.034	4,981	0.044
Total output	**553,145**	**4.886**	**517,211**	**4.569**
Out - In	**0**	**0.000**	**-3,875**	**-0.034**
Filter Water	209,289	1.849	189,497	1.674
Product acid	117,645	1.039	118,181	1.044
Cake moisture	67,292	0.594	64,977	0.574
Acid losses	0	0.000	1,245	0.011
Into system	**428,311**	**3.784**	**403,018**	**3.560**
Out of system	**428,298**	**3.784**	**403,105**	**3.561**
Out - in	**-13**	**0.000**	**87**	**0.001**

CONCLUSION

The Raytheon AspenPlus® model is an analytical tool that will assist in the optimization of the design of the Raytheon Isothermal Reactor/Crystallizer for the production of phosphoric acid. This tool allows for the rigorous calculation of the entire range of ionic species that occurs in the reactor, and can thus predict optimal operating conditions for any particular rock composition that may be in the feed to the reactor. It will allow the reactor to be designed to a range of rock assays, and will also allow a reactor to be “tuned” to any change in feed rock assay.

Over the next few months, the Raytheon AspenPlus® Model will be checked against a number of operating Raytheon Isothermal Reactor/Crystallizer installations, and validated against their individual operating conditions. Once thoroughly validated, it will then be used for design and for operational checks.

Figure 1



References

[i] Belle, W. Douglas, and Pelham, Daniel L. “Phosphoric Acid Plant Design for the 21st Century - A Virtual Reality with 3D CAD”. AIChE Clearwater Conference, May 1997.

[ii] Felice, Charles J., Martinez, John L., and Hilakos, Steve. “21st Century Phosphoric Acid Plant Designs - (Bigger is Better). AIChE Clearwater Conference, May 1998.

[iii] Mathias, Paul, and Mendez, Mike. “Simulation of Phosphoric Acid Production by the Wet Process.” AIChE Clearwater Conference, May 1998.

[iv] Becker, Pierre. “Phosphates and Phosphoric Acid - Raw Materials, Technology, and Economics of the Wet Process”. 2nd Edition, Revised & Expanded. Marcel Dekker Inc. New York. Basel. Hong Kong. Data Sheet M3, pages 666 & 667.

[v] Becker, Pierre. “Phosphates and Phosphoric Acid - Raw Materials, Technology, and Economics of the Wet Process”. 2nd Edition, Revised & Expanded. Marcel Dekker Inc. New York. Basel. Hong Kong. Pages 89-91.

[vi] Becker, Pierre. “Phosphates and Phosphoric Acid - Raw Materials, Technology, and Economics of the Wet Process”. 2nd Edition, Revised & Expanded. Marcel Dekker Inc. New York. Basel. Hong Kong. Pages 89-91.