

THE
HEMI ERA
IN PHOSPHORIC ACID

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SUMMARY

This article explains why Hemi (hemihydrate) has become the preferred process for making phosphoric acid in the 21st century. The related Hemi-Di process begins like the Hemi process and adds process steps for extra benefits. The Dihydrate (Di) process served as the standard of the industry for several decades. Other phosphoric acid processes including Di-Hemi and a short-cut Hemi-Di have also found their niche.

The term hemi refers to calcium sulfate hemihydrate. A phosphoric acid plant produces far more gypsum (calcium sulfate) than phosphoric acid. A dihydrate process makes the dihydrate form of gypsum, and a hemi plant makes hemihydrate gypsum - involving higher combination of temperature and concentration. During the last few decades people have developed ways to enjoy hemi's high concentration advantage without suffering its potential chaos.

HEMI PROCESS

The Hemi (hemihydrate) process produces phosphoric acid directly from filtration at typically 40-43% P₂O₅ concentration. Most Hemi plants use phosphate rock as received – without drying or grinding. Two entire plant sections are usually rendered unnecessary – evaporation to ~42% P₂O₅ and 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 small 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 26-42% 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

HEMI-DI PROCESS

This advanced process begins with a Hemi reactor and filter section, but 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% recovery
- Very low sulfuric acid requirement
- Energy benefit from needing little or no steam to concentrate acid
- Eliminate 26-42% evaporators
- Usually eliminate rock grinding
- Low cooling water requirement
- Gypsum purity is suitable for making a variety of by-products
- Higher analysis fertilizer

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. The filter product phosphoric acid is typically only 25-28% P_2O_5 , so further concentration 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

Disadvantages include:

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

THE HEMI ERA IN PHOSPHORIC ACID

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THE HEMI PHOSPHORIC ACID PROCESS

As in nearly all commercial phosphoric acid plants, phosphate rock reacts with sulfuric acid to produce phosphoric acid and gypsum crystals. The Hemi process operates at a high concentration of phosphoric acid, where the gypsum crystals exist as the hemihydrate form of calcium sulfate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$).

The most widely used Hemi process was developed by Fisons in the 1960's and later became the Hydro process. The process name was changed from Hydro to Yara in 2004, but staffing of the licensing division was not changed. Hemi and Hemi-Di plants have been built using processes by Nissan, OXY, PCS, and others.

The alternative dihydrate process operates at a much lower concentration of phosphoric acid, where the gypsum crystals exist as the di-hydrate form of calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

HIGH ACID CONCENTRATION

Hemi and Hemi-Di plants can produce phosphoric acid directly from filtration at concentrations ranging from 38% to 50% P_2O_5 , but optimum is usually around 42%. Most dihydrate phos acid plants make 25-28% P_2O_5 product.

ENERGY ENHANCEMENT

The 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. When the final product is DAP, no steam heating is required to concentrate the phosphoric acid, because the acid as produced is more than strong enough. 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 , which is strong enough for DAP feed, compared to dihydrate process acid at 26% P_2O_5 . Over 3 megawatts of electric power is saved by not having to grind most types of rock, and by having a much smaller acid evaporation section - or perhaps none at all.

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 - worth roughly \$40 million annually (based on 8 cents/kwh). The energy advantages of the hemihydrate process account for about 16 megawatts of this

power - worth roughly \$10 million/year - approximately \$20/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.

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 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.

NO EVAPORATION OR STEAM REQUIRED WHEN MAKING DAP

If the only product is DAP, it is not necessary to concentrate phosphoric acid. Thus no phosphoric acid evaporators would be required, and no steam would be needed to concentrate the acid. Filter product acid from a Hemi plant is more than adequate for DAP feed acid.

This was clearly demonstrated at Belledune, Canada, where phos acid evaporators and process steam boilers were never needed. The Belledune DAP plant diluted some of the Hemi filter product acid to 38% P_2O_5 and used that as DAP scrubber acid. However, in many situations it may not be practical to meet modern atmospheric emission regulations at the DAP stack when scrubbing fumes with 38% P_2O_5 phosphoric acid, because scrubbing efficiency suffers when such a high concentration of scrubber acid is used.

Where DAP air emission standards are rigorous (as with the US EPA, World Bank, and other modern standards) more efficient DAP scrubbing is required. The recommended procedure to meet the DAP plant air emission requirement is to use 30-35% P_2O_5 for scrubbing at the DAP plant. Further scrubbing improvement can be attained by using "Double Mole" fume scrubbing (2-stage countercurrent acid scrubbing) for fumes from the DAP pre-neutralizer and granulator. The 30-35% P_2O_5 acid for DAP scrubbers would be withdrawn as #2 filtrate from the Hemi filter(s). Most of the DAP plant feed acid would be provided as #1 filtrate (with or without clarification) at approximately 42% P_2O_5 concentration - fed directly to the DAP pre-neutralizer (reactor). Average phosphoric acid feed to the DAP plant would exceed the 38% P_2O_5 concentration that is required in many modern DAP plants.

If products such as MAP or TSP are made, some evaporation of phosphoric acid would be required. However, the Hemi process would still retain the same concentration and energy efficiency benefits relative to a dihydrate plant.

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 (but decreasing) portion of central Florida phosphate is much too coarse to feed directly to any phos acid plant. Pebble rock could be ground to -2mm size in relatively low energy impact, hammer, or roller 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 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. Rod milling of the damp pebble would also be acceptable, but is probably unnecessarily expensive in capital and power cost.

Dry grinding with a ball mill would be acceptable, but unnecessarily expensive, because the Hemi process does not require the fine grinding that is inherent with use of a ball mill. Conventional wet ball milling would not be possible, because wet ball mill slurry containing about 38% water is too wet for the Hemi plant water balance.

PHOSPHATE ROCK CONSUMPTION

Recovery of P_2O_5 as measured in the filter cake will be roughly equal for the Hemi or dihydrate process (varying considerably with type of rock, condition of the plant, and how hard the plant is pushed for capacity). The Hemi process benefits from less loss of product elsewhere in the plant, which should help recovery by at least 1%. This comes from elimination of any losses relating to handling of 26% P_2O_5 acid, or from the evaporation facilities that can be eliminated.

There is an added recovery benefit for plants which recirculate gypsum pond water. Dicalcium phosphate which crystallizes within the gypsum crystals will re-dissolve in the recirculated pond water. Much of this re-dissolved phosphate is recovered when the same pond water is used to wash the filter cake. This amounts to nearly 2% recovery benefit. Overall P_2O_5 recovery in a Hemi plant would thus be about 2.3%

better than in a dihydrate plant, based on equal filter cake loss for both plants, as summarized below:

| P₂O₅ Recovery Example, Hemi vs. Dihydrate | | |
|---|--|--|
| | HEMI | DIHYDRATE |
| FILTER RECOVERY (Based on filter cake) | 95% (3.5% CS loss, 1.5% WS loss, minor CI loss) | 95% (3.5% CS loss, 1.5% WS loss, minor CI loss) |
| 26% Acid Handling & Evaporation Losses | 0 | -1% |
| Miscellaneous Losses: (From filter pans or belt grooves, flash cooler entrainment, spills, leaks, and other acid handling) | -2% | -2% |
| Recovery from pond water wash of filter cake: (@50% recovery) Re-dissolved dicalcium phosphate (C.S.): Water soluble (w.s.) losses: | +1.75% +1.75% | 0 +2.2% |
| Overall P₂O₅ Recovery | 96.5%(2.3%better) | 94.2% |

LOW H₂SO₄ CONSUMPTION

Sulfuric acid requirement for a Hemi plant is very low for three reasons:

- The ratio of free sulfate to P₂O₅ in a hemi plant is far less than in a dihydrate plant, reducing sulfuric consumption by 2-2.5% (based on the Yara process).
- Less sulfuric acid reacts with aluminum impurities in the phosphate rock, saving a few tenths of a percent.
- Better overall P₂O₅ recovery, as described in the preceding table (~2.3%)

The combined benefit of these effects is that a Hemi plant will use 5% less sulfuric acid than the dihydrate plant of equal P₂O₅ recovery.

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 the following page.

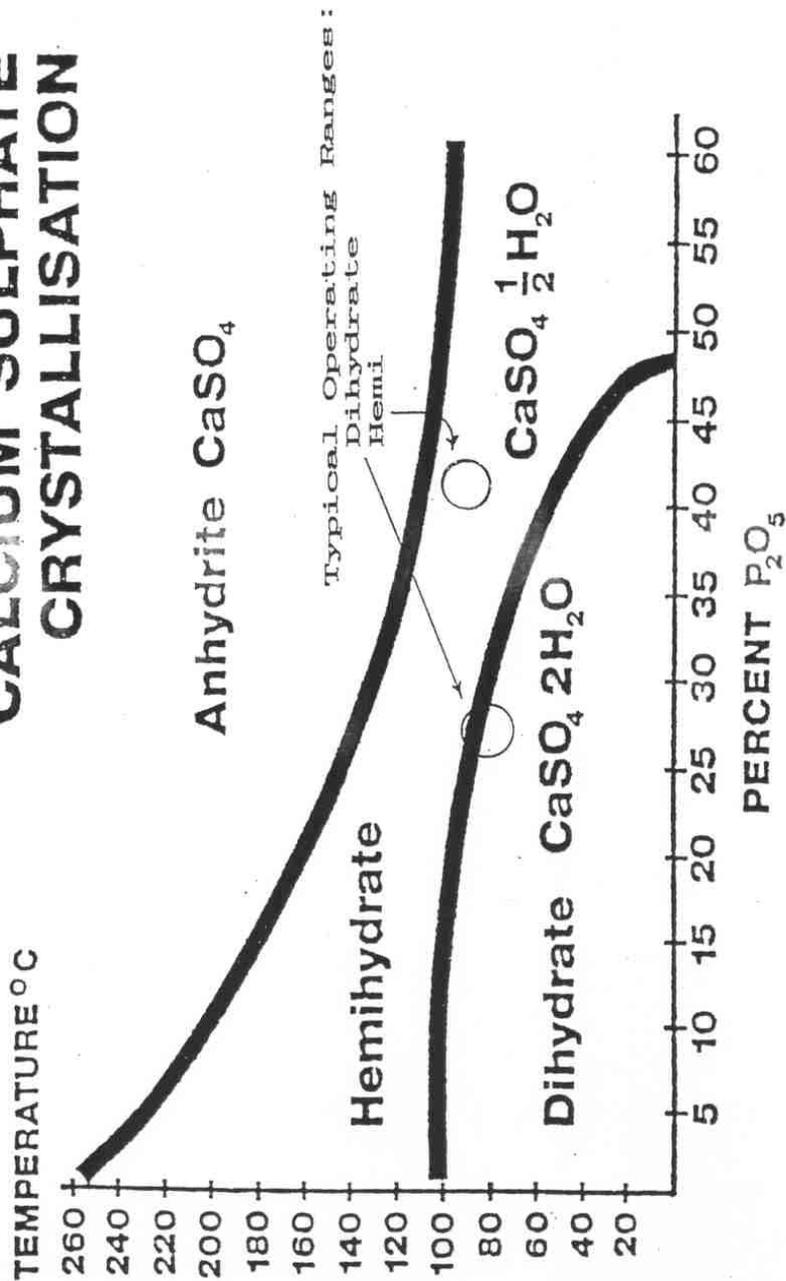
Dihydrate plants must limit reactor concentration in order to keep below a wide transition zone between hemihydrate and dihydrate. When concentration or temperature gets a little too high, the gypsum crystals form as a mixture of dihydrate and hemihydrate crystals. These crystals are small, which reduces 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. Nevertheless, 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 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 in some hemi-di plants which push reactor acid concentration to 48-50% P_2O_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.

EFFECT OF REACTION CONDITIONS ON CALCIUM SULPHATE CRYSTALLISATION



LESS COOLING WATER REQUIRED

There is 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°C (92-95°F) required for 52-54% P₂O₅ 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. The cooling pond and associated pumps and piping are a fraction the size of comparable equipment in a dihydrate plant.

SIMPLER ACID STORAGE AND CLARIFICATION

Phosphoric acid storage and clarification facilities are reduced to 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.

A dihydrate plant would typically require storage and clarification for 26% and 40% acid, plus agitated storage (and sometimes clarification) for 52-54% acid.

CORROSION

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 should normally be at least 317L, or 904L with highly corrosive acids. Belt filter vacuum boxes are typically 904L.

For the highly corrosive BuCraa acid at Arcadian, we used expensive alloy G-30 for new agitators, but several existing Ferallium 255 agitators were left in service. After several years it appeared that the less expensive Ferallium 255 may have been more cost effective – even in that severely corrosive service.

PURER PHOS ACID YIELDS HIGHER FERTILIZER ANALYSES

Phosphoric acid from a hemihydrate process is purer than that from a dihydrate 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 can be raised to reduce 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. The plant used 67 BPL central Florida rock. Before the Hemi conversion it was difficult to meet 18-46-0 DAP grade, using settled 40% P_2O_5 acid. Upon startup of the Hemi process, grade jumped to about 47.5% P_2O_5 , and easily exceeded the 18%N requirement, using un-settled 40% acid. A simple modification was employed to prevent over-formulation of DAP. Coarser filter cloths were used to add solids to filter product acid, thus adding gypsum as a diluent to bring DAP grade down to the required 18-46-0 specification.

The Hemi process has four effects which improve purity of ~41% acid, compared with dihydrate process acid that is evaporated to the same concentration. There will be less sulfate, aluminum, fluorine, and solids, as described:

SULFATE

The Hemi process operates with around 2% free sulfate in 41% P_2O_5 acid. Sulfate concentration will be much less than in acid from a dihydrate process, which typically has 2.5% sulfate in 26% P_2O_5 - equal to 3.9% sulfate when evaporated to 41% P_2O_5 .

ALUMINUM

Hemi reaction conditions and solubility situation cause more aluminum to be insoluble and be discharged with the gypsum. Therefore, there is significantly less aluminum in the acid. This effect varies with feed source. Tests can provide quantitative information for any rock source.

FLUORIDE

Hemi reaction/solubility conditions cause more fluoride to be discharged with the gypsum. Also, more fluoride evolves as a gas from the reaction section. Therefore, there is significantly less fluoride in Hemi filter product versus dihydrate acid which is concentrated to the same 41% P₂O₅.

SOLIDS

Hemi filter product typically contains less than 1% solids at 41% P₂O₅. Dihydrate acid often contains much more solids, although additional clarification can compensate.

Effects of Hemi acid on DAP grade can be calculated for any specific situation. The figures below represent a typical central Florida phosphate plant.

DAP GRADE EFFECT FROM HEMI IN A TYPICAL PLANT

| Component | <u>% in 41% Acid</u> | | | | <u>Ratio vs. P205</u> | | | <u>Effect on DAP % P205</u> | |
|------------------------------------|----------------------|-------|-------------|-------|-----------------------|--------|---------------|-----------------------------|---|
| | HEMI | DI | Diff. | | HEMI | DI | Diff. | Calculated | Expected |
| SO ₄ | 2.0 | 3.9 | -1.9 | | 0.049 | 0.096 | -0.047 | +1.04 | +1.0 |
| Al ₂ O ₃ 0.8 | 1.5 | -0.7 | | 0.020 | 0.037 | -0.017 | +0.38 | +0.3 | |
| F | 1.2 | 2.0 | -0.8 | | 0.029 | 0.049 | -0.020 | +0.43 | Nil * |
| Solids | 1.0 | 3.0** | <u>-2.0</u> | | 0.024 | 0.073 | <u>-0.049</u> | <u>+1.09</u> | <u>+1.0</u> |
| TOTAL EFFECT: | | | -5.4 | | | | -0.133 | +2.94% | +2.3% P₂O₅ |

* The lower %F in 41% hemi acid would provide a different benefit versus dihydrate with a dual-acid-strength DAP process, where the dihydrate acid involved would be a combination of 26% and 54% P₂O₅ acids.

** Dihydrate % solids is based on 1.9% solids in 26% P₂O₅ and no settling of 41% P₂O₅ acid.

Similar calculations predict a potential of 0.9% N increase, although in actual practice, ammoniation absorption is likely to be limited to less than this, and ammoniation would be controlled to limit %N to that which is required.

The amount of DAP grade boost may be more than a single-plant operation needs. This can be an added benefit for a large complex where one plant is Hemi, and other plants are dihydrate plants. The Hemi acid would be blended with dihydrate acid to provide a more moderate increase in grade of all of the DAP, TSP, MAP, or other products.

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_2O_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 such rock could lead to breakthroughs in utilizing phosphate reserves in places like South Florida.

THE HEMI-DI PROCESS

A variant of the Hemi process is the Hemi-Di process, which employs a second “transformation” reactor, followed by a second filtration. The Hemi-Di process minimizes raw material costs, produces cleaner gypsum, has cleaner cooling pond water, can accept more cake wash water, and allows product acid concentrations from 42 to 50% P_2O_5 .

The transformation reactor provides conditions wherein hemihydrate crystals dissolve while dihydrate crystals are forming. This allows most of the phosphate that had been trapped within the hemi crystals to dissolve in the acid solution. These dihydrate crystals are then washed with water, providing extremely high P_2O_5 recovery of 98-99%.

Many gypsum utilization process require high purity gypsum, which can be produced from a Hemi-Di or Di-Hemi process.

A Hemi-Di process provides an opportunity to recover sulfuric and phosphoric acid by recycling weak solutions, such as raffinate from a phosphoric acid purification process or from spent scrubber acid.

Uranium recovery from phosphoric acid can be greatly enhanced with a Hemi-Di process. This occurs because a high uranium-to- P_2O_5 ratio occurs in a certain weak acid filtrate stream with the Hemi-Di process.

CASE HISTORIES

Four Hemi or Hemi-Di phosphoric acid engineering projects with which the writer was involved are described here. These include:

- Engineering for two conversions of existing dihydrate plants to the Hydro Hemi process.
- Consulting as owners' engineers for a new Hemi phosphoric acid plant for Indo-Jordan.
- Basic engineering for conversion of a very large dihydrate phos acid plant to the Yara Hemi-Di process.

A major justification for all four projects was elimination of all of the steam and processing for concentrating phos acid from about 26% to 42% P_2O_5 . This was accompanied by corresponding reduction of cooling water requirement and elimination of any need to handle 26% P_2O_5 acid. The Hemi plants made effective use of the purity benefits of Hemi acid. The Hemi-Di plant was designed to produce high purity gypsum for further processing.

BELLEDUNE HEMI CONVERSION

The Belledune Hemi conversion proceeded very smoothly and provided what the client described as "one sweet plant to run". It was running at capacity only 19 days after start-up. Rate increased to 110% of design a few days later. All guaranteed performance criteria were exceeded. The plant became what some people believe to be the world's easiest running phosphoric acid plant. The plant superintendent observed that Hemi could tolerate upsets like raw material changes far better than the previous dihydrate process.

Product acid was used to make DAP without the expensive concentration step. The old concentrators were abandoned, all process steam requirement was eliminated. Hemi operation resulted in almost none of the serious reactor and flash cooler scaling that had affected the dihydrate plant. Purity of acid directly from filtration (without any clarification) was so good that DAP grade immediately jumped to about 18.4-47.5-0 – far above the required 18-46-0 analysis. To limit DAP grade, acid solids content was raised by using very coarse filter cloths.

ARCADIAN HEMI CONVERSION

The Arcadian Hemi conversion started even faster than Belledune – only 2 days. Its P₂O₅ recovery of 96% is the world's best for a Hemi plant. Within a month the plant was operating well above design capacity, and all performance criteria were so good that the client accepted the plant without the usual guarantee test run.

The Hemi process enabled Arcadian to abandon its expensive rock grinding operation and to reduce steam use for acid concentration by 70%. Maintenance cost was substantially less than with the old dihydrate operation. Product acid is used to make food grade phosphoric acid and premium quality liquid fertilizers.

Raffinate from a food grade acid purification plant and spent scrubber acid from a superphosphoric acid plant were consumed in the transformation section - providing recovery of most of the phosphoric and sulfuric acid in those streams.

| HEMI CONVERSIONS - BELLEDUNE & ARCADIAN | | |
|---|---|---|
| Plant Location | Belledune Fertilizer Ltd New Brunswick, Canada | Arcadian Fertilizer (now PCS) Geismar, Louisiana, USA |
| Phosphate Rock | Central Florida (original) Morocco (later operation) | BuCraa (western Morocco) |
| Reactor | Prayon - 9 compartments | Prayon - 9 compartments |
| Filter | Bird Prayon 24C | Bird Prayon 24C |
| Conversion Process | Hydro (now Yara) HH Hemi | Hydro (now Yara) HH Hemi |
| Capacity, STPD P₂O₅: | | |
| Before Conversion | 500 | 540 |
| Design | 550 | 720 |
| Actual Sustained | 600+ | 800+ |
| Peak | 700 | 900 |
| P₂O₅ Recovery (filter cake): Guaranteed / Actual | 93% / 95% | 95.5% / 96% |
| Startup Date | Sept., 1986 | Sept. 1990 |
| Time to 100% Capacity | 19 days | 2 days |
| Comments | Very little scale accumulation in reactor or flash cooler. No evaporation or clarification required to make DAP. Client: "One sweet plant to run." | Extremely easy start-up. Consumes raffinate and scrub- ber acid from other plants. Product makes food grade acid & premium liquid fertilizers. |

INDO-JORDAN HEMI PLANT

The Indo-Jordan phosphate chemical complex at Eshidiya, Jordan produces 54-56% P₂O₅ phosphoric acid for shipment to India DAP plants. The Hydro (Yara) Hemi phosphoric acid plant uses a variety of phosphate rocks from the adjacent JPMC Eshidiya mine. It was designed to use a combination of damp concentrate, screened dry rock, and rock dust. Phosphoric acid is concentrated from about 43% to 56% P₂O₅. The purity benefit of hemi acid enables the plant to produce 56% P₂O₅ at the same boiling point as with conventional 54% P₂O₅ acid. This saves much freight cost when shipping the acid to India.

The hemi gypsum is conveyed directly from the filters to an advanced design dry stacking system. Crucial know-how was provided by JPMC (one of IJC's owners) to enable the conveying and stacking system to operate reliably.

The plant easily exceeds its design capacity of 700 t/d P₂O₅, and has operated profitably every year since start-up. IJC now successfully uses a substantial portion of "sub-commercial" rock that had been considered to be of no practical value.

| INDO-JORDAN - NEW HEMI PLANT | |
|--|--|
| Plant | Indo-Jordan Chemicals Co. (IJC), Eshidiya, Jordan |
| Phosphate Rock | Eshidiya, Jordan - various grades |
| Reactor | Hydro - 3 cylindrical tanks |
| Filters | 2 @ 85 m ² Eimco Belt Filters |
| Process | Hydro (now Yara) HH Hemi |
| Capacity (MTPD P₂O₅): | |
| Design | 700 |
| Actual Sustained | 870 (limited by sulfuric acid supply) |
| Peak | 900+ |
| P₂O₅ Recovery (filter cake) | 94.2% |
| Start-up | 1997 |
| Comments | Designed for damp concentrate, screened rock, and rock dust. Now also consumes much sub-commercial rock. Remote desert location. Dry gypsum stacking. |

LARGE HEMI-DI CONVERSION

The client needed to modify an existing dihydrate phosphoric acid plant to produce high quality gypsum, suitable for further commercial processing. Several process were available that could meet the gypsum quality criteria. The Hydro/Yara Hemi-Di process was selected because it provides:

- Extremely high P₂O₅ recovery (~98.5%)
- Energy & processing benefits of making 42% P₂O₅ acid directly from filtration
- Avoids the major expense of grinding the phosphate concentrates
- Proven track record in several plants worldwide
- Excellent technical support - licensing, engineering, and follow-up

We performed the basic engineering to convert the plant to the Yara HDH Hemi-Di process. Others have done the detailed design and much of the construction. Unfortunately, the plant was sold, and this attractive conversion project is on hold.

| LARGE HEMI-DI CONVERSION | |
|---|--|
| Plant | Not disclosed |
| Phosphate Rock | Jordan, Yunnan, Egypt |
| Reactor | Jacobs Dihydrate |
| Filters | Delkor Belt Filters |
| Process | Yara (formerly Hydro) HDH Hemi-Di |
| Design Capacity | large |
| P₂O₅ Recovery (filter cake): Guaranteed / Expected | 98% / 98.5% |
| Startup | Partly completed, but on hold since 2005 |
| Comments | Gypsum would be suitable to be utilized. |

YARA (HYDRO) HEMI & HEMI-DI PROCESS EXPERIENCE

The Hydro or Yara Hemi process has been chosen since 1970 for twelve Hemi plants and eleven Hemi-Di plants which have been built, converted, or are underway worldwide. The process name was changed from Hydro to Yara in 2004, but staffing of the licensing division was not changed. The plants are listed in the following two tables.

| YARA (HYDRO) HEMI PLANTS | | | | | |
|---------------------------------|-------------------------|--|---|-------------|------------------------------|
| CLIENT | Location | Design t/d P₂O₅ | Actual mt/d P₂O₅ | Year | ROCK |
| Windmill ** | Holland | 200 | | 1970 | C.Fla., Togo, Moroc. |
| HCI | Cyprus | 130 | | 1982 | Algeria, Jordan, Togo |
| Windmill ** | Holland | 330 | | 1983 | C.Fla., Togo, Moroc. |
| Royster | Fla., USA | 590 | 650 | 1985 | C. Fla. Spiral conc. |
| Belledune | Canada | 500 | 600 | 1986 | C. Florida |
| Arcadian (PCS)* | La., USA | 655 | 800 | 1990 | BuCraa |
| Saranya* | Brazil | 480 | 580 | 1994 | Brazil |
| Indo-Jordan* | Jordan | 700 | 870 | 1997 | Eshidiya Jordan |
| Western Mining* | Australia | 1500 | 1650 | 1999 | Queensland |
| Ma'aden | Saudi Arabia | 3 @ 1460 | Bidding | 2009 | Al Jalamid, Saudi |

* Operating

** Two Windmill Hemi plants were converted into one Hemi-Di plant in 1991.

Royster, Belledune, and Arcadian were converted from Prayon dihydrate plants.

| YARA (HYDRO) HEMI-DI PLANTS | | | | |
|--|--------------------|---|-------------------------------|----------------------------------|
| CLIENT | LOCATION | m t/d P₂O₅ | YEAR | ROCK |
| RMKH Trepka | Yugoslavia | 160 | 1974 | Jordan |
| Albright & Wilson | England | 500 | 1980 | Morocco |
| CSBP | Australia | 500 | 1981 | C. Florida |
| Pivot | Australia | 100 | 1981 | C. Florida |
| Supra^{***} | Sweden | 360 | 1986 | C. Fla, Morocco, Togo |
| Chinhae | South Korea | 250 | 1990 | C. Florida, China |
| Hydro-Agri ^{**} | Holland | 620 | 1991 | C. Florida, Morocco |
| Hong He Zhou[*] | China | 210 | 1993 | Jian Chuan China |
| NFC[*] | Thailand | 700 | 1997 | Jordan, Morocco |
| Sterlite[*] ^{***} | India | 420 | 1999 | Jordan |
| Not disclosed^{****} | — | Large | Holding since 2005 | Yunnan, Egypt, Jordan |

* Operating

** Two Windmill Hemi plants were converted into one Hemi-Di plant in 1991.

*** Much of the Supra plant equipment was relocated to Sterlite in India.

**** Conversion from dihydrate

Additional information on the Hemi and Hemi-Di processes and operating experience at several of the referenced plants can be found in references cited at the end of this article, including previous papers which the author presented at Clearwater in 1991, 1995, and 1999.

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REFERENCES

- Pierre Becker, "Phosphates & Phosphoric Acid", 2nd Ed., Marcel Dekker Inc., NYC, 1989.
- BuShea, et al., "Application of BSF Technologies CTC3 to a Phosphate Fertilizer Complex", AIChE Spring National Convention, Orlando FL, March '90 and AIChE Clearwater Convention, May '90.
- 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.
- G.W. Hartman & L.J. Friedman, "The Royster Power Program - Start-up and Initial Operating Experience" AIChE Convention, New Orleans LA, April,'86.
- John H. Wing, "From Phosphate Rock to DAP at Lower Cost", AIChE Clearwater Convention, May,'99.
- John H. Wing, "The Case for Converting Phos Acid Plants to Hemi", AIChE Clearwater Convention, May,'95.
- John H. Wing, et al, "Hemi or Hemi-Di - Our Future", AIChE Spring National Meeting, New Orleans LA, April,'92.
- John H. Wing, et al, "Hemi or Hemi-Di? - Arcadian Converts Phos Acid Plant from Dihydrate to Hemi", AIChE Clearwater Convention, May,'91.
- John H. Wing, "Hemihydrate Phosphoric Acid Plant Conversion at Belledune, Canada", AIChE Meeting, Lakeland FL, Oct.,'87.
- John H. Wing, "Florida Phosphate Technology - 2000", AIChE Clearwater Conv.,May,'89.
- Anonymous, "HiTech Solutions, Inc. - Contractor Profile". *Phosphorus & Potassium* magazine, Jan.-Feb. '93, page 26.

ABOUT THE AUTHOR

John H. Wing - Vice President of HiTech Solutions, Inc. - has a Bachelor of Chemical Engineering degree with Honors from the University of Florida and a Master of Engineering in Administration from University of South Florida. He has served the phosphate industry for over three decades in process design, consulting, project management, technical service, process development, and production supervision.

He has designed modifications and expansions of several phosphoric acid, DAP, MAP, & TSP plants. He performed the process design for 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 and Arcadian Hemi conversions and for a large Hemi-Di conversion. He was project manager for the Arcadian Hemi conversion, and consulted as owner's engineer for the Indo-Jordan Chemical Co. Hemi plant in Jordan.

He has written technical papers on:

Hemi and Hemi-Di processes (6 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

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

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