THE CASE FOR CONVERTING PHOS ACID PLANTS TO

HEMI

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SUMMARY

The Hemihydrate phosphoric acid process provides major advantages in energy efficiency, product purity, and elimination of most evaporation requirements. Advances during the past decade provide a process which has been proven to be more reliable and easier to operate than dihydrate processes, with comparable capacity and improved overall product recovery.

Major advantages of the Hemi process include:

Energy Efficiency
Saves most or all evaporation steam requirement

Evaporation and Cooling Water
Eliminates much or all requirement for evaporation equipment, cooling water, and operating expense

Product Grade
Greatly increases grade of DAP, MAP, or TSP

Rock Grinding
Eliminates rock grinding when using concentrate
Simpler rock grinding when using pebble

The Hydro Hemi Process provides phosphoric acid at typically 41% P_2O_5 from the filter, compared with typically 26% P_2O_5 with dihydrate processes. This high concentration of filter product acid eliminates most or all steam, cooling water, and equipment requirements to evaporate acid.

Advantages of the Hemi process versus dihydrate for a typical scenario using central Florida rock are as indicate in the following table.

HEMI Advantages vs. Dihydrate		
	When making 40% P_2O_5 for DAP	**When making 54% P_2O_5 for other products**
Steam for Evaporators	**None req'd**	**70% less**
Number of Evaporators	**None req'd**	**Half as many**
Condenser Water (evaps.& flash cooler) Flow Rate: Heat Load:	**85% less 77% less**	**37% less 62% less**
Electric Power Production (@1,000 STPD P205)	**11 MW more 82,000 MWH/year $4 million @ 5c/kwh**	**11 MW more 82,000 MWH/year $4 million @ 5c/kwh**
Rock Grinding Power With Concentrate With Pebble	**No Grinding 70% less**	**No Grinding 70% less**
Grade of DAP, MAP or TSP	**+ aprox. 2% P_2O_5 + aprox. 1/2% N**	**+ aprox. 2% P_2O_5**

THE HEMI PROCESS

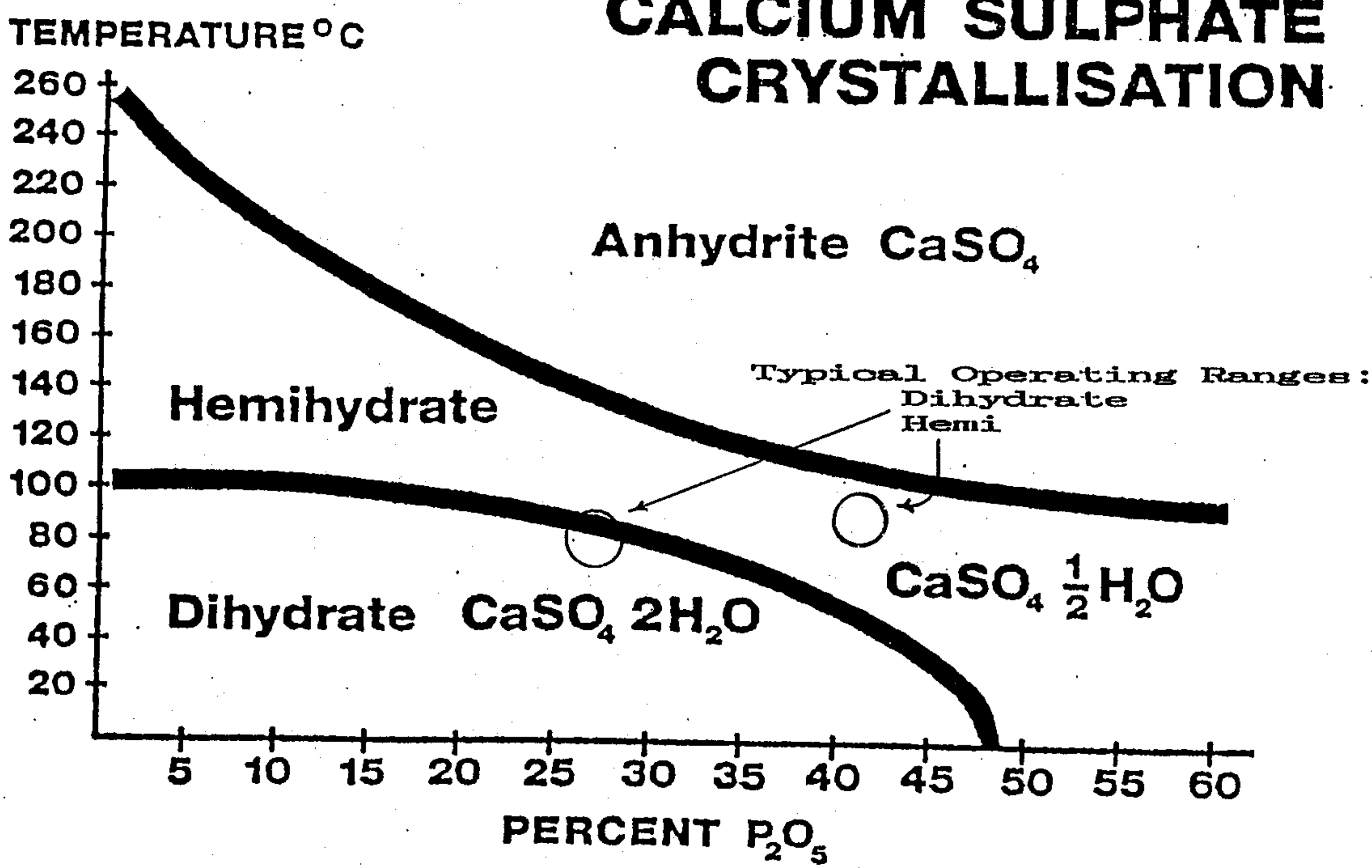
The Hydro Hemi process was developed by Fisons, which is now part of the Norsk Hydro Group. This process is used in 8 Hemi plants and 9 Hemi-Di plants which have been built, converted, or are underway worldwide. In both the Hemi process and the dihydrate process, phosphate rock reacts with sulfuric acid to make phosphoric acid and calcium sulfate. The calcium sulfate forms with a half molecule of water (called hemihydrate) in the Hemi process, and with two molecules of water in the dihydrate process. The Hemi process operates at higher temperature and concentration than dihydrate processes.

Either process can operate stably, provided that conditions are clearly in either the dihydrate or hemihydrate zone of calcium sulfate formation. This is illustrated in the attached graph of calcium sulfate crystallization. Dihydrate processes have a disadvantage, because as a matter of economic necessity, they must operate close to the transition between dihydrate and hemihydrate formation.

Hemi plants operate further from the hemi/di transition range. This allows a Hemi plant to be more stable and to scale less in the reactor, flash cooler, and filter than a dihydrate plant. This advantage has been clearly demonstrated in Hemi plant operation. Modern Hemi plants successfully avoid problems which might arise when conditions change from hemi to dihydrate during filtration. This too has been demonstrated in Hemi plant operation. Hemi plants have proven to be more stable, are easier to operate, and incur less scale formation than dihydrate plants. Visits to operating Hemi plants can be arranged to demonstrate these claims to potential users of the Hemi process.

The Hemi process involves dividing the reactor into two zones, with controlled recirculation rate between the two zones. A Hemi plant can produce filter product acid at concentrations ranging from 38 to 50% P_2O_5. Where energy cost is modest, or where there is no need for higher concentration, hemi plants typically make 41% P_2O_5 filter product.

EFFECT OF REACTION CONDITIONS ON CALCIUM SULPHATE CRYSTALLISATION



RECENT HEMI CONVERSIONS

Three existing Prayon dihydrate plants have been converted to the Hydro Hemi process in North America. These include Arcadian in 1990, Belledune in 1986, and Royster in 1985. The writer was responsible for process engineering for the Arcadian and Belledune Hemi conversions. Both started up quickly, easily exceed design rate and recovery, and operate smoothly. These plants have proven to be more reliable and easier to operate than they had been as dihydrate plants. Performance and descriptions are summarized below.

HEMI CONVERSIONS

	Belledune	Arcadian
Company	Brunswick Smelting	Arcadian Fertilizer
Location	Belledune New Brunswick Canada	Geismar Louisiana USA
Phosphate Rock	Central Florida (orig.) Morocco (recently)	BuCraa (northwest Africa)
Reactor	Prayon 9 compartments	Prayon 9 compartments
Filter	Bird 24C	Bird 24C
Capacity (STPD P_2O_5) Before Design Actual Sustained Actual Peak	 500 550 550+ 700	 540 720 900 1,000
P_2O_5 Recovery: (filter cake) Guaranteed Actual	 93% 95%	 95.5% 96%
Startup: Date/Time	Sept. '86 / 19 days	Sept. '90 / 2 days

The Belledune Hemi conversion started relatively quickly and easily. It was running smoothly at design rate 19 days after startup, and was increased to 110% of design rate a few days later. The production superintendent calls it "one sweet plant to run." When Arcadian personnel observed the Belledune plant before converting their own plant, they reported unaccustomed boredom in watching the plant run steadily and seeing the instruments draw straight lines.

The Arcadian Hemi conversion started even faster - achieving design conditions within two days. It operates steadily well above its design rate, and with 96% recovery - probably the world's best for a Hemi plant. Maintenance cost per ton has been less than for dihydrate operation.

The Royster plant at Mulberry, Florida was converted to Hemi in 1985. It had initial difficulties due to use of the wrong anti-scalant, the wrong defoamer, and some mechanical problems. The difficulties were not due to the process per se. After these problems were corrected, the plant ran reliably at capacity. Later the plant was converted back to a dihydrate plant of increased capacity. Reasons for selecting dihydrate for the expansion included ease of conversion. For example, an existing old second filter was OK for dihydrate but would have needed new pans and other modifications for Hemi operation. Royster's economic justification for Hemi was hurt by a very low price for exported power, and by their requirement for much of the phos acid to be at a low concentration.

The Serrana plant in Cajati, Brazil was converted from dihydrate to Hemi in 1994. Capacity was increased from 360 to 480 mtpd P_2O_5. It achieves filtration rate of 16 mtpd P_2O_5 /m^2 on an Eimco belt filter, using Brazilian rock.

The next Hydro Hemi plant will be a grass roots 700 metric tpd plant, which is being designed for Indo-Jordan Chemical Co. at Eshidiya, Jordan. It will have a 3-vessel reaction section and twin belt filters. Phosphoric acid will be produced from Jordan rock and then shipped to India and made into DAP.

HiTech Solutions is providing consulting to joint venture owner SPIC-SMO of India as owner's engineers, reviewing the design, participating in design conferences, and eventually assisting with startup.

ENERGY EFFICIENCY

Production of filter product acid at typically 41% P_2O_5 provides energy utilization benefits that are usually the biggest factor in justifying a Hemi conversion. A 1,000 TPD P_2O_5 phosphoric acid plant will save about 1850 TPD in evaporator steam by making filtered acid at 41% instead of 26% P_2O_5. This steam would typically be used to generate about 9 megawatts of electric power.

In a typical scenario a phosphate chemical complex provides about all of its own electric power requirements. The additional power would be exported to the owner's mine or to the power grid for sale. If exported power is sold, its price will be crucial.

A 1990 AIChE paper by Kenneth BuShea and others described a situation wherein a low value (less than $0.025/KWH) might be received without special arrangements. However, they go on to say that "With long term guarantees of power production and reliability, additional capacity credits are available, and power sold to the utility would be worth approximately $0.045 to 0.06/KWH." The National Energy Policy Act of 1992 and related state legislation may help phosphate companies receive a fair price for exported power, or to export power to a mine.

The 1,000 STPD Hemi conversion in the scenario described above would export about 9 megawatts of power. Another 2 MW reduction in rock grinding and evaporation power consumption would bring the total to 11 MW, which is over 80,000 MW annually. If a price of 5 cents per KWH were received for exported power, this power would be worth over $4 million/year, or $13/ton of P_2O_5.

EVAPORATION AND COOLING WATER BENEFITS

Elimination of the need to concentrate acid from 26 to 41% P_2O_5 will obviously solve an evaporation capacity bottleneck. If a Hemi conversion eliminates the need to add an evaporator, a major portion of the capital cost of the Hemi conversion can be credited.

Likewise the Hemi conversion will eliminate the need for cooling water to and from the first stage evaporator condensers of that plant. Most of the cooling load of a phosphoric acid plant is for the first stage evaporators, so the cooling pond or other cooling system duty will decrease drastically.

A Hemi plant has substantially less flash cooler duty and requires less flash cooler condenser water than a dihydrate plant. Thus a Hemi conversion would eliminate any flash cooler bottleneck, and reduce cooling water flow and heat load.

The approximate percentage reduction of total condenser water flows and related cooling load is summarized in the "Hemi Advantage vs. Dihydrate" table on page 3.

Elimination of 26% P_2O_5 acid and first stage evaporation obviously eliminates operating costs and product losses associated with this equipment. Losses will likely reduce on the remaining evaporators, because they can operate with less load per unit.

PRODUCT GRADE

Phosphate producers in Florida generally face steadily decreasing quality of phosphate rock. Results are operability problems in phosphoric acid plants, and increasing difficulty in meeting grade specifications with DAP and TSP. The Hemi process can generally handle low grade rock more easily than the dihydrate process, and its higher acid purity usually makes it easy to meet grade in the DAP, MAP, or TSP product.

Hemi acid is purer than dihydrate acid that has been evaporated to the same concentration. There is less sulfate, aluminum, and fluoride, and usually less solids in Hemi acid than in dihydrate acid. The purer acid makes it easy to meet fertilizer product grade requirements. The Belledune Hemi plant experienced a sudden jump in DAP grade to around 47.5% P_2O_5 with Hemi acid, whereas previously it had not been easy to achieve 46% P_2O_5. The over-formulation was a much easier problem to solve than under-formulation. Belledune avoided over-formulation by switching to very open cloths on the phos acid filter, and by not clarifying the 40% P_2O_5 acid.

The effect of Hemi acid for one central Florida DAP producer was calculated to be an increase of 2.3% P_2O_5 and potentially 0.9% N. Some improvement could be achieved with better clarification of dihydrate acid, but a net improvement of around 2% P_2O_5 and 0.5% N is realistic. This is more grade improvement than is usually needed. If one phosphoric acid plant in a complex with two or more plants is converted, the entire DAP output from the complex might be brought up to grade.

If all of the DAP feed acid is Hemi acid, I recommend that the feed acid be a single concentration (39-40%), rather than the typical 26% and 54% P_2O_5 feeds. The low fluoride content of Hemi acid makes it less likely to encounter the potential plume of sub-micron ammonium fluoride particles. Nevertheless, it would be best to provide "Double Mol" acid scrubbing. Double Mol scrubbing generally pays for itself in reduced ammonia losses, while also reducing fluoride emissions. A dual-acid-concentration DAP plant which is fed from both a Hemi plant and a dihydrate plant should receive its weak acid from the dihydrate plant.

ROCK GRINDING

The Hydro Hemi process can handle rock which is much coarser than that required for a conventional dihydrate process. Typical particle size specification is 100% passing 10 mesh BSS (1.68 mm; about 1/16 inch)

Concentrate

Floatation concentrate is easily fine enough that it requires no grinding. The 8-12% moisture in typical damp concentrate is also acceptable. Therefore, phosphate concentrate can generally be fed to a Hemi plant as is, with neither drying nor grinding.

Pebble

Pebble needs only to be ground to under 10 mesh. This does not require the large energy and expensive equipment of a ball mill. Ground rock slurry from a wet ball mill cannot be fed into a Hemi process, because it leaves more water in the rock than the process water balance can tolerate.

An existing plant with a wet ball mill can either switch to using only concentrate (which needs no grinding), or grind damp pebble in another type of mill. Impact mills (similar to hammer mills) appear to be suited for grinding damp pebble for a Hemi plant, and chain or hardened cage mills might also be considered. Any of these types of mills would use a fraction of the power that a ball mill of the same capacity requires.

CAPACITY AND RECOVERY

The Hydro Hemi process provides capacity and filter recovery comparable to better dihydrate plants. This can be verified in more detail for each prospective conversion. Both the Belledune and Arcadian conversions provided substantially more capacity than the plants had achieved as dihydrate plants. Recovery based on filter cake analysis averages 95% at Belledune with central Florida rock, and 96% at Arcadian with BuCraa rock.

In addition to the recovery as measured in filter cake, the Hemi process provides additional recovery benefits of about 3% of the P_2O_5 and 5% of the sulfuric acid fed, relative to dihydrate plants, as explained below:

Low SO_4/P_2O_5 Ratio in Product - 2% of H_2SO_4

The Hemi process operates with a much lower SO_4/P_2O_5 ratio in the filter product acid than common dihydrate processes. This reduces the sulfuric acid consumption by about 2% compared to dihydrate plants. Sulfuric acid consumption is also reduced by other factors described below, which benefit recovery in general.

Reduce Evaporator Losses - 1%

Elimination of the need to evaporate acid from 26 to 41% P205 eliminates acid losses associated with handling and evaporating the lower concentration acid. After a Hemi conversion, the existing evaporators will not need to handle much load, so they can operate a lower rates, which reduces entrainment loss.

P_2O_5 Recovery from Pond Water - 2%

Most phosphoric acid plants use recirculated water for gypsum sluice, filter cake wash, cooling, etc. With such a system, about 60% of any water soluble phosphoric acid loss is eventually recovered via the filter cake wash water.

(Cont.)

CAPACITY & RECOVERY - P_2O_5 from Pond Water (Cont.)

The biggest source of phosphate loss from a phosphoric acid plant (either Hemi or dihydrate) is dicalcium phosphate (dical), which is embedded in every calcium sulfate crystal. Dical loss amounts to around 3 to 4% of the P_2O_5 fed to the plant. In a dihydrate plant, the dical remains mostly locked within calcium phosphate crystals. However, in a Hemi plant, the calcium sulfate hemihydrate crystals dissolve and re-form as calcium sulfate dihydrate crystals in the gypsum handling system. The dical is released, and if there is some strong acid present, most of it remains in solution as phosphoric acid (or monocalcium phosphate) in the gypsum decant water. There is sulfuric acid and fluosilicic acid in this water, which acidifies the dical according to the following reactions. (Water of hydration is not shown for simplicity.)

$CaHPO_4$	+	H_2SO_4	--->	H_3PO_4	+	$CaSO_4$
Dical		sulfuric acid		phos acid		calcium sulfate
$CaHPO_4$	+	H_2SiF_6	--->	H_3PO_4	+	$CaSiF_6$
Dical		fluosilicic acid		phos acid		calcium silicofluoride

The results of this phenomenon are that the sulfate and fluoride content of the water decrease, and the phosphate content of the water increases. The pH of the water increases, because these reactions replace stronger acids with weaker phosphoric acid. When the calcium sulfate re-crystallizes as dihydrate, there will be calcium sulfate and silicofluoride, but very little co-precipitated calcium phosphate.

The benefit to recovery is that most of the dical which had been counted as filter cake loss gets recovered when the water is recycle as filter cake wash water. It is estimated that this adds 2% to the P_20_5 recovery in a Hemi plant (over and above the minor amount that re-dissolving of dical occurs in a dihydrate plant). This is based on 3.5% dical loss (analyzed as citrate soluble P_2O_5) 80% re-dissolving in a Hemi plant (vs. 10% re-dissolving in a dihydrate plant), and recovery of 60% of the re-dissolved P_2O_5 via filter cake wash water.

CONVERSION OF EXISTING PLANTS TO HEMI

The Prayon Attack Tank reactor has proven to be well suited to conversion to the Hydro Hemi process, as demonstrated at Belledune and Arcadian. Its multiple compartments provide excellent environments for reaction and crystal growth. Other reactor designs can also be converted to the Hydro Hemi process. Modifications are made to provide two reaction zones, controlled recirculation, good agitation, etc.

Most modern tilting pan (Bird), belt (Delkor, Eimco, Pannevis, Philippe, etc.), or table (Ucego) filters can be used for the Hemi process. An existing dihydrate filter can be converted to Hemi service by adding a third wash (if not already provided) and several smaller modifications. A system to route a proprietary anti-sclalant to the filter would be installed.

It would be inappropriate to generalize about the contents or cost of a Hemi conversion, because requirements vary greatly with the situation. In addition to the basic modifications to the reactor and filter, related systems must be evaluated and brought into compliance with requirements of the Hemi process. Such systems include rock feed, scrubbing, product handling, water, defoamer, disposal of gypsum, and co-generation of electric power.

Even with Belledune and Arcadian - which have the same model reactor and filter - the basic Hemi conversion was very different. Both plants had additional requirements which added perhaps 50 to 80% to the cost of a basic conversion, yet they easily justified conversion.

More information about the Hydro Hemi and Hemi-Di processes and their track record are contained in the article for the AIChE Spring '92 National Meeting "Hemi or Hemi-Di - Our Future" by Sam Houghtaling and John Wing.

HiTech Solutions Inc. is North American licensee for the Hydro Hemi and Hemi-Di processes. HiTech also offer consulting and engineering services for these processes elsewhere in the world.

THE HEMI-DI PROCESS

The Hydro Hemi-Di (HDH) process provides unexcelled P_2O_5 recovery, with a corresponding reduction in P_2O_5 emission to the plant water system. The gypsum is substantially purer than with Hemi or dihydrate processes - a major advantage where gypsum is recovered as a by-product. In addition the Hemi-Di process provides all of the benefits of energy efficiency, reduced evaporation, acid purity, minimal rock grinding, etc. that the Hemi process offers.

The Hemi-Di process involves two reaction systems and two filtration systems. Capital cost and operating complexity are increased, although the second reactor and filter systems are simpler than the first ones. Recovery is typically 98-99%, and this high recovery provides a strong incentive for making the extra investment.

The first reactor is a Hemi reactor, much like that of the Hemi process. Slurry from the Hemi reactor is filter and then washed, not with water but with weak acid from the second (dihydrate) reactor. The product of strong (typically 41% P_2O_5) acid is taken from the Hemi filter.

Hemihydrate cake from the Hemi filter is sluiced into a second (dihydrate) reactor. Here the hemihydrate crystals mix with a solution of weak phosphoric and sulfuric acid. The hemihydrate crystals dissolve and re-precipitate as dihydrate crystals. Co-precipitated dicalcium phosphate (dical) and any un-reacted rock from the Hemi crystals are released into this weak acid solution, and little of the dical or un-reacted rock are lost with the dihydrate crystals. The result is extremely low loss of un-reacted rock (C.I. loss) or dical (C.S. loss) in the dihydrate filter cake. Slurry from the dihydrate reactor is washed with water on the dihydrate filter. The combination of weak wash solution and multiple washes minimize the water soluble filter cake loss.

Eight Hydro Hemi-Di phosphoric acid plants have been built since 1974, and the following two plants are being designed:

350 mtpd plant for Sterlite in India - making 43% P_2O_5 from Jordan rock
660 mtpd plant for NFC in Thailand - making 49% P_2O_5 from Florida, Morocco, Phalaborwa, or Jordan rock

ENVIRONMENTAL ADVANTAGES

Environmentally Friendly Electric Power

The energy efficiency of the Hemi process allows electric power to be produced from steam that would otherwise be spent evaporating acid. Production of electric power from waste heat provides energy with incremental net results of:

No Air Pollution
No Water Pollution
No Solid Waste
No Potential Environmental Hazards
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.

Cleaner Pond Water

In the Hemi process, dicalcium phosphate from the filter cake reacts with stronger acids in the recycled pond water. This raises the pH by replacing strong acids (H_2SO_4 & H_2SiF_6) in the recycled water with an equivalent amount of a weaker acid (H_3PO_4).

The Hemi-Di process is unexcelled for low losses of P_2O_5 to a recycled pond water system. The result is the lowest P_2O_5 content in this common recycled water system that is achievable by any wet process for phosphoric acid manufacture.

Smaller Cooling Pond

A Hemi plant needs only a fraction of the cooling duty as a dihydrate plant, as indicated in the table on page 3. Reduced cooling pond requirement would be of value for a grass roots plant, or for one which otherwise would have needed a larger cooling pond.

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ABOUT THE AUTHOR

John Wing - Vice President of HiTech Solutions, Inc. - has a Bachelor of Chemical Engineering from Univ. of Florida and a Master of Engineering in Administration from Univ. South Florida. His 31 years in the phosphate industry includes process design, project management, consulting, technical service, process development, and production supervision.

He has designed modifications and expansions of several phosphoric acid, DAP, MAP, and GTSP plants. He performed the process design for fluosilicic acid recovery systems at Conserv in Florida and Sterlite in India. He provided conceptual design for five phosphoric acid evaporators and about thirty scrubbers.

For Hemi plants he performed the process design for the Belledune and Arcadian Hemi conversions, was also project manager for the Arcadian Hemi conversion, and consults as owner's engineer for the Indo-Jordan Chemical Co. Hemi plant in Jordan. He has written five technical papers on the Hemi and Hemi-Di processes.

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

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