SELECTING A PHOSPHORIC ACID PROCESS

Di, Hemi, & Hemi-Di Processes for New Plants & Conversions

John Wing, P.E.

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SUMMARY

Most of the world's phosphoric acid is produced by either a dihydrate (Di), hemihydrate (Hemi) or the hemi-dihydrate (Hemi-Di) process. Which process is best for that new phosphoric acid plant? Should an existing plant be converted to another process? How about converting and expanding in the same project? The answers don't come easily.

This presentation deals with issues to consider when making these decisions. Each process has its advantages and disadvantages. Capital and operating costs for the plant as a whole vary greatly depending on which process is selected. Entire plant sections for grinding rock, handling of weak acid, or clarifying product acid are either necessary or not, depending on the process. There major differences between processes regarding size of facilities required to concentrate acid or to cool process water. Operating costs vary greatly due to differences in energy efficiency, raw material consumption, ability to consume water, and requirements for steam, cooling water, and reagents.

Opportunities to recover valuable by-products are greatly affected by which process is employed. Uranium recovery has recently re-emerged as an important issue, since even environmentalists promote nuclear power's ecological advantages over fossil fuels. Potential developments in uranium recovery from Hemi-Di plants might make this even more attractive. The opposite is true for the Hemi process, which may be incapable of practical uranium recovery. The Di process continues to be a proven source for uranium recovery. The Hemi-Di process provides the highest quality gypsum for a variety of gypsum utilization needs. The Di process can provide the greatest recovery of fluosilicic acid.

This presentation highlights issues affecting capital and operating costs as well as by-product recovery. The processes will be compared for new facilities and for potential conversions of existing plants. A third area with quite different incentives is when an existing facility might be expanded in capacity while converting to a new process.

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John Wing, P.E., 1121 Waters Edge Drive, Lakeland FL 33801, USA
Phone: 1-863-666-6555 Email: johnwingpe@verizon.net

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CHARACTERISTICS OF DI, HEMI, & HEMI-DI PROCESSES

IT'S ALL IN THE GYPSUM

Phosphoric acid plants are really gypsum plants, because they make much more gypsum than phosphoric acid. Since gypsum is often a bothersome waste product, the plants are named for the valuable second product - phosphoric acid. However, the various processes that are utilized are named for the type of gypsum that is produced. Gypsum is calcium sulfate with various amounts of water of hydration attached to the calcium sulfate molecules. The key to successful operation of a phosphoric acid plant is to make good gypsum. Characteristics of good gypsum are large crystals that filter well and a minimum of phosphate content within the gypsum crystals.

Gypsum crystals are in the Di (dihydrate) form at lower concentration and temperatures, and in the Hemi (hemihydrate) form at higher concentration and temperature. The Dihydrate (Di) process makes gypsum in the form of calcium sulfate dihydrate, which has two water molecules per calcium sulfate molecule. The Hemi process makes gypsum in the form of calcium sulfate hemihydrate, which has half a water molecule per calcium sulfate molecule. The hemi and di zones are illustrated in the "Calcium Sulfate Crystallization Graph" on page 6.

Either a hemihydrate or dihydrate process can have stable operation if the conditions are clearly in either the hemihydrate or dihydrate zone. Problems occur between the zones, because the crystals don't know which form they are supposed to be, resulting in poor crystals and formation of scale. Think of the transition zone boundary as a "line of dragons" that needs to be avoided where possible. Special techniques are necessary where conditions must cross this transition zone, such as occurs on a Hemi filter. The Hemi process became successful only after good "dragon-fighting" techniques were developed for filtration and gypsum disposal.

DIHYDRATE PROCESS

This was the conventional process for most of the 20th century. Dihydrate plants have made the phosphoric acid for most of the high analysis phosphate fertilizer that has ever been produced. This process has a long track record or reliable operation, but it lacks the energy efficiency and many of the operating advantages of the Hemi process. Most phosphate rocks must be finely ground before processing.

Operating conditions in the Di process stay below the Hemi/Di transition boundary, but it is economically necessary to push as deeply as practical into that boundary zone. The filter product phosphoric acid is typically only 25-29% P_20_5, so substantial further concentration of product acid is required before making phosphate fertilizers. Innovations have been used to expand capacity of some dihydrate plants to more than double their original capacity.

Dihydrate process advantages include:

- Long track record of experience
- Predictable performance
- High capacity relative to equipment size
- Moderate recovery and sulfuric acid requirement
- Proven potential for recovery of uranium by-product
- Best for recovery of fluosilicic acid by-product

Disadvantages include:

- Fine grinding of rock is normally required
- Acid must be further concentrated to make most phosphate fertilizers.
- Large steam and cooling water requirement

HEMI PROCESS

The Hemi (hemihydrate) process produces phosphoric acid directly from filtration at 40-45% P_20_5 concentration. Most Hemi plants use phosphate rock as received – without drying or grinding. Two entire plant sections are usually rendered unnecessary:

- Evaporation to ~42% P_20_5
- Rock grinding (when using concentrate or other rock smaller than 2 mm)

Cooling water, acid storage, clarification, and steam distribution systems are reduced to a fraction of their conventional size. Capital cost for the phosphate complex is roughly 20-25% less than for a dihydrate-based complex, which would require rock grinding, evaporation, larger cooling water and steam distribution systems, and often elaborate acid clarification systems.

Modern Hemi phosphoric acid plants tend to be easier to operate and require less cleaning than dihydrate plants. One reason is that the reaction takes place in a stable range of hemihydrate crystals. In contrast, dihydrate plants must (out of economic necessity) operate near the unstable transition between dihydrate and hemihydrate.

Hemi process advantages include:

- Minimum capital cost
- Energy benefit from needing little or no steam to concentrate acid
- Eliminate 27-42% evaporators
- Usually eliminate rock grinding
- Low cooling water requirement
- Moderate phosphate recovery
- Added recovery benefit where gypsum water is recirculated
- Low sulfuric acid requirement
- Easy to run and maintain; tolerant of process upset
- Higher analysis fertilizer due to purer acid

Hemi has become the preferred process for making phosphoric acid in the 21st century. Early Hemi plants were difficult to operate because of scaling problems that occurred because of having to cross the zone of transition between Hemi and Di gypsum crystals. During the last few decades people have developed ways to enjoy hemi's high concentration advantage without suffering its potential chaos.

HEMI-DI PROCESS

This advanced process begins with a Hemi reactor and Hemi filtration section, but it adds a transformation reactor and a second filtration. The payoff for the added cost and complication is extremely high recovery and high quality gypsum.

Hemi-Di advantages include:

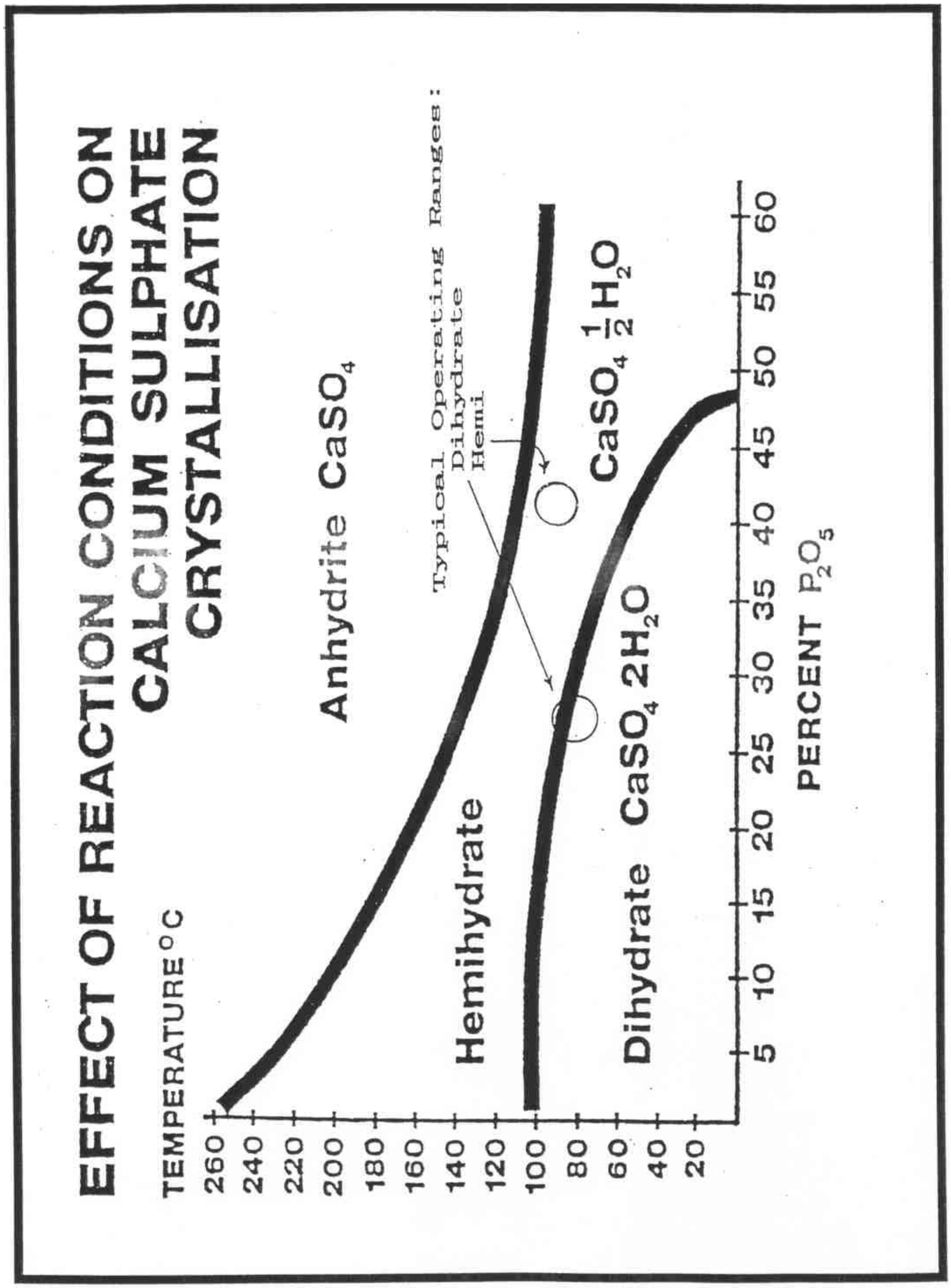
- 98-99% P_20_5 recovery
- Very low sulfuric acid requirement
- Energy benefit from needing little or no steam to concentrate acid
- Eliminate 27-42% evaporators
- Usually eliminate rock grinding
- Low cooling water requirement
- Gypsum purity is suitable for making a variety of by-products
- Potential for enhanced uranium recovery (to be confirmed)
- Higher analysis fertilizer

OTHER PROCESSES

Other phosphoric acid processes including Di-Hemi and a short-cut Hemi-Di have also found their niche. If that's not enough, ask someone from Prayon to explain the Hemi-Di-Hemi process. Jim Hebbard can amuse you regarding the FIPR process, which operates in the mono-calcium phosphate mode. There are other processes that don't even make gypsum, because they don't use sulfuric acid, (so what I said earlier about phosphoric acid plants being gypsum plant isn't always true). This presentation will deal with only the three most common processes – Di, Hemi, and Hemi-Di. I don't know much about the other processes to cover them adequately, although I once convinced a client not to pursue a Di-Hemi process.

Calcium Sulfate Crystallization Graph

Courtesy of Hydro



COMPARING PROCESSES

Selection of the optimum process requires careful evaluation of capital and operating costs, requirements for raw materials and reagents, quality of products and by-products, utility situation, opportunities to recover valuable raw materials, and a variety of other issues. Every project has its own set of needs, costs and opportunities, so a detailed evaluation is necessary to pick the process. Factors which often vary so greatly that they have overwhelming influence on process selection include:

Performance of phosphate rock in the various processes
Phosphate rock cost, delivered
Sulfur cost, delivered
Value of exported electric power
Gypsum utilization or disposal situation
Opportunity to recover uranium

The main issues are discussed below in a qualitative manner, based on typical or average situations. Any project that is being seriously considered should involve a comprehensive evaluation of each of these issues, including cost information that is specifically tailored to the site.

To help provide an overview of issues to consider, the three processes are rated in the attached “Di, Hemi, and Hemi-Di Processes Comparison Table” on page 19. This table relates to average situations, but one must recognize that any individual project may have circumstances that are far from typical.

CAPITAL COST – REACTOR/FILTER SYSTEM

A Di process will usually have the least expensive main reactor. Experience with dihydrate reactors over several decades has demonstrated that many plants are operating at capacities that are more than double original design capacity. Such experience is utilized to confirm that new reactors can be much smaller than those of a few decades ago. Hemi reactor size requirement has also tended to decrease as plant experience is gained, but the Hemi process has a shorter track record to draw from.

Filter size requirement varies greatly with the type of phosphate rock that is utilized. Pilot plant testing of the phosphate rock can predict filtration rate before the plant is designed. It has been my observation that filtration rate tends to average somewhat higher with a Di process than with a Hemi process. However, there are many exceptions, so a valid comparison between the two processes must consider experience in real plants and pilot plant testing.

Since the Hemi process operates at hotter temperatures, metals tend to corrode somewhat faster than in the Di process. Consequently, metals in agitators, pumps, and filter wetted parts will usually be somewhat more expensive in a Hemi plant. Flash coolers in Hemi reactors can be significantly smaller and require less circulation rate than those in Di plants. However, Hemi plants require more fume collection capacity and efficiency than Di plants.

The entire reactor/filter system for a dihydrate process will usually be smaller and less expensive than for a Hemi process. A Hemi-Di process requires a Hemi reactor/filter system followed by a simpler and smaller dihydrate reactor/filter system. Consequently, reactor/filter capital cost is very high in a Hemi-Di plant.

CAPITAL COST OF OTHER PLANT SECTIONS

The Hemi process has advantages outside of the reaction and filtration sections that tend to allow the total plant capital cost to be significantly less than with a Di process.

The first advantage is that the Hemi reaction does not require the phosphate rock to be ground as finely as does the Di process. The popular Yara (Hydro) Hemi process can use rock particles as large as 2 mm (9 mesh), compared to a typical 35 mesh requirement with the Di process. This means that a Hemi plant can use phosphate concentrate and other phosphate up to 2 mm in size without any processing. In contrast, a Di process usually requires rock to be finely ground in a ball mill, requiring major expense for capital, operation, maintenance, and energy.

A Di plant makes filter product acid at around 27% P_20_5 concentration, compared to about 42% P_20_5 acid from Hemi filters. Consequently it requires additional evaporators to concentrate this acid, along with substantial investment for additional cooling water and acid storage facilities.

A Hemi plant normally has lowest capital cost for a new plant, because it usually avoids rock grinding (except with pebble-sized rock), it requires much less (if any) evaporation of acid, cooling water is minimized, there is no 27% P_20_5 acid to handle, and product acid clarification is usually unnecessary.

Although a Di process might have a less expensive reactor and filter section, it would require all of those extra plant sections and expanded capacities. Consequently, the whole plant containing the Di process would normally cost around 20-25% more than a Hemi process plant.

A Hemi-Di process shares Hemi's advantages of eliminating or down-sizing of those plant sections. However, Hemi-Di requires a second (but simpler) set of reaction and filtration facilities, which roughly offset savings in other sections. I would guess that the whole Hemi-Di plant would cost no more than a whole Di plant, when cost of rock grinding, evaporators, acid handling, and cooling are considered.

PHOSPHATE ROCK & SULFURIC ACID REQUIREMENT

Most loss of product in a phosphoric acid is in the filter cake, so **filter recovery** has the largest influence on how much raw materials are required. This must be evaluated on a case by case basis. Licensors guarantee performance including recovery at the filter cake for the specific plant and conditions. Di and Hemi plants typically achieve filter recovery in the mid-90% range, with Di plants averaging perhaps a percent or so higher than Hemi plants. Hemi-Di recovery (based on filter cake) is typically 98-99%.

There will be considerable **additional losses beyond filter cake losses**. Phosphoric acid is lost by entrainment from flash coolers and evaporators, leakage from seals, filter mechanical losses, dumping of acid during maintenance and cleaning, and accidental spills. The total of such losses may amount to a percent or two of product in a typical plant. Hemi & Hemi-Di plants have much less evaporator entrainment losses, because very little evaporation of acid is required. Only Di plants are exposed to losses from handling 27% P_20_5 acid because Hemi & Hemi-Di don't produce the weak acid. Hemi-Di plants have additional exposure to general material handling losses around reactors and filters, because they have more reactors and filters.

There can be opportunities to **recover what had been lost**. Many plants recirculate the acidic water from the gypsum stacks and/or cooling water systems. Some of this acidic water is used to wash the filter cake. Most cake wash water proceeds through the filter and ends up in product acid. Thereby, over half of all phosphoric acid which had been lost into this acidic water is eventually **recovered from the recirculated water**.

Any plant that recirculates acidic water from the gypsum stack will recover most of the water soluble losses in the filter cake. However, water insoluble losses from a Di plant (or the Di filter in a Hemi-Di plant) remain locked in the dihydrate gypsum crystals, so it cannot get recovered. This refers to losses that are reported as CI losses (citrate insoluble – un-dissolved rock) and CS losses (citrate soluble – co-precipitated dicalcium phosphate in gypsum crystals – the majority of filter losses).

A **Hemi** plant that recirculates acidic water from the gypsum stack has an added recovery benefit. This is because the hemihydrate gypsum crystals will release co-precipitated dicalcium phosphate out of the crystals and into the surrounding water.
will **recover most of the water soluble losses from the filter cake**. For example, a typical Hemi filter cake contains co-precipitated dicalcium phosphate (citrate soluble P_20_5) equivalent to 3.5% of the feed. After discharging from the filter the hemihydrate crystals gradually dissolve while forming dihydrate crystals. The co-precipitated dicalcium phosphate dissolves in the acidic water, and very little re-precipitates into the dihydrate crystals. Thus about half of that 3.5% loss (1.75%) gets recovered when recirculated water is used to wash the filter cake.

P_20_5 Recovery Rankings for the three processes are typically as follows. High recovery means low phosphate rock requirement.

1st: **HEMI-DI**
High recovery 98-99% is the reason for this fancy process

2nd: **HEMI with Recirculation of Water from Gypsum Stack**
Recovery of an extra couple percent of lost P_20_5 gives Hemi the advantage over Di.

3rd: **TIE: HEMI & DI**
Di usually has a slight edge with recovery based on filter cake, but Hemi avoids evaporator entrainment and weak acid handling losses.

A Hemi reactor needs significantly less sulfuric acid than a Di reactor, primarily because of the reduced ratio of sulfate to phosphate in the reactor acid. Acid from Hemi reactors typically contains 2% free SO_4 and 43% P_20_5 (a ratio of 0.46), whereas Di reactor acid is typically 2% free SO_4 and 27% P_20_5 (a ratio of 0.74). Another small advantage with Hemi is that slightly less sulfuric acid reacts with aluminum impurities. In the Yara (Hydro) **Hemi** process these effects amount to needing about **2.5% less sulfuric acid** than with a Di process with similar recovery.

Sulfuric acid consumption will track with P_20_5 recovery, except that Hemi & Hemi-Di have about 2.5% advantage – due primarily to low-sulfate product. The processes typically rank in this order regarding sulfuric acid consumption: **Hemi-Di, Hemi, and Di.**

ACID CONCENTRATION

Most dihydrate phos acid plants make 25-29% P_2O_5 product. Higher product concentration is impractical, because it would involve pushing operating conditions into the unstable hemi/di transition boundary.

Hemi plants produce phosphoric acid directly from filtration at concentrations between 38% and 46% P_2O_5. Optimum concentration has been around 43% P_2O_5, which is near the “sweet spot” where a Hemi plant performs best. Rapidly increasing energy value may entice anyone who operates or designs a Hemi plant to raise product concentration to further enhance energy efficiency. Higher product concentration would require somewhat larger reactor and filters, and recovery might decline. However, these trade-offs may be wise, considering the energy benefits to be gained.

Hemi-Di plants benefit from water balance and cake washing situations that make it practical to make even higher concentrations of phosphoric acid – ranging from 40% to 50% P_2O_5.

ENERGY EFFICIENCY

Energy efficiency is essential in dealing with global warming. The Hemi process' forte is efficient use of energy. Its high product acid concentration avoids the need for the huge quantity of evaporator steam that would otherwise be required to make product concentration suitable for further processing. Ongoing trends of soaring energy costs and need to conserve energy will further magnify this advantage in coming years.

The biggest source of energy for a typical phosphate chemical complex is sulfuric acid production. Surplus heat from burning of sulfur is absorbed by steam, which is used to generate all electric power required by the complex plus an export of power.

Energy efficiency of a phosphate complex is greatly enhanced by use of the Hemi phosphoric acid process. A 1,500 T/D P_2O_5 phosphoric acid plant will save about 2500 T/D in evaporator steam by making filtered acid at 42% P_2O_5, compared to dihydrate process acid at 26% $P_2O_{5.}$ This surplus steam would typically be used to generate electric power. Total electric power production is near 60 megawatts for a 1500 metric T/D P_2O_5 phosphate complex. This is worth $35 to $50 million annually, based on electric power values of 7 to 10 cents/kwh. The energy advantages of the hemihydrate process account for about 16 megawatts of this power – worth $9-15 million/year or $18-30/ton of P_2O_5. The surplus electric power could be exported to the power grid for sale, or it could be wheeled to the owner's mine or other nearby facilities. Future electric power values are likely to increase substantially as other sources of energy become increasingly expensive.

A 1500 T/D Hemi or Hemi-Di plant would typically save another 3 MWs of electric power by not having to grind rock, and by having much smaller acid evaporation requirement.

Hemi & Hemi Di plants also save the electric motor power that Di plants need to operate additional evaporators, cooling water pumping, and acid handling facilities. Hemi-Di plants do require substantial power for the second reactor and filters, thus offsetting part of the motor power savings.

It is important to note that any utilization of energy from waste heat is environmentally friendly. This electric power is produced with incremental net results of no pollution, no greenhouse gas, no solid waste, and no consumption of fuel. **No other source of energy can top this for ecological responsibility** - whether it uses coal, oil, gas, nuclear fuel, wind, or solar energy.

Energy Efficiency rankings for the three processes would be:

1st:	**HEMI**	Needs little or no evaporator steam Avoids rock grinding (usually) Less power for evaporation, acid handling, and cooling water
2nd:	**HEMI-DI**	Same advantages as Hemi However, the second reactor and filters need more power.
3rd:	**DI**	A distant last place.

AVOIDING ROCK GRINDING

The Yara (Hydro) Hemi phosphoric acid process can use rock which is much coarser than that required for conventional dihydrate processes, so grinding is not required for most of the world's phosphate rock sources. Particle size requirement for Yara Hemi is typically -9 mesh (-2 mm), versus -35 mesh (0.42 mm) for typical dihydrate processes. The Hemi process can handle damp rock with up to about 15-20% moisture. Most commercial phosphate rock sources worldwide are suitable in particle size and moisture content for feeding directly to a Hemi plant without drying or grinding. This includes coarse concentrate and some screened phosphate rocks.

An important exception is that the pebble rock which makes up a significant portion of central Florida phosphate is much too coarse to feed directly to any phos acid plant. Pebble rock could be ground to -2 mm size in relatively low energy roller, impact, or hammer, mills with closed circuit screening. This pebble rock is available dripping wet with about 10% moisture, and drying would be quite expensive. Consequently, the recommended method would be to grind the damp rock without drying, followed by wet screening and recycle of damp +2 mm material to the mill. Such milling requires only a fraction of the power and capital cost that a ball mill requires.

OPERATOR, MAINTENANCE, AND CLEANING COST

Both Hemi and Hemi-Di benefit from elimination of rock mills and evaporators, and have smaller acid handling and cooling water sections than a Di plant. Hemi reactors and flash coolers stay cleaner than those in Di plants. Di filters stay cleaner than Hemi filters. A Hemi-Di process has a second reaction and filtration second to operate and maintain. A Hemi plant should have a significant advantage over either Di or Hemi-Di, because there is much less equipment to operate and maintain.

Hemi reactors have a major stability advantage, because they operate in a stable zone, well above the hemi/di transition boundary. Substantial changes in temperature and concentration can be tolerated without approaching the transition. Operating control is less critical, and the reactor is more forgiving to upset conditions or sudden changes in rock feed characteristics. This accounts for praise by those that operate the plants that they are easier to operate, more stable, and more forgiving than dihydrate plants. There is relatively little scale formation in the reactors and flash coolers, because of operating in the stable zone, and because there is lower solubility of calcium sulfate.

Hotter conditions in Hemi reactors and filters cause faster corrosion to agitators, filter metal surfaces, etc. Optimum metals for Hemi service are typically one step up from metals that would be optimum for dihydrate service. Hemi reactor agitators are typically in the 904L or Ferallium 255 class, although existing 317L agitators have lasted fairly well in plants that were retrofitted from di to hemi. Upper agitator shafts in either hemi or di reactors require rubber coating. Filter pans are normally 317L or either process, but Hemi plants with highly corrosive acids should use 904L. Belt filter vacuum boxes are typically 904L.

OPERATING STABILITY

Either a hemihydrate or dihydrate process can operate stably if the conditions are clearly in either the hemihydrate or dihydrate zone. The hemi/di transition zone is illustrated in the “Calcium Sulfate Crystallization Graph” on page 6.

Dihydrate plants must limit reactor concentration in order to keep below a transition zone between hemihydrate and dihydrate. When concentration or temperature gets a little too high, the gypsum crystals form as a mixture of dihydrate and hemihydrate crystals. These crystals are small, which reduces filtration rate. Wherever the slurry cools, scale forms inside the reactor, pumps and piping. For economic reasons dihydrate plants must push slightly into the transition zone, but good control can minimize problems. If a dihydrate reactor is allowed to get seriously over optimum temperature or concentration, filtration becomes extremely slow, and equipment scaling is severe. Crystals in a typical dihydrate plant are a mixture of some hemihydrate among mostly dihydrate crystals. Dihydrate plants tend to have far more scale formation in reaction and flash cooling systems than hemi plants.

Hemi reactors have a major advantage, because they operate in a stable zone, well above the hemi/di transition zone. Substantial changes in temperature and concentration can be tolerated without getting into the transition zone. Operating control is less critical, and the reactor is more forgiving to upset conditions or sudden changes in rock feed characteristics. This accounts for praise by those that operate the plants that they are easier to operate, more stable, and more forgiving than dihydrate plants. There is relatively little scale formation in the reactors and flash coolers, because of operating in the stable zone, and because there is lower solubility of calcium sulfate.

The “Calcium Sulfate Crystallization Graph” shows a hemi/anhydrite transition above the hemi zone. In actual practice this transition is so high that it is rarely a problem, except occasionally in some hemi-di plants which push reactor acid concentration to 48-50% P_20_5.

In a Hemi plant conditions in filtration pass thru the Hemihydrate/Dihydrate transition line. Crossing this transition caused problems for early Hemi plants. However, technology has been developed which allows this transition to be crossed with minimal scaling in the filter system. Part of this technology has been use of an anti-scalant reagent that greatly slows the conversion of hemihydrate crystals to dihydrate crystals, thus reducing scaling. Anti-scalant is not always necessary, as was demonstrated at Belledune, where the anti-scalant system was abandoned.

COOLING WATER REQUIREMENT

Hemi & Hemi-Di plants have less need for the huge flow of cooling water normally required by phos acid evaporator condensers - perhaps none at all. A relatively small flow of cooling water is required for flash cooler condensers, fume scrubbing, equipment washing, etc. This water does not need to be as cool as the 33-35^{0}C (92-95^{0}F) required for 52-54% P_20_5 evaporators in a dihydrate phos acid plant. Water at around 38°C (100°F) will be adequate for scrubber water, equipment wash, etc., and more than adequate for flash cooler condenser water. Hemi & Hemi-Di plant cooling pond and associated pumps and piping are a fraction the size of comparable equipment in a Di plant.

ACID STORAGE AND CLARIFICATION

Phosphoric acid storage and clarification facilities in a Hemi or Hemi-Di plant are about one third that required for a dihydrate plant. There will be agitated storage tanks for 42% acid (and possibly some 30% acid for DAP scrubber feed). Clarification is not necessary because the 30% and 42% phosphoric acids have both come from filtration, and because the high purity of Hemi acid makes further clarification unnecessary for product analysis purposes.

A Di plant would typically require storage and clarification for 26% and 42% acid, plus agitated storage (and often clarification) for 52-54% acid.

PHOSPHORIC ACID PURITY & BENEFITS TO FERTILIZER ANALYSIS

Phosphoric acid from a Hemi or Hemi-Di plant is purer than that from a Di process, with lower sulfate, aluminum, fluoride, and solids content. DAP, MAP, and TSP produced from this acid will be about 2 percentage points higher in P_2O_5 than that from a dihydrate plant. This facilitates production of on-grade DAP and TSP from phosphate with high impurity levels. MAP grade would rise, thus reducing shipping cost.

Effect of acid purity on DAP nitrogen content is more difficult to predict, because %N is affected not only by product purity, but also by efficiency of ammonia absorption. Calculated DAP grade benefit is over 0.5 percentage points in N, but this assumes adequate ammonia absorption.

Effect of Hemi acid purity on DAP grade was demonstrated at the Belledune plant, which was converted to Hemi in 1986, using 66-67 BPL central Florida rock. Before the Hemi conversion is was difficult to meet 18-46-0 DAP grade, using settled 40% P_20_5 acid. Upon Hemi start-up, grade jumped to about 47.5% P_20_5 and easily exceeded the 18% N requirement, using un-settled 40% acid. A simple modification was employed to prevent over-formulation of DAP.

REAGENT REQUIREMENTS

Nearly all phosphoric acid reactors require defoamer, and I have not noticed significant difference between Di and Hemi reactors. However, Arcadian/PCS found that when using BuCraa rock from the Western Sahara region of Morocco, no defoamer was required with the Di process or after conversion to the Hemi process.

Yara prescribes a proprietary anti-scalant to minimize formation of scale within filters in a Hemi plant (but not in a Hemi-Di plant). This costs roughly \$1/ton P_20_5. An exception was that the Belledune Hemi plant discontinued use of the anti-scalant and removed the system. That was with a Bird tilting pan filter, using phosphate rock from central Florida and Morocco.

Hemi and Hemi-Di plants sometimes add clay to the hemi reactor to modify crystal shape and/or absorb corrosive free HF.

Hemi-Di plants sometimes add clay to the second reactor to facilitate transformation of hemi gypsum crystals to dihydrate form.

WATER CONSUMPTION INTO THE PROCESS

A Di process must consume much more water into the process than a Hemi or Hemi-Di process, largely due to the effect on water balance for producing 27% versus 42% P_20_5 product. Water consumption can be good, bad, or of little consequence, depending on the circumstance. A plant receiving ground rock slurry from a wet ball mill would have to have a Di process. That much water would drown a Hemi reactor. However, a Hemi reactor does not need finely ground rock, so a wet ball mill should not be involved anyway.

There may be other reasons to want to consume extra water into a reactor. For example, one client expressed interest in a Hemi conversion, but the plant received 70% sulfuric acid at very low cost. There was too much water in 70% H_2SO_4 for the Hemi process to work, so the plant kept its Di process. The Di process could have an advantage where phosphate rock is received as a slurry by pipeline, because it might be able to consume the entire slurry without de-watering. Such rock slurry would have to be partly de-watered to feed a Hemi plant.

For plants in a desert or other location where water is very expensive, the Hemi reactor's lesser need for water is an advantage. The Hemi plant also has an advantage at the gypsum discharge end. Free moisture in filter cake is about the same for a Di or Hemi filter. However, Hemi filter cake contains far less water of hydration, because of the difference between calcium sulfate hemihydrate versus calcium sulfate dihydrate. Plants in deserts often discharge gypsum to the gypsum stack as filter cake, rather than as slurry. In such plants the difference in total water content in the gypsum is important.

Hemi gypsum cake is “self drying” because hemi gypsum absorbs most of the free water from the filter cake as gypsum converts from hemi form to dihydrate form. In desert conditions, this leads to another advantage of discharging Hemi filter cake. This “self drying” gypsum will never seep free water downward. Thus there is no real need for using an expensive water-proof liner under a hemi gypsum stack. In some situations it might be necessary for the plant owner to convince regulatory authorities not to mandate a multi-million dollar expense for a useless liner.

The same self drying gypsum advantage is achieved with a Di-Hemi or Hemi-Di-Hemi process. It is not achieved with a Hemi-Di process, because Hemi-Di discharges dihydrate gypsum from the Di filters.

PROCESSING IMPURE ROCK

There is increasing evidence that the Hemi process performs well with some types of phosphate rock that are impractical to process with conventional dihydrate processes. This includes rock with very low P_20_5 concentrations and unusually high levels of iron, aluminum, and magnesium impurities. Such rock is either left in the ground, blended with higher grade rock, or processed for further purification. Ability to process low-grade rock could lead to breakthroughs in utilizing phosphate reserves in places like South Florida.

One Hemi plant successfully uses a large amount of “sub-commercial” rock that had been considered practically worthless for processing. A company that has both Hemi and Di plants routinely routes the lowest grade rock to the Hemi plant, because it processes it more easily. At Belledune the original Di plant was unable to make on-grade DAP from clarified acid; when the plant was converted to Hemi, it immediately exceeded DAP grade by a wide margin.

GYPSUM UTILIZATION

Gypsum from phosphoric acid plants can be utilized to produce a variety of products. Such phospho-gypsum has been used for road-bed material, cement ingredient, sulfate fertilizer, agricultural soil conditioner, or gypsum wall board. Further processing of the gypsum can produce limestone, ammonium sulfate, sulfuric acid, glass, and ceramics. The Florida Institute for Phosphate Research (www.fipr.state.fl.us) is heavily involved with an international effort to develop many uses for billions of tons of phospho-gypsum. FIPR has stated that “research indicates that a beneficial, commercially appropriate and environmental neutral use for PG (phospho-gypsum) would be preferable to dumping or perpetual storage in stacks.” This effort is supported by international and regional phosphate organizations including IFA, IMPHOS, AFA, and Mosaic, as well as the OECD, IAEA, and other organizations.

In the United States it is unfortunate that the EPA banned use of phospho-gypsum in 1992 – essentially mandating perpetual storage for billions of tons of this potentially valuable material. This resistance seems to be an overreaction to the minor radioactive content of phospho-gypsum. Although original flawed data that led to this conclusion has been repudiated, efforts to have the EPA re-evaluate their stance have proceeded extremely slowly.

Processes that utilize gypsum from phosphoric acid plants often require the gypsum to have limited concentration of phosphate and fluoride impurities. Suitable high purity phospho-gypsum can be produced from either a Hemi-Di process or a Di-Hemi process. Gypsum of moderate purity is obtained by re-washing gypsum cake from phosphoric acid filters.

Hemi, Di-Hemi, and Hemi-Di-Hemi processes produce gypsum filter cake that is self-drying, which can be a major advantage for drying requirements when gypsum is utilized. This self-drying occurs because hemihydrate gypsum absorbs most of the free water from filter cake when it converts to dihydrate gypsum.

URANIUM RECOVERY

Phosphate rock contains uranium in concentrations up to a pound (half a kilogram) of U_3O_8 per ton of rock. Uranium can be recovered by solvent extraction from phosphoric acid from dihydrate plants containing about 25-29% P_20_5. This extraction is preceded by extensive clarification and pre-treatment of the phosphoric acid. Much uranium was recovered from phosphoric acid a couple of decades ago. A sudden downturn in uranium price forced recovery plants to shut down.

Now nuclear power plants are finding favor as economically and environmentally attractive sources of electric power. Despite concerns about disposal of spent fuel, nuclear power plants are often considered a more environmentally friendly power source than fossil fuels. They emit no air or water pollution and no greenhouse gasses. The Nuclear Regulatory Commission is handling 16 applications for nuclear power plants in the USA, and expects to receive 32 by 2012.

Uranium prices have soared to double or triple what they were a couple decades ago. Even so, uranium costs only a fraction as much as oil per unit of power produced.

The **Di process has a proven track record** of successful uranium recovery. The Hemi process is not attractive for uranium recovery. Its high product acid concentration makes uranium extraction difficult, and uranium content in the acid is low.

Uranium recovery **might be exceptionally attractive with a Hemi-Di** process. This is because a high uranium-to-P_20_5 ratio occurs in a certain weak acid filtrate stream with the Hemi-Di process. It appears that it would be far easier to extract uranium from this stream than with the conventional extraction from 27% P_20_5 acid, and quantity of uranium might increase. However, this process has **yet to be proven** and developed.

FLUOSILICIC ACID RECOVERY

Fluosilicic acid (FSA) is sometimes recovered from phosphoric acid plants. When it contains relatively high concentrations of P_20_5 (0.1-0.25%), it is sold at relatively low price for use in fluoridating municipal water. When P_20_5 is limited to a few hundred ppm, it is sold at a higher price for making aluminum fluoride.

The Di process excels in opportunity to recover FSA, because FSA can be recovered from the evaporators that concentrate acid from 27-42% acid, as well as from the higher concentration evaporators. Hemi and Hemi-Di processes eliminate the need to evaporate acid from 27 to 42% P_20_5, so this opportunity to recover FSA from 27-42% evaporators does not exist. However, some FSA is recovered from Hemi reactor fumes or from flash cooler vapors, as well as from evaporators for higher acid concentrations.

EFFECT OF RECENT TRENDS

Some recent trends will have a major impact on process selection. Soaring fuel costs will obviously place major emphasis on the energy-efficient Hemi and Hemi-Di processes. An added benefit of any such means of recovering waste heat is that it will help combat global warming.

Recent sharp increases in cost of sulfur and phosphate rock make it more attractive to invest in the added recovery benefit of the Hemi-Di process.

A flurry of interest in new nuclear power has escalated the value of uranium. The Di process and probably the Hemi-Di process produce acid from which uranium can be extracted economically.

If and when the US EPA gets around to relinquishing its ban on utilization of gypsum, various uses of this valuable by-product will be pursued. The Hemi-Di process produces gypsum with the high purity that is essential for some of these uses.

DI, HEMI, & HEMI-DI PROCESS COMPARISON TABLE

(Ratings with 5 being excellent)

CRITERIA	DI	HEMI	HEMI -DI	REMARKS (for typical or average situations, with exceptions)
Capital Cost, Reactor & Filters	5	4	2	Di has smallest Reac. & Filt. H-D has 2 Rx & Filter stages
Capital Cost, Other Sections	2	5	5	Hemi & H-D need no rock grinding, less evaporation, acid storage, & cooling water
Operating Cost & Benefits	2	4	5	Di needs rock grinding & much evap. H-D: high recovery
Energy Efficiency, Total Plant	1	5	4	Di needs rock grinding, much more steam & cooling water
Product Acid Concentration	1	4	5	Di 25-29% P_2O_5, Hemi 40-45%, H-D 40-50%
Evaporators & Steam Req't	1	4	4	Hemi & Hemi-Di make DAP with little or no evaporation.
P_2O_5 Recovery at Filter	3	2	5	Di ~96%, Hemi ~95%, Hemi-Di ~98.5%
P_2O_5 Losses Other Than Filter	3	4	3	Hemi & H-D avoid handling 27% acid. H-D has 2nd Rx & Filter
Recovery of Losses from Recirculated Water	3	5	1	Works only where water recirculates from gypsum stack.
Sulfuric Acid Consumption	3	3	5	2% benefit to Hemi & H-D due to low SO_4 in product, etc.
Rock Size Requirement	1	4	4	Di needs <0.4 mm (35 mesh). Hemi & H-D can use <2 mm (9 mesh)
Cooling Water Requirement	2	4	4	Hemi & H-D need no 42% evap. condenser water
Product Clarification, Storage	1	4	4	Hemi & H-D have no 27% acid; often need no clarification
Product Acid Purity	2	4	4	Hemi & H-D acid can make fertilizers with 2% more $\%P_2O_5$
Capacity per Size of Eqip.	4	3	2	Di has smallest equip. H-D requires 2nd reactor & filters
Reagent Requirements	4	3	3	Hemi may need anti-scalant Hemi & Hemi-Di may use clay or silica.
Familiarity & Experience	5	4	3	Most existing plants are Di, but many are Hemi & H-D.
Complexity of Operation	2	4	2	Di needs grinding, much evaporation, etc. Hemi-Di has 2nd Reactor & Filters
Uranium Recovery	4	0	5?	Hemi-Di may be best, but needs development.
Gypsum Utilization	2	2	4	Hemi-Di gypsum is purest.
Fluosilicic Acid Recovery	4	2	2	Hemi & H-D have no 27-42% evap's, hence less FSA.

CONVERTING FROM DI TO HEMI OR HEMI-DI

When should one consider converting an existing Di plant to Hemi or Hemi-Di? A key issue is that the Hemi process requires very little evaporation of product acid. The huge quantity of steam that had been going to the evaporators becomes available, so the decision is largely based on how much value can be obtained from all of that steam. The surplus steam would normally be used to generate electric power. If there is surplus capacity in an existing power co-generation facility, and if this power can be used effectively or sold at a good price, then there is major justification for converting the plant to the Hemi process. When electric power was cheaper, it was difficult to justify the expense of new power co-generation facilities. Now electricity is so valuable that this old rule of thumb no longer holds true.

If a Di plant needs another evaporator, one should consider converting to Hemi instead of buying the evaporator. Since a Hemi plant avoids the need to concentrate acid from 27 to 42% P_20_5, conversion to Hemi would eliminate any shortage of evaporation capacity. The capital that is saved by avoiding one new evaporator may cover most of the cost of a Hemi conversion. Furthermore, a Hemi conversion would greatly reduce need for steam, cooling water, and acid storage facilities – potentially bringing additional capital cost savings.

If a Di plant is having difficulty meeting grade with DAP or TSP, a Hemi conversion would increase P_20_5 content in DAP, TSP, or MAP by 2 percentage points. It should also help N concentration, depending on ability of the product to consume ammonia. Where there are two or more phos acid plants, converting only one of them to Hemi may solve DAP or TSP grade problems for the entire facility.

The Belledune Fertilizer plant in New Brunswick Canada is an example of a very profitable Hemi conversion. The plant might have been shut down because of high cost and difficulty in meeting DAP grade. After converting an old Prayon Mark 2 dihydrate to Hemi in 1986, cost were slashed by totally eliminating the evaporation section and associated fuel cost for generating steam. Recovery averaged 95%, and capacity easily topped the modest increase in design rate – limited only by raw material and product requirements. The superintendent called it “one sweet plant to run.” Belledune continued to operate for a decade, and was considered one of the world’s easiest running phosphoric acid plants. DAP grade became easy to reach, using 40% acid that needed no settling to remove solids.

Further conversion to Hemi-Di involves major expense for the second reaction and filtration facilities. Justification for this expense comes from the major reduction in raw material cost that is achieved by Hemi-Di’s 98-99% recovery efficiency. Recent increases in phosphate rock and sulfur prices make Hemi-Di especially attractive.

CONVERTING TO HEMI OR HEMI-DI WHILE EXPANDING

Additional economic opportunities arise when simultaneously converting an existing dihydrate plant to Hemi or Hemi-Di while expanding capacity. First, a major expansion can be made without adding evaporators, because Hemi needs so little evaporation. Second, the existing cooling water system will accommodate a major expansion, because of savings in evaporator condenser cooling water requirements. Third, the rock grinding section is likely to be eliminated, so no expansion is required there.

The acid storage tank area may not need expansion when a Di plant is converted to Hemi or Hemi-Di of substantially greater capacity. Tanks that had been used for 27% acid storage will become available for other acid storage service. Acid clarification requirements are reduced or eliminated, because the Hemi acid will be purer.

Arcadian (now PCS) in Louisiana made good use of those down-stream advantages when they expanded capacity by a third while converting to the Hydro Hemi process. After hearing of Belledune's success, Arcadian converted its Prayon Mark 2 plant with Bird filter to Hemi. Expenses beyond the reactor and filter sections were minimized because:

- Rock Grinding was totally abandoned and by-passed, with un-ground BuCraa rock feeding from a rock washing filter directly to the reactor.
- Elimination of the requirement to concentrate acid from 27 to 42% P_20_5 allowed existing evaporators to make more capacity.
- One evaporator was dedicated to boosting concentration from 54% to 60-62% P_20_5 for feeding a super-phosphoric acid facility, thus increasing super-acid rate.
- Requirements for cooling water were reduced.
- No new phos acid storage facilities were required.

The Arcadian Hemi plant started very easily – achieving design capacity and conditions within two days. The plant easily performed so well that the client accepted it without doing the customary performance test run. It frequently ran at 110% of design capacity, and occasionally achieved up to 130% of design capacity. Recovery consistently exceeded 96%. Arcadian and Belledune's experience demonstrated that Prayon reactors and tilting pan filters are well suited to conversion to the Hemi process.

The exceptionally high quality Hemi acid was welcome as feedstock to a food-grade phosphoric acid plant and a super-phosphoric acid facility. Arcadian's liquid fertilizer product was considered to be the best in the domestic industry.

Expansion while converting a Di or Hemi plant to Hemi-Di can be facilitated by using the existing filters in the dihydrate section of the Hemi-Di process. Dihydrate filtration in a Hemi-Di plant needs only about 60% of the filter area as hemi filtration. The old filters may be big enough to act as dihydrate filters in a new and larger Hemi-Di plant.

REFERENCES

Pierre Becker, “Phosphates & Phosphoric Acid”, 2nd Ed., Marcel Dekker Inc., NYC, ‘89.

BuShea, et al., “Application of BSF Technologies CTC3 to a Phosphate Complex”, AIChE Nat’l Convention, Orlando, 3/90 and 1990 AIChE Clearwater Convention

J. David Crerar & Barry T. Crozier, “Practical Retrofitting to the Hemihydrate Process and Plant Performance Data”, AIChE Meeting, Lakeland FL, Mar. ‘87.

B.T. Crozier, “Fisons Hemihydrate Process - A Decade of Energy Savings”, The Fertilizer Institute Round Table, Atlanta, Oct.’82.

John Gobbitt, “Hemihydrate Phosphoric Acid Plant Retrofits at Geismar and Chinhae”, AIChE Clearwater Convention, May, ‘90.

Joseph W. Guida, “Phosphoric Acid and Uranium Recovery - Take 3" *Fertilizer International,* Jan-Feb., 2008

G.W. Hartman & L.J. Friedman, “The Royster Power Program - Start-up and Initial Operating Experience” AIChE Convention, New Orleans LA, April,’86.

Sam Houghtaling & John Wing, “Hemi or Hemi-Di - Our Future”, AIChE Spring National Meeting, New Orleans LA, April,’92.

Sam Houghtaling & John Wing “Hemi or Hemi-Di? - Arcadian Converts Phos Acid Plant from Dihydrate to Hemi”, AIChE Clearwater Convention, May,’91.

John Wing, “The Hemi Era in Phosphoric Acid”, AIChE Clearwater Convention, June,’06

John Wing, “From Phosphate Rock to DAP at Lower Cost”, AIChE Clearwater Convention, May,’99.

John Wing, “The Case for Converting Phos Acid Plants to Hemi”, AIChE Clearwater Convention, May,’95.

John Wing, “Hemihydrate Phosphoric Acid Plant Conversion at Belledune, Canada”, AIChE Meeting, Lakeland FL, Oct.,’87.

John Wing, “Florida Phosphate Technology - 2000", AIChE Clearwater Conv., May,’89.

Anonymous, “Hemi Forever?” *Fertilizer International*, July-Aug. 2007, pages 43-48.

Anonymous, “HiTech Solutions, Inc. - Contractor Profile”. *Phosphorus & Potassium* magazine, Jan.-Feb. ‘93, page 26.

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 in other engineering and phosphate production companies.

He did process engineering for new plants, modifications and expansions for many phosphoric acid, DAP, MAP, & TSP plants. He designed fluosilicic acid recovery systems at Conserv in Florida, Sterlite and Hindalco in India, and IJC in Jordan. He provided conceptual design for six phosphoric acid evaporators and several dozen fume scrubbers.

For Hemi plants he performed the process design for the Belledune Hemi conversion, the 3-train Ma'aden plant which is in progress, and conversion of a very large dihydrate plant to Hemi-Di. He was project manager and process engineer for the Arcadian Hemi conversion. He consulted as owner's engineer for the Indo-Jordan Chemical Co. Hemi plant in Jordan and has provided subsequent technical services for the same plant.

He has written technical papers on:

- Hemi and Hemi-Di processes (7 papers)
- The future of the phosphate industry
- Phosphoric acid evaporation
- Cooling pond systems
- "Can a Little Altruism Enhance an Engineer's Career Satisfaction?"
- Article segments for *Phosphorus & Potassium* magazine
  - (now *Fertilizer International)*

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

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John Wing, P.E., 1121 Waters Edge Drive, Lakeland FL 33801, USA
Phone: 1-863-666-6555 Email: johnwingpe@verizon.net