

## **The FIPR MonoCal WPA Process**

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## ABSTRACT

### FIPR MonoCal WPPA Process

The Florida Institute of Phosphate Research (FIPR) has been funding development of a monocal process for production of wet-process phosphoric acid (WPPA) for over 12 years. This is the first public disclosure of the FIPR technology.

The term "MonoCal," refers to dissolving the feed phosphate rock in an initial low-sulfate, high dissolved-calcium zone in a relatively conventional dihydrate WPPA facility. The current emphasis of this work is development of a cost-effective environmentally-favorable process that can stand on its own or act as a front-end to existing WPPA plants.

We have discovered that almost 100% of the feed fluorine can be tied up as low-solubility Calcium fluoride or silica fluorides in the gypsum and product acids. Although tests have not been carried out on a whole-plant circuit (for example, volatilization of F in flash coolers) the potential to reduce the environmental impacts and need for lime treatment of process waters at WPPA plants is obvious. Additionally, pilot plant runs have indicated that a significant Sulfate savings should be achievable.

At the current state of development, the FIPR process modifications can be recommended as the basis for a world-class single tank reaction system or front end modification of older-style "Iso-thermal" or Rhone-Poulenc design plants, with improved rates, excellent control, good product recovery and reduced environmental impact.

Since the MonoCal modifications result in an inexpensive, extremely stable, easy to control process, the potential in third-world markets is large. FIPR would primarily like to see the technology developed to make a favorable impact on the economics and environmental profile of Florida-based plants.

## INTRODUCTION

The Central Florida Section of the American Institute of Chemical Engineers provided an opportunity for us to begin discussing this technology at Clearwater, FL on May 25, 1996. Please re-read **Factors Affecting Recirculation Rate Choices in Wet Process Phosphoric Acid Production<sup>1</sup> ("Factors")**, available in the FIPR library, for a chatty view of dihydrate plant operation.

Contract agreements limited what we could discuss about monocal operation at that time. Since then much has changed. Most significantly we have developed new technology not disclosed in prior art.

We have reviewed the early patents (Case et al) and are aware of the potential for high co-crystallized P<sub>2</sub>O<sub>5</sub> losses first published in the Becker and Frochen paper at the 1956 ISMA conference in Stockholm<sup>2</sup>. We have experienced and discussed with other practitioners problems that occur when trying to grow filterable crystals from a mono-calcium phosphate solution by addition of sulfuric acid.

The early monocal patents were never commercialized because, in our opinion, the developers were not fully aware of the extremely complex nature of the physical processes involved. WPPA production, even the hemi-hydrate processes, is still largely "black art," about which little is published and every engineer holds his/her own opinions and trade secrets.

We have added to this proprietary technology that improves filtration and reduces fluoride gas emissions. We have overcome many of the early problems such as crystal bloom and high CS (co-crystallized, citrate-soluble P<sub>2</sub>O<sub>5</sub>) losses. We have investigated pilot plant configurations and vessel sizes that should scale to 1000 tpd P<sub>2</sub>O<sub>5</sub> and beyond.

More work is desirable, but that is always the case. If your process situation faces a need that you see answered somewhere in the balance of this presentation, contact the author at [LithiaTechnology.com](http://LithiaTechnology.com) or G. Michael Lloyd at FIPR (Florida Institute of Phosphate Research in Bartow, FL).

## **MonoCal Operation--Fluoride Volatility**

Reducing the phosphoric acid plant reactor recirculation rate to increase dissolved calcium levels in the rock dissolving area has many advantages (see the paper, "Factors," op.cit.). In this paper we are concentrating on just one, the effect of high Attack calcium on acid fluoride volatility.

Raising the molar concentration of calcium in the rock-dissolving zone of the Attack and letting the sulfate concentration drop has the major effect of reducing the volatility of acid fluoride gases throughout the reaction and crystallization system. We believe, from data showing reduced silica dissolution, that HF (hydrogen fluoride) concentrations or activities are reduced or eliminated. In turn the volatilization of SiF<sub>4</sub> (silicon tetra-fluoride) ceases.

The elimination of the Attack/Reactor scrubber as a source of acid fluoride gases into the phosphoric acid scrubbing system has major implications for plant operation. A major source of toxic acidity is removed from the cooling pond or scrubber water system. This will greatly reduce eventual neutralization and closing costs for the pond systems.

Coughing, choking fumes from poorly ventilated Attacks have always been a health and safety issue. Many times this cost shows up in corrosion and maintenance expenses. Reduced buildup of silica depositions in scrubbers and ductwork can save much operating manpower. MonoCal addresses all these issues.

For plants operating entirely with recirculated water, much of the need to neutralize water on an on-going basis is eliminated<sup>3</sup>. It is estimated that one-third to one-half of the fluorine present in the feed phosphate rock is volatilized during rock attack and gypsum crystallization.

## **Neutralization Costs**

Considering burned or hydrated lime at \$100/short ton, the cost to neutralize half of the feed fluorine is equal to about \$16 per ton of product P<sub>2</sub>O<sub>5</sub>. This is a very significant cost of production. Of course, this consideration brings up the question of neutralization of the cooling water circuit.

Our work has not included estimation of the volatility of fluorides from Reactor flash coolers or later evaporation or concentration of the product phosphoric acid. That volatility depends largely on the nature of the fluoride in the product filtrates. We have reason to believe that much of the fluoride can be tied up as fine particulate calcium fluoride<sup>4</sup>. In this case the overall cost of neutralization of fluorides can be reduced even further.

## **Operating Flexibilities**

The need to maintain a portion of the Phosphoric Acid reactor at one sulfate (calcium) level, and another at a higher sulfate level may seem a needless complication. In practice it has not been found to be difficult at all.

Since a large portion of the phosphate rock goes into solution in the MonoCal zone of the Attack system, the amount of un-dissolved rock in the areas where sulfuric acid is introduced directly is very much lower than normal. This has the immediate effect of eliminating or minimizing sulfate-level variations in the Reactor controls. The near-elimination of rock "sulfate-coating"<sup>5</sup> is one of the prime advantages of the MonoCal process.

Variations in the level of solution sulfate are strongly related to other control problems such as filtrate strength and crystal size distributions. Obviously, if the rate of formation of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  slows or increases, the amount of free water in the Attack system changes also. As total Attack residence times drop towards two hours this sensitivity increase.

Buildup of scale deposits on equipment surfaces is difficult to estimate from pilot plant operation. Our experience is that reduced sulfate swings reduce the rate of nuisance deposition of gypsum and silica fluorides which seem to bind the gypsum. This includes the annoying, very insoluble dual salt of sodium-potassium silico-fluoride.

## **Reactor Configuration**

We have only sketched out in general the FIPR modifications, and how they can be applied to an existing or new plant design. This paper cannot provide proprietary information for which the Florida Institute would like to obtain licensing revenue. However, we can provide enough information for you to decide if further conversation is justified.

First, let me say very clearly, every attempt to convert an existing plant to something like monocal operation has resulted in many, many thousands of dollars of losses and expenses. This is true of all early pilot plant exercises also. We do not make claims of proprietary technology because we "think" it will work. We have seen it work in pilot configurations.

FIPR has spent upwards of \$500,000 developing this technology, both for itself and for clients. The portions that constitute significant extensions to the prior art were designed and tested under my supervision by persons not being paid by FIPR at the time of the technology extension, but certainly inside FIPR facilities.

The proprietary aspects concern the understanding and implementation of procedures and method to foster gypsum cluster crystal development in monocal solutions. Without these, co-crystallized  $P_2O_5$  losses are higher and slurry filterability unpredictable. There will be a little more on these subjects just before the Endnotes to this paper.

The FIPR MonoCal reactor design consists of an expanded rock dissolving compartment which receives only a portion of the recirculation in the crystallization - sometimes called "digestion" - area of the reactor.

This restricted recirculation deprives the rock dissolving area of sulfuric acid and causes the accumulation of excess dissolved calcium. We have operated several FIPR-owned pilot plants at a variety of dissolved calcium levels from 2 to 4% CaO.

The resultant MonoCal solution is then introduced into the main crystallization area of the reactor in such a fashion as to promote cluster crystals<sup>6</sup>. This is a proprietary step.

Understanding the mechanism that causes clustering is necessary in understand how the FIPR MonoCal modifications reduce co-crystallized  $P_2O_5$  gypsum losses. This comes with the technology package.

### **Status of MonoCal Development**

The history of the wet process phosphoric acid (WPPA) industry is one of incremental changes. Any experienced process engineer can relate to you numerous "obvious" improvements that were near-disasters. The MonoCal modifications are much more than "incremental."

We hoped in several of the last pilot plant configurations to leap-frog the latest Dorr-Oliver and Prayon generations of plants in recoveries and production rates. While we feel we are more than competitive in filtration rates at a given product acid  $P_2O_5$  strength, recoveries have run around 95% across the reactor and filtration. We believe they can be higher in this process.

We have spent so much time and effort understanding the factors that affect filtration that we were unable to adequately address the apparent lack of acid fluoride gas volatilization during Reactor operation.

In an earlier pilot plant investigation of a monocal flowsheet from another researcher, we first noted that the further we ventured into "conventional" operation the worse the fuming became. We have clear (actually foggy window) proof that the amount of glass-etching and lung-searing emissions are very much less with MonoCal operation.

When operating at the prescribed conditions, one may take a deep breath from the top of an operating MonoCal reactor and detect only a damp rock odor. Amazing!

This puts us in a very strong competitive position, since the MonoCal process is the only one that can claim major environmental benefits.

To have commercial value a process must have commercial benefits. This means providing equal or better production at lower costs. How this plays out depends very much on each plant's particular situation. If you are currently expending large amounts of money neutralizing hydrofluosilicic acid from a conventional plant, you must at least consider how MonoCal can help you.

If you have, or are considering a single tank reactor of the iso-thermal or Rhone-Poulenc design, we can reduce your costs, improve your rates and help the environment.

If further work matures some of the "Areas of Future Research - Potentials" addressed below, then existing large plants may reduce product costs and improve profitability by adapting the MonoCal modifications.

If you have to meet government regulations requiring you to do something about fluoride or HF emissions, we think we are the only process in town worth considering.

### **MonoCal vs Hemi hydrate**

The latest generations of hemi hydrate plants have very high specific production capability, good filtration rates and recoveries and an appetite for sophisticated controls and expensive alloys. Environmentally, they may pose a problem.

We are not in a position to decide if a MonoCal-type front end could pose solutions for the frequent excess hydrofluosilicic acid (FSA) situation of modern hemi plants. We need to know is if the calcium fluoride we believe is formed in the MonoCal front end will re-dissolve under the vigorous and hot attack conditions of a typical hemi-hydrate phosphoric acid plant.

So far, this is an unknown. We do surmise that some  $\text{CaF}_2$  is formed in some of the existing hemi plants because of reduced sulfuric acid requirements. In that case the fluoride must be physically large enough to be resistant to re-dissolution.

Plants that produce more than marketable amounts of  $H_2SiF_6$  are forced to neutralize the excess with lime, recycle some of the FSA to the DAP or Phos Acid reactors, where it hurts granulation, lowers rates and recoveries. Some make aluminum fluoride. Although a number of new aluminum smelters are coming on-line, particularly in the Mideast, there has been resistance to FSA-based  $AlF_3$  because of its fine particle size<sup>7</sup> or dustiness..

### **Areas of Future Research - Potentials**

We believe very strongly that a profitable retrofit of an existing single tank reactor or Iso-thermal style reactor could be based on the MonoCal information we have on hand. However we would be the first to agree that more work is desirable.

Firstly, most of our data is from relatively small pilot plants, 10 to 20 grams per minute rock feed rate. Secondly, we have been hampered in the fluoride analytical area by lack of access to anything like quick sample turnaround. Not a single one of our runs was based on what would optimize fluoride capture.

Thirdly, there have been great, even enormous variations in lab results on the same samples from various laboratories. We know this is a common complain of all researchers. But it can be solved.

Some runs were made at 40 - 42%  $P_2O_5$  reactor acid concentrations, but before we learned to optimize filtration rates. Yet the gypsum samples showed exactly no hemi hydrate contamination by X-ray crystallography. We love to speculate what can be done with this fact. Perhaps increasing reactor  $P_2O_5$  so that Ralstonite will form. The Ralstonite molecule,  $MgAlF_6Na \cdot H_2O$  gets rid of a lot of unwanted ingredients and has been observed in 40% acid clarification.

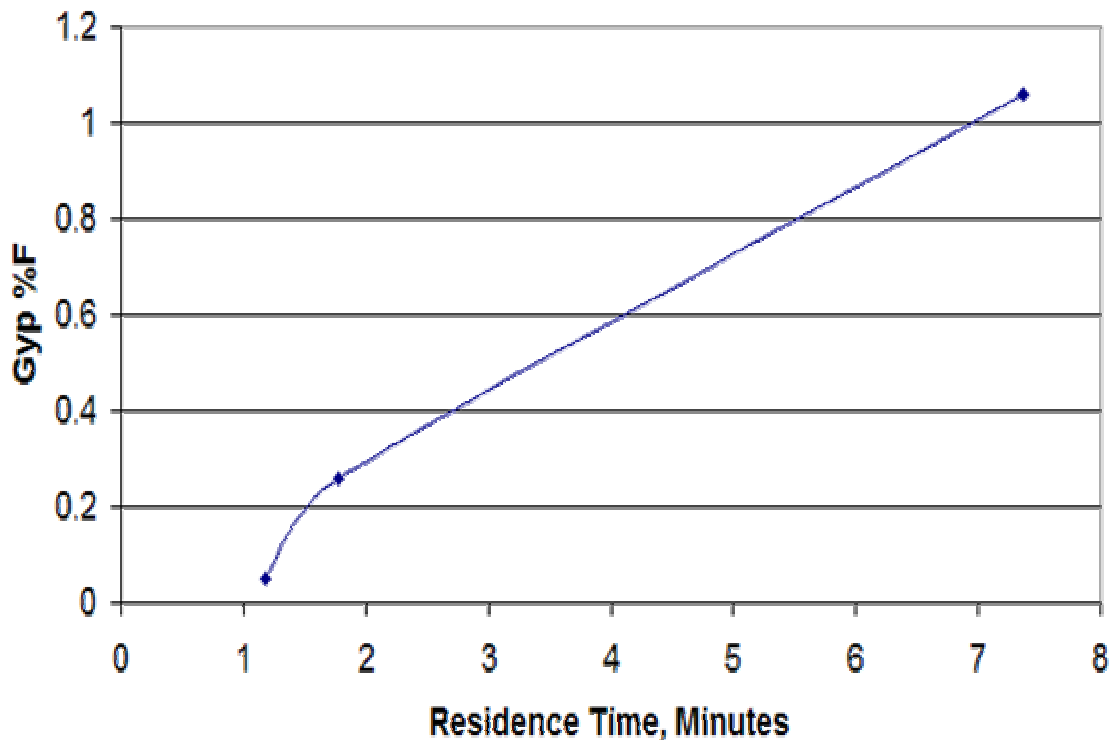
You may not need to be told that 180°F and 42%  $P_2O_5$  is supposed to be within the hemi hydrate range of operation - see the second chart on Page 10.

Only a single sample of MonoCal gypsum was measured for pH. A standard 5% sample in di-ionized water measured 3.45 pH after normal acid/fresh water washing. This indicates roughly how much additional acidity must be neutralized to run a neutral (7 pH) conveying scheme. Questions are, can this sample be improved? Is there room here for further environmentally sound plant modifications?

We have experienced variable periods of iron and aluminum reduction. One recent set showed 17% reduction (from rock) in the 27%  $P_2O_5$  first filtrate. We expected more.

Early on, we thought we saw up to 8% reduction in sulfuric acid consumption. Even though our pilot plant facilities have improved, we have not seen this again. Yet there is a major difference. Our last three efforts were made with a small fraction of the rock-dissolving residence time as the earlier work. We can see the difference in the gypsum. Yet if we are tying up acid fluoride, some low-vapor pressure fluoride species must be involved.

### Gypsum Fluoride



The issue of rock-solving residence time is a dilemma. The last MonoCal pilot plant work at FIPR used a very small rock compartment because C.I (Citrate Insoluble) losses have always been near nil with this process. Unfortunately, earlier runs with this configuration involved no gypsum fluoride analyses. The information in the above chart was not recognized until that final work was complete. It would have been relatively simple to evaluate this variable if we had been aware of its significance.

## Reactor Calcium Control

The following page is from one of Everett Case's monocal patents. There is much to disagree with in this data, but it shows some of the solubility considerations involved with increasing dissolved CaO in reactor slurries.

Exceeding the solubility of mono-calcium phosphate will surely lead to excessive phosphate losses. We believe that when slurries containing solid  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  are added to the primary reactor filtration suffers also.

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SHEET 1 OF 2

FIG. 1

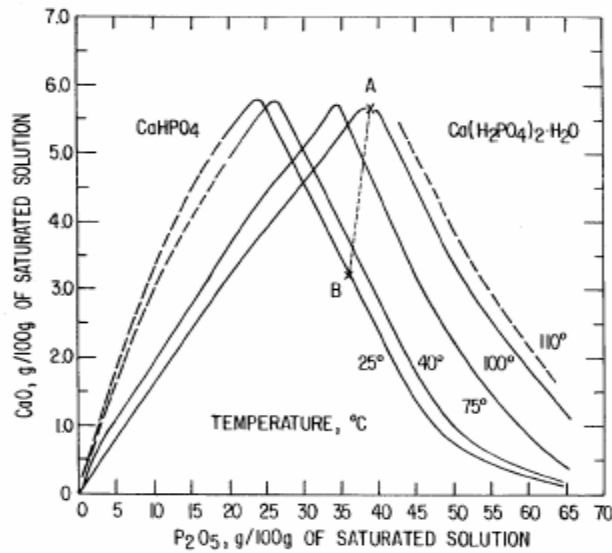
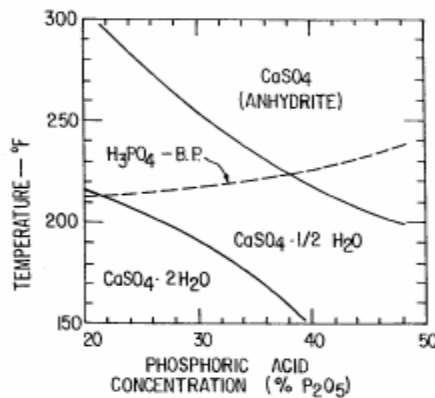


FIG. 2



INVENTOR  
EVERETT N. CASE

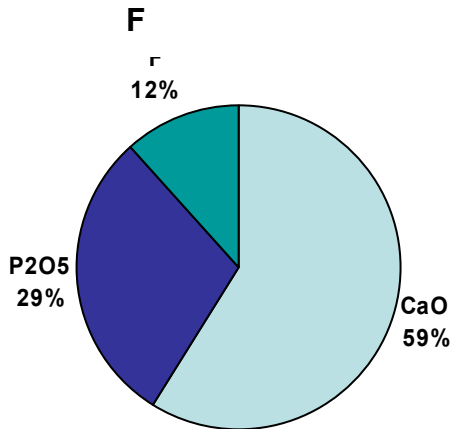
BY *McLean, Nelson & Strickland*

ATTORNEYS

Rock dissolving calcium levels were set by the recycle rate back to the rock compartment and remain quite stable. We measured soluble calcium from the same samples as sulfate samples, but using a AA Photo-Spectrometer with calcium lamp. The method was usually quick and accurate.

### Fluorine in Phosphate Rock

The fluoride ion is about 12% of the molar composition of rock phosphate considered as P<sub>2</sub>O<sub>5</sub>, CaO and F:



This means that for every ton of P<sub>2</sub>O<sub>5</sub> produced 0.11 tons of fluorine must be handled in some way. We have already discussed the problem of excess FSA production.

Accurate fluoride material balances around operating plants are rare and subject to controversy. We have used the estimate that 50% of the fluoride precipitates as Chukrovite and the like in a plant with cooling pond and wet gypsum conveying. The figure is obviously lower for a plant with only cooling towers.

The fact that most new world production is in areas with restricted water usage or tighter environmental restrictions is driving the acceptance of cooling towers with their higher liming costs. This makes the MonoCal process even more significant to those areas.

### Influence of Agitation on Our Work

Agitation played an enormous role in the improving of the FIPR MonoCal pilot plant filtration rates. We knew going into the last tests that agitation was going to be important because of its affect on C.S. losses in this process. We did not know how sensitive rock dissolving compartment agitation was going to be in terms of filtration rates.

The primary process operator for the last runs was a former IMC Chief Operator. He had taught himself that level and agitation were the prime determinants of defoamer usage, and ran the pilot plant accordingly.

The result was a background production of small crystal scraps that accumulated quickly during periods of agitated downtime. The MonoCal reactor always responded well to these episodes. When a more Prochem Maxflo-like agitator was fabricated, and rock compartment agitation speed reduced, episodes of poor filtration became rare.

We also modified the main reactor agitation to a large-blade design. The last FIPR MonoCal pilot reactor design incorporated a main U-shaped vessel with a central divider. One agitator pumped down on one side of the baffle and the second pumped up on the other side. The recirculation rate was estimated at nearly 300:1.

This design is why we can say with some confidence that single tank operations can be adapted to MonoCal operation with the addition of a simple additional rock compartment.

These agitation changes are also related to C.S  $P_2O_5$  losses. There is a complex interplay between nucleation of new crystal material and its subsequent re-dissolution. Agitation plays a large part in this balance since the initial crystal nuclei tend to be higher in  $P_2O_5$  than the bulk of the gypsum crystals.

It makes sense to tackle a single-tank conversion as a next step but we are open to any opportunities that may arise.

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<sup>1</sup> Hebbard, George M, Factors Affecting Recirculation Rate Choices in Wet Process Phosphoric Acid Production, Paper 1.4, The 1996 Clearwater Conference of the Central Florida Section, American Institute of Chemical Engineers. Copies available in FIPR Library, Bartow.

<sup>2</sup> Frochen, J and Becker. Crystallisation and Co-crystallisation in the Manufacture of Phosphoric Acid, , P., ISMA Technical Conference, Stockholm, Sweden, 14-18 September 1959. LE/59/59 21 pp.

<sup>3</sup> See later discussion of neutralization costs.

<sup>4</sup> The Florida Institute of Phosphate Research in Bartow, Florida has excellent X-ray diffraction equipment. Unfortunately, the diffraction pattern of calcium fluoride is almost exactly the same as for normal gypsum. We have been unable to distinguish the various kinds of particulate fluorides in the MonoCal circuits.

<sup>5</sup> Most of the surface area of even finely ground phosphate rock is inside the porous rock particles. When solution sulfate levels rise above a certain target zone, diffusion of calcium from the pore openings is blocked, cause an immediate rise in solution sulfate levels. In a conventional dihydrate reactor under manual control such swings are a regular occurrence (several episodes per shift) for any but the best trained and experienced operators.

<sup>6</sup> Clustered gypsum crystals immobilize what would be a large population of smaller crystals into a single mass. At one time it was thought that such clusters or raspberries were individual crystals joined together. Scanning electron microscope work at FIPR has plainly shown that almost all "clusters" result from the growth of new crystal planes from the central faces of existing crystals.

Clustering improves filtration rates and washing not because surface area is reduced but because cake flow hydrology is improved.

<sup>7</sup> One wonders why granulation or pelletizing might not solve this problem. However, since our goal is to use the calcium in phosphate rock to neutralize acid fluoride we cannot become experts in this area.