MUD CHEMISTRY?

An Insider Reveals the Soft Side of Phosphate Technology

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Ask a phosphate chemical expert a serious question about technology of the industry. The response often starts with “Well....” Pretty soon the conversation turns to a tale about something that once happened at some plant or something that somebody figured out once upon a time.

Whatever became of expectation that technology should provide precise answers? Well, the industry may have come a long way from the days of bone phosphate of lime and superphosphate (which wasn’t all that super). However, clear cut answers are no easier to achieve. We’re accused of practicing mud chemistry.

COMPARISON WITH SULFURIC ACID TECHNOLOGY

If you want precise answers you need look no further than the sulfuric acid plants that are in the midst of every phosphate chemical complex. Now there is a showplace of precise technology! My friend Shiv Shukla flits around the world with a laptop computer that contains all knowledge about sulfuric acid plant design & operation (website http//sulphuric.tripod.com/). Ask him a question, and he soon starts spouting precise information about material flows, concentrations, temperatures, heat transfer, and even corrosion rates. Awesome! Sulfuric acid experts seem so brilliant, whereas phosphoric acid experts, well....

How can sulfuric acid technology be so much more precise than phosphate technology? Well, for one thing, a sulfuric acid plant has only two feeds – sulfur and air – and neither changes much. Even when you concede that sulfur has a bit of trash in it and air has its various components and temperature swings, that is still a very, very simple feedstock. The drying tower quickly converts the inlet ambient air into clean dry air. A filter removes any trash from the sulfur, so the plant operation sees only pure air and pure sulfur. The product itself is sulfuric acid – almost pure and at whatever exact concentration that is desired. So simple!

COMPLEXITY OF PHOSPHORIC ACID TECHNOLOGY

In contrast phosphate technology is overwhelmed with complexity. There is an endless variety of feedstocks, all sorts of weird reactions going on, crystallization patterns that defy understanding, solids dropping down, fumes going up, scale forming everywhere, foam covering everything, and a myriad of idiosyncracies thrown in for good measure. How can anyone deal with such a mess with any kind of scientific approach?

The complications begin with the phosphate rock feed. The main ingredient of phosphate rock is apatite. My spell checker never heard of "apatite", whereas it can spell "mud chemistry" (a bad start). Apatite has many forms, the most common being fluorapatite – a complicated compound with the formula $Ca_{10}(PO_4)_6F_2$. There's 42 atoms in each apatite molecule, and it has a hefty molecular weight of 1009. Complicated enough! However, this is only the first of perhaps 100 ingredients in phosphate rock that significantly affect performance of a phosphoric acid plant.

The Florida Institute for Phosphate Research (FIPR) recently documented analyses of up to 28 elements that are significant in numerous phosphate rocks from around the world. The elements are:

phosphorus	calcium	silicon	magnesium
aluminum	iron	fluorine	sulfur
sodium	potassium	chlorine	molybdenum
manganese	copper	strontium	barium
arsenic	cadmium	zinc	lead
mercury	chromium	nickel	titanium
vanadium	uranium	selenium	

carbon (as carbonates, organic matter, etc.)

These elements plus hydrogen and oxygen combine to form innumerable compounds. Compounds and minerals of significance in phosphate rock include these:

fluorapatite	hydroxylapatite	hydroxyl-fluor-carbonate apatites	
chlorapatite	various other mixed apatite compounds		
francolites	calcite	carbonatites	hematite
dolomite	crandallite	goyazite	gorceite
wavelite	varisite	strengite	dufrenite
beraunite	aluminophosphates	illite	opaline
tectosilicates	micas	biotite	muscovite
jerrite	capite	saranyite	kauwenbite
henryite	ronite	pyrochlore	feldspar
kaolinite	smectites	palygorskite	sepiolite
geothite	beraunite	nepheline	pyroxenes
amphiboles	biotite	phlogopite	magnetite

This list could go on and on, but I think this makes the point that phosphate rock is exceedingly complicated stuff. I will admit to spicing it up with just a few items that do less to name real minerals than to honor some friends. Some of those people deserve to have a more valid source than myself name a mineral in their honor. I concocted "jerrite" to thank Jerry Cape for teaching me a little of what he knew about beneficiation. However, Jerry informed me that there really is a jerrite mineral, so I concocted "capite" for my list. It would be fitting if some bona fide organization were to really name a mineral after one of the local phosphate mineral experts like Jerry.

The one other feed to a phos acid reactor is sulfuric acid, usually at a concentration of 93 or 98% H_2SO_4. Defoamer is almost always added to the phosphoric acid reactor. Other supplemental materials may be added, including clay, flocculant, crystal modifier, anti-scalant, active silica, etc. Even before any reactions begin, a phosphoric acid plant has exceedingly complex feedstock.

These compounds either react in the phosphoric acid reactor, or later in the process, or when making fertilizer products, or they fail to react. The primary reaction in most phosphoric acid plants produces gypsum crystals. This gypsum is impure calcium sulfate in either dihydrate or hemihydrate form. The size, shape, and exact composition of these gypsum crystals is affected by nearly everything – including concentration of phosphate, sulfate, and many of those 28 elements in the feed.

Many of the multitude of compounds that form in phos acid contain aluminum. Aluminum is a gigolo element that casually forms loose electronic bonds with molecules outside of its own molecule. Such immoral behavior encourages formation of many complex compounds, and also results in many strange effects on crystal structure. For example, variations in aluminum content changes the shape of hemihydrate crystals from looking like matchstick to looking like rose blossoms.

Sudden changes in temperature, sulfate concentration, etc. cause formation of many crystal nuclei, which has the disadvantage of reducing crystal size. Many of the components have serious harmful or sometimes beneficial effect on corrosive action of the acid. Some impurities significantly affect viscosity of the acid and slurries. Even obscure minor elements like selenium are thought to affect the balance between dihydrate and hemihydrate form of gypsum. Agitators and pumps beat on gypsum crystals, making them smaller.

I suspect that even God is hard-pressed to understand everything that goes on in a phosphoric acid reactor. Well, maybe not. My point is that it's impossible for us mere mortals ever make precise predictions of phosphoric acid plant performance when there is so much going on.

There was once a sophisticated attempt to develop a mathematical model of a phosphoric acid reactor, involving capable organizations like Aspen, FIPR, and the help of many people in the industry. A huge amount of information on all aspects of phosphoric acid technology was fed into the model, and formulas were developed to try to make sense of everything. The program took over an hour to run on a computer. This alone impressed me, because I was working on a spreadsheet that calculated scores of streams in a phos acid process flowsheet. What I has considered to be a big program would crank out in a blink of an eye. My friend Shiv's sulfuric acid plant program didn't take much longer than that. I was mightily impressed that a phos acid program was big enough to run for an hour. Alas, even that elaborate program never achieved much success in modeling the operation of a phosphoric acid plant.

GRANULAR FERTILIZER TECHNOLOGY

I've previously made presentations to you folks regarding advanced technology for granular fertilizer plants. However, I must admit that granulation of fertilizer is quite resistant to technology. The multi-fold impurities within the phosphoric acid feed often have great effect on how well the granules form in the granulator. Some impurities help hold the granules together, while others make granulation difficult. Some ingredients form side reactions that harm product quality or render some of the phosphate inactive.

Granulation itself is a mix of a lot of art and considerable science. A skillful operator will adjust a multiple of variables so that the material leaving the granulator contains a high portion of on-size granules. A well-engineered granulator is also essential for good granulation. There have been numerous important improvements to the basic design of pre-neutralizers, granulators, granulators, dryers, mills, conveyors, elevators, and other equipment. Numerous process innovations have been developed that have greatly improved performance and reduced processing costs in granulation plants. These include dual mole acid scrubbing (invented by Dick Maginnis), the BFL vaporizer-scrubber, and pipe reactors of various designs. HiTech Solutions developed a recycle control system that continuously senses particle size distribution and instantly makes adjustments to keep it in the optimum range.

POCKETS OF REAL TECHNOLOGY

There are aspects of phosphate technology that constitute true technology. Many aspects of phosphate chemical technology can be calculated – mundane stuff like heat and material balances, some heat transfer (before scale starts to form and slow things down), and fluid flow (until that same scale mucks things up).

All of us in the phosphate chemical industry can be eternally grateful to the late Pierre Becker, who documented a tremendous amount of real phosphate technology in his book *Phosphates and Phosphoric Acid* (Marcel Dekker, Inc., New York). This book has been an invaluable source book of real phosphate technology for two decades.

Our own AIChE Clearwater Convention, as well as the nearby Lakeland Phosphate Conference and other phosphate conferences around the world are a valuable source of real phosphate technology and of the mud chemistry that are essential parts of our know-how.

The industry is fortunate to have the excellent services of the Florida Institute for Phosphate Research just down the road in Bartow, Florida. FIPR has consistently been a great source of phosphate technology, and their library contains a wealth of information. FIPR is spearheading a worldwide effort to develop a wide variety of ways to utilize what is actually the phosphate industry's biggest product – gypsum. IFDC provides fertilizer development technology worldwide, and publish a very useful *Fertilizer Manual*.

There is a computer program that successfully correlates amounts of various complex compounds that post-precipitate while phosphoric acid aged in storage tanks. Another computer program predicts performance of the big cooling ponds that handle water re-use and do the cooling at many phos acid plants.

I recently encountered some impressive technology in action for a thermal process that makes high-purity superphosphoric acid from some extremely low-purity phosphate materials. The "Improved Hard Process" (IHP) uses lots of break-through technology involving advanced-design kilns, classy heat transfer, understanding of eutectic points, and many concepts that we don't see in the wet phosphoric acid end of the industry. I encourage my colleagues in the phosphate industry to keep an eye on the IHP as its process development moves from pilot plant operation into a practical demonstration plant.

Maybe the IHP will provide a way to utilize material that we think of as trash, or material that would require excessive beneficiation cost, or other material that some clever mine planner might come up with. Central Florida phosphate people might be interested in IHP's ability to utilize the lower zone phosphate ores of the southern extension without transferring impurities to the main stream phosphate rock product. Old tailings and debris sites are other candidates for consideration. Byproduct from IHP is a dry agglomerate, rather than the gypsum that wet phos acid plants produce. There may be potential uses for the agglomerate in reclamation or aggregate uses.

THE MINERALS PART OF THE PHOSPHATE INDUSTRY

I'll leave it to the experts on geology, mining and beneficiation to say whether the minerals end of the industry deals with mud chemistry. However, whenever I visit their sites I get mud on my boots. They do deal with some interesting technology, including geological reactions that often take over a hundred million years.

IS IT MUD CHEMISTRY OR SOFT TECHNOLOGY?

Although the "mud chemistry" claim has some validity, I think a more accurate term would be "soft technology." In an industry where we politely avoid calling phosphatic clay "slimes" and use various euphemisms instead of saying "low grade rock", we should also opt for the more civilized characterization of our technology. So:

~~MUD CHEMISTRY~~ **--------> SOFT TECHNOLOGY**

HOW SHOULD WE WORK WITH SOFT TECHNOLOGY?

The softer the technology, the more important it is to listen hard to what others in the industry have to say. Only a limited amount of technology can be derived from books, technical articles, calculations, and other traditional sources. Soft technology tends to come from more casual sources. A key to learning and sharing of soft technology is to network with people who deal with all parts of our industry.

A prime source of important phosphate technology is the people in operations. They deal with many of the idiosyncracies of phosphate operations daily, and what they tell you could be invaluable. Feedback from those who work "where the rubber meets the road" can aid in troubleshooting problems or can lead to design of operator-friendly plants that operate more easily and effectively. Similarly, those who maintain phosphate plants can provide insights that help their colleagues in operations, tech service, or plant design to enable plants to operate more reliably and with lower maintenance cost. Vendors who offer equipment and services to the industry can be a valuable source of know-how regarding many details of equipment or service related issues.

WHO BENEFITS FROM EFFECTIVE USE OF SOFT TECHNOLOGY?

The first benefactors of better utilization of soft technology are the various plants that produce phosphate products more effectively. However, the beneficial effects of what we do in the phosphate industry continue throughout the entire chain of distributors, farmers, food processors, and users of upgraded products and by-products of all sorts. Most people in the world eat food from crops that have been nourished by phosphate. All of us in this industry had a hand in producing that phosphate. The end result is that all of us in the phosphate industry are helping billions of people worldwide by promoting harvests in greater quantity and quality.

Of particular importance are an estimated 800 million desperately hungry people around the world who need more food from more productive farms. A child starves to death every five seconds. Phosphate fertilizer plays a crucial role in dealing with this tragic situation.

It is recognized that making a contribution to society is a person’s deepest desire. The efforts that we make as part of our daily routine within the phosphate industry are benefitting most of the people in the world. Everyone in the industry can take satisfaction in accomplishing whatever specific task we do as part of our job, whether it’s fixing a pump, operating a filter, writing a letter, or getting up to our knees in ~~mud chemistry~~ soft technology. All of us in the phosphate industry are helping to feed the world, prevent starvation, and save lives of millions of people we’ve never met.

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ABOUT THE AUTHOR

John Wing - President of the consulting firm John Wing, P.E. - has a Bachelor of Chemical Engineering degree with Honors from University of Florida and a Master of Engineering in Administration from University of South Florida. He has served the phosphate industry for decades in process design, consulting, project management, technical service, process development, and production supervision. He was vice president of HiTech Solutions and was employed by other engineering and phosphate production companies. He has performed work for nearly all of the phosphate chemical plants in the United States and several foreign operations.

He does process engineering for new plants, modifications and expansions for phosphoric acid, DAP, MAP, & TSP plants. He has provided process and conceptual design for six phosphoric acid evaporators, scores of fume scrubbers, and five fluosilicic acid recovery systems.

John has helped pioneer implementation of the energy-efficient Hemi process by doing process design for the Belledune and Arcadian Hemi conversion, the 3-train Ma'aden plant in Saudi Arabia, and for converting the Oswal dihydrate plant in India to Hemi-Di (a project that started but then stalled). He consulted as owner's engineer for Indo-Jordan Chemical Co.'s Hemi plant in Jordan and has been providing subsequent technical services and modifications for the same plant.

Technical papers include:

- Hemi and Hemi-Di processes (7 papers)
- Comparison of the three main phosphoric acid processes
- The future of the phosphate industry
- Phosphoric acid evaporation
- Cooling pond systems
- "Can a Little Altruism Enhance an Engineer's Career Satisfaction?"
- Featured in three recent articles in *Fertilizer International* journal.

He is a Fellow of AIChE, a registered Professional Engineer, and past Chairman, Vice Chair, and Secretary of the Central Florida AIChE Section.

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