

**Factors Affecting Recirculation Rate Choices
in Wet Process Phosphoric Acid Production**

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ABSTRACT

A Wet Process Phosphoric Acid plant is a complex interplay of concentrations, solubilities, super saturations, phase changes and interfering reactions. Operating personnel really have only a very few handles they can twist to try to optimize conditions, maintain steady state, and solve the compromises of product strength, production rate, feed quality and recoveries.

This paper discusses a few factors that go into setting some of these compromises, and points out how an often ignored but inexpensive adjustment can be used to help maintain steady state in a multi-compartment reactor.

BODY

All of us are familiar with process plants and plant runs where conditions just seem to "click" together to make for excellent operation. Unfortunately, we often don't have the time to sort out what worked, and must resort to trial and error the next time we operate near those conditions or use those kinds of feeds.

One example is wet process Phos Acid attack systems, which never seem to run as well when freshly cleaned as they do after a few weeks of operation. Another is granulation plants that labor until a certain product rate is reached, then seem to crank out product without a hitch as long as "the system is kept hot."

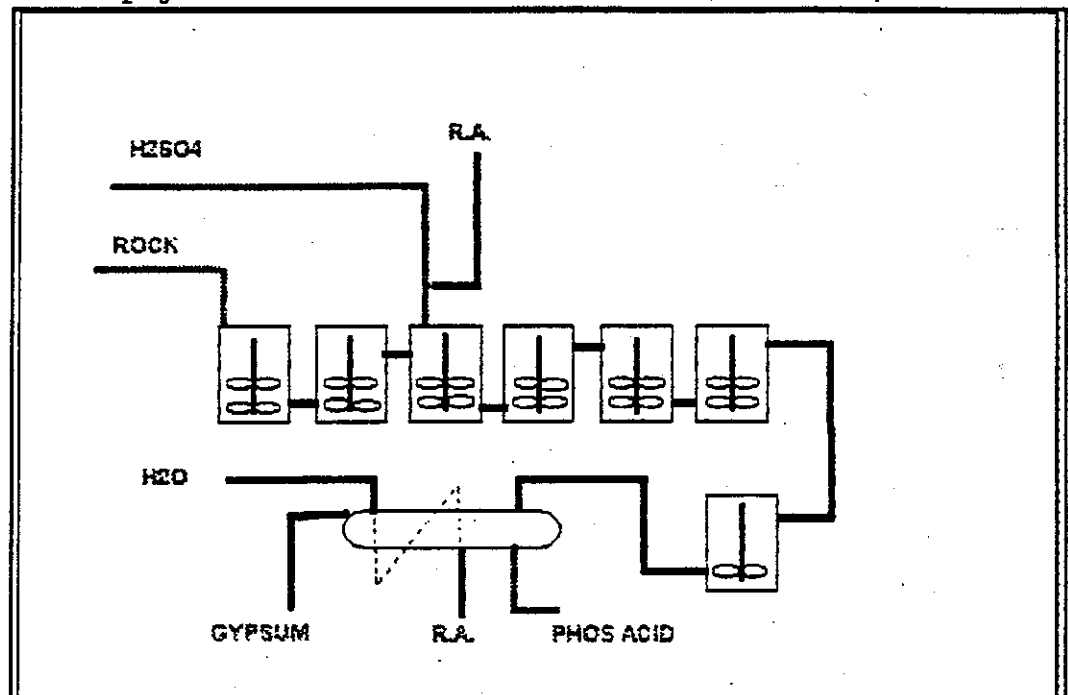
While we may never know all the ins and outs of these various sweet spots, as a tennis buff might call them, we can learn something about the control of attack supersaturation by recirculation change.

It has previously been described¹ how variations in the free sulfate just before fresh sulfuric is added can change the crystal habit from clusters to tabular and back. Changing the sulfate level at only one point in a recirculated system involves either dividing the sulfuric addition points or varying the recirculation rate itself. We will spend some minutes on this latter option.

This paper does not confine itself to multi-compartment reactors, but for the sake of clarity we will use the common six compartment front end Prayon design for a model. That design is all too familiar to most of us.

Lets assume that we are operating with an overflow to the filter feed system of 2.1% total sulfate. Our plant is reasonably optimized, and with our filter setup we have 0.25 % water soluble P_2O_5 loss. Cl & CS are in control and total recovery is 95% (cake).

Production Control or Traffic notifies us that the rock mix for the next seven shifts will be a dark, South County rock - pebble and concentrate - that we have identified with low reactivity in the past. What do we do?



In the past, "Nothing" might have been the best answer, as a wait-and-see attitude was considered conservative.

Now-a-days, most plant superintendents would drop the attack sulfates a little to counter the lower reactivity and tendency to "coat rock." Good operators will look at the ball mill feed and make that decision for themselves.

But there is a better way. Since we know that a lower reactivity will probably result in reduced rates, or will surely do so if we let the attack get out of control, we should initially plan for more residence time in the rock dissolution sections. Logically, we should drop rates ahead of time. Or should we?

Five years ago the above discussions might have resulted in raised voices and strained nerves. Today, most plants have their own set response to this scenario, and they are not all the same.

The better way is to reduce slurry recirculation rates in proportion to reduced feed rates and maintain a constant final sulfate to the filter feed compartments. If the operators do this as soon as they see "black rock" hitting the mill², chances are that very little filter capacity will be lost and the attack level will be drawn down to allow room to maneuver when the new feed hits.

[In the case where feed rock reactivity does not change, a reduction in recirculation might normally be accompanied with a relocation of sulfuric addition point(s). If recirculation is being changed because of reactivity, leave the sulfuric addition point alone.]

The end result of this action will be a higher total production that would have been made with no change and lost sulfate control. Plus, since the operator has made a proactive change, he is in control and is reasoning out what is happening.

In a few minutes we are going to discuss why recirculation rates are set where they are. First, we'll discuss a few of the ways various producers are using to vary the attack recirculation rate on-line and without sheave changes. These are (in order of good design):

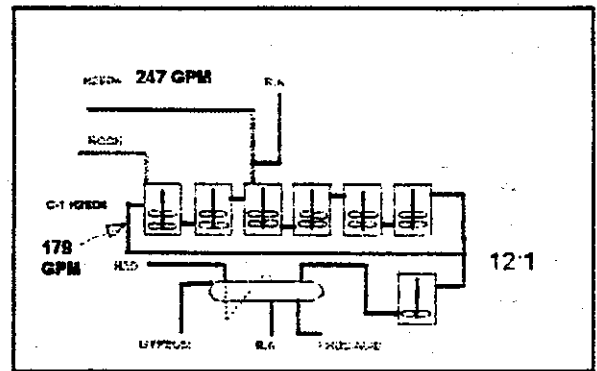
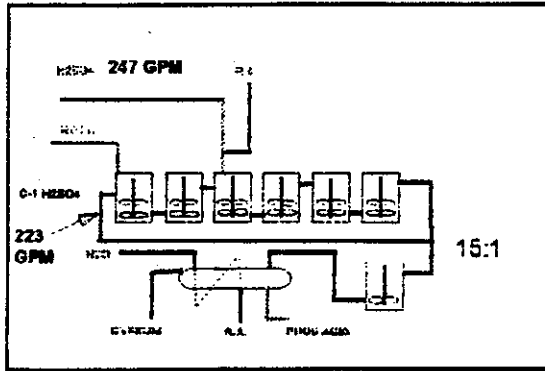
Methods of Changing Recirculation Rates

- **Hydraulic Speed control of Couch or Morris Recirculating Pumps**
- **Hydraulic or Variable AC Flash Cooler Pump Speed Controls**
- **Kicking On or Off Various Combinations of Fixed Speed F.C. Pumps**

All of these have proved to work. In the case of early plants or modified plants where all of the recirculation passes through the Flash Coolers and the Flash Cooler Pumps, option three is the most economical if there are at least three Flash Cooler pumps. Otherwise the cost can initially appear quite high.

There are other compromises involved in changing the flow through Flash Coolers, but when we are talking about compensating for lower rock reactivity, they usually do not apply. If, on the other hand, we are successful in our attempt to maintain high rates, the cost may well be a higher cooler scaling rate--not too bad a compromise when compared to the loses that might otherwise occur.

Probably the most important effect of reducing the recirculation rate is to reduce the quantity of sulfuric being added to the rock dissolution area. (See Appendix II for explanation.) Depending on the attack sulfate level and recirculation rate, the amount of sulfuric acid in the slurry recirculating from the end of the attack system back to rock dissolution may exceed the feed sulfuric acid rate to the plant. This sulfuric sets up a competition between rock dissolution and sulfate buildup on the rock particles.



With

finely ground dry 72 BPL rock in 1962 this was not much of a problem. Today's 58 BPL gray rock is harder and less weathered. A major effect of lower reactivity is to reduce the instantaneous rate of calcium liberation, thus throwing the balance towards reaction of sulfate at the rock surface rather than in the bulk liquid or at gypsum crystal surfaces.

Over the years most manufacturers have come to equate higher recirculations with higher production and better recoveries. We will return to this idea later, but let's now look closer at the idea of recirculated sulfate.

It's an interesting fact that two people may do the same right (or wrong) thing for completely different reasons. Or others, following what the pioneers are doing, may experience poor results and stick with the old ways until bought out. Then there are industrial secrets. The analogy of the British carrot ("The reason British pilots can see so well in the dark is carrots. There is no such thing as radar.") fits some of the changes made by producers to WPPA production. The more strongly someone protests these concepts, perhaps the more stronger they actually agree.

Most operating personnel are still convinced that it is wrong to allow the mole ratio of solution CaO to H_2SO_4 to go above 1.0, into the 'negative' free acid region. It is expected that citrate soluble losses P_2O_5 will increase. But further research shows that CS losses are controlled by another mechanism which will not be discussed in this paper. (An analysis of the Fröchen and Becker paper at '59 ISMA in Appendix I touches on how this idea started.

Accept for now that correct operation, under control, in the negative free acid region will not cause drastic increases in co-precipitated P_2O_5 . For the sake of argument we'll propose controlled operation in this range to test the response of your particular plant. Now, having disposed of that carrot, what do we handle this new procedure?

There may be, in a particular plant, good reasons to run with the final attack sulfate at a particular level, be it 1.7%, 2.1, or 2.6% H_2SO_4 . That is outside the scope of our discussion. As noted above, we can maintain that same final sulfate and reduce the sulfate in the rock dissolving area by reducing recirculation. This will have a number of ripple effects.

The first is, of course, to reduce the amount of recirculated sulfate. Then we will immediately see higher rock dissolving rates which will load the front end of the attack with dissolved calcium. We will likely see shifts in crystal habit which we may, or may not like. It will likely only be a problem if we shift from tabular crystals to clusters, but we can probably live with that change (Ref 1 again).

In the short term more rock will go into solution so the final compartment (say #6, in our model) will drop in sulfate. If the operator knows this will happen he can nudge the sulfuric flow up a few gallons per minute for one attack recirculation cycle.

If the less soluble rock has already hit the attack, sulfates will have started to rise, and the recirculation change will simply maintain the status quo. Given a choice, I think most operators will watch the rock and try to catch the transition rather than monkey with sulfuric.

And what about a rate change? At first glance that might make sense. But recall that we would then have a smaller amount of rock entering the rock dissolution area, and an even lower amount dissolving, because we have left the same high recirculation, with its load of sulfuric. A rate change may be necessary, but it should always be matched with a proportional or greater reduction in recirculation.

Less this seem mere mad speculation, note that people who have problems growing filterable crystals at reduced rate have used this technique for years. Most don't understand why it works. Reducing the recirculation is a proven way to prevent a plant from going into the doldrums with reduced rate.

At least one plant has installed variable speed hydraulic drives to adjust recirculation. [Which brings up a major point. There is an almost universal feeling in each producer or plant designer I have spoken with that they are privy to more good ideas than any of their competitors. Thus, open sharing of ideas would only reduce their profitability. I don't think this is true. Most of the major producers have something of their own to contribute, but the sum of the whole would benefit the Florida phosphate industry more than the sum of the individual advantages restricted to single plants.]

I should mention at this point that an attack is very sensitive to control around the recirculation rate where rock starts to coat during rock dissolution. A plant that runs a typical 0.2 to 0.5% Cl loss on normal rock is probably operating with a constant rate of rock coating. In the normal three to four hour residence time, most of the coating is penetrated and its P_2O_5 becomes available.

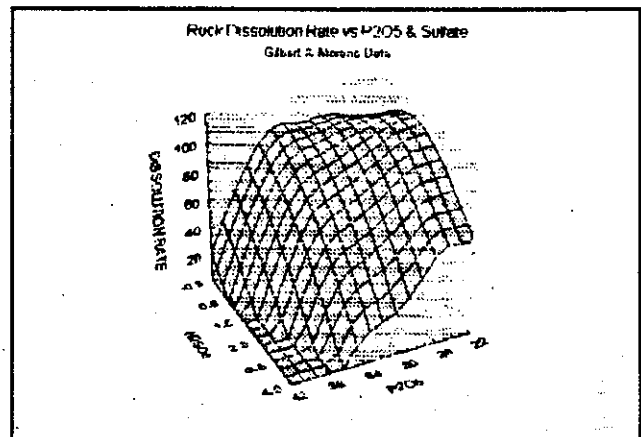
The same plant, operated at a lower free acid in rock dissolution, will behave completely differently. The major difference is the response to sulfate excursions. Appendix II discusses this in terms of the ratio of recirculated sulfuric acid to feed sulfuric.

Let's say that any one of the seeming endless factors that can initiate a sulfate swing occurs. An example might be a lagging rock slurry feed pump that uses the instantaneous dry tons per hour signal from the flow instrumentation to maintain constant feed rate instead of a true integrated tons delivered signal. The controller may bring the flow back to setpoint, but without true error integration, some rock feed will have been lost.

Here we would expect a sulfate spike of some magnitude and several hours duration.. For the plant operating with a high dissolving free acid, the rock solubility will drop proportionately less than will the plant with a low free acid. Thus, the spike may be more predictable and less accentuated for the high free acid case.

To see this more clearly, we can look at the data from Gilbert and Moreno³ (I&EC, 1968). The slope of dissolution rate with sulfate is steeper at lower sulfates. Note also the obvious: the rate of rock dissolution does depend on dissolving area free sulfate.

Where does this leave us? A plant with higher free acid in rock dissolution shows greater sulfate stability, is thought by some to have higher recoveries, and matches the operating manual recommendations of 30 years ago. But it just doesn't like today's unreactive rocks.



Producers that have used EVOP (evolutionary operation, a simple statistic procedure for optimizing continuous or batch processes) have generally moved towards an attack total sulfate of 2% or less. And experience has shown that matching recirculation rates to rock calcium feed rates has a more dramatic effect in plants with high rock dissolving area free acids. When this is done, a sort of natural EVOP will lead towards lower attack sulfates. This may be because with this control, the previously apparent response of CS losses to absolute attack sulfate levels is reduced or eliminated.

Why High Recirculation?

As production rates have been pushed higher in plants by combinations of improved mixing, better sulfuric acid dispersion, and general optimization, increasing recirculation has become a major design goal. In a number of cases the high dollar expenditures have accomplished nothing more than matching, at the higher rates, the original rock:recirculation rates. The first effect of increasing rates was usually an increased delta-T in the flash coolers, and recirculation was increased to reduce scaling problems.

In discussions with respected persons in the design area, a weak pattern emerges: Most but not all of today's senior process engineers remember that the original goal was to increase the free acid in the rock dissolving area, thus reducing CS losses in accordance with the Fröchen & Becker paper⁴.

In those plants where the flash cooler flow is more of a side stream, increase in recirculation, by and of itself has been a mixed bag. Very positive results have been obtained by forcing the flash cooler discharge directly into the rock dissolving zones. The small nuclei from the cooled slurry are very soluble in the higher calcium environment of rock addition. But this is a subject for another paper.

The main thrust of the above discussions was to point out the benefit of recirculation adjustment to control free acid in the critical rock dissolving area while allowing attack final sulfates to be set wherever desired. It should be obvious that a lower sulfate should encourage the dissolution of a less reactive rock even at the same residence time. Giving the less reactive rock more residence time and a lower sulfate goes even further towards preventing loss of undissolved (Cl) P_2O_5 and reducing attack upsets.

If a lower recirculation rate is all that good, why don't we all save recirculation horsepower and go that route? The answer is based in the many theories for increased attack recirculation.

Even aside from CS P_2O_5 losses considerations, there has always been an undertone of thought that better mixing through increased recirculation meant better plant performance. It was thought that higher mixing rates equated to lower concentration gradients and a lower rate of formation of new nuclei. The desired result is usually a larger crystal to filtration.

This thinking culminated in U.S. Patent 3,416,889 ⁵, granted in 1968 for an early high recirculation single tank vacuum reactor. Harold B. Caldwell, assignor to the Whiting Corporation, put it this way:

"Localized differentials in temperature and concentration are thereby effectively minimized to provide a substantially uniform level of calcium sulfate supersaturation throughout the mass of reaction slurry which reduces the number of nuclei formed."

A draft tube pump, single tank reactor also eliminates the significant problem of bypassing or short circuiting. It does this at the expense of sacrificing individual reaction zones that can be optimized or designed for the particular unit operation happening therein.

Let's expand on this. Although the model for our recirculation discussion is the multi-tank reactor, it is not necessarily the best reactor design. Quite a number of people here today operate single tank reactors or the Iso-Thermal high recirculation design. Some of the single tanks are in reality multiple compartments cunningly nested within a single overall tank. The Iso-thermal is as far away from a multi-zone reactor as it is possible to get. The Caldwell design emphasized this factor.

In the case of the Iso-Thermal the high recirculation rate means that localized high supersaturations are reduced, but also that the rock dissolves in effectively the same liquor the crystals are growing from. It is not possible to reduce the recirculation rate sufficiently to cause a deficiency of sulfate during rock dissolution. There is less ability to compensate for lowered rock reactivity.

Some iso-thermal plants had a rock pre-wetting tank for mixing rock and return acid. However, it is not easy for this design to take advantage of that feature. Pre-wetting of wet or dry rock with return acid has a lot of potential but can cause more problems than it solves if not carried out correctly. Among other problems is foaming from rock carbonates.

To summarize the case against isothermal reactors of most sorts, the inherent design limits the ability to set reaction conditions separately in rock dissolving and crystal growth sections. In it's defense, the uniformity of mixing does reduce some problems of the multi-tank reactor such as rock solubility/operator over-reaction harmonic sulfate swings.

Oddly enough, a compromise can be found in the most unusual place: The hemihydrate dual draft tube reactors of the Fernando Ore designs at White Springs. That system has provisions for optimizing the sulfate in the rock dissolving area while at the same time running a somewhat isolated sulfuric balance in the nucleation and crystal growth areas of the plant. The expense is dual tank operation.

Unfortunately, the mechanism for CS formation in hemihydrate is different from that in dihydrate phospho-gypsum. V. N. Rudin, D. O. Ivanov, P.V. Klassen, and I.V. Melikov of NIUF-NTI⁶ in Russia have recently claimed an "Increase of Efficiency and Phosphorus Yield in the Existing Processes of Phosphoric Acid Production in the Presence of the Seeding Crystals." I don't have the date reference for this paper but the paper is on file at F.I.P.R. in Bartow.

Rudin et al claim that a significant reduction can be made in co-crystallized P_2O_5 by the addition of proper seed crystals. They claim that hemihydrate crystals are made up of agglomerates of a large number of tiny hexagonal crystals. This is not the case for di-hydrate gypsums I am familiar with. A medium number of relatively large crystals perhaps....

Major changes for the iso-thermal reactor are on the horizon that will allow this design to reach it's true potential and reduce the internal compromises. I think it possible that at sometime in the future a modified iso-thermal will be the most popular style of wet process phosphoric acid reactor. But the same tricks might work for single tank designs also. The next 15 years should see more changes in our field than the last 45!

Appendix I: Effect of Sulfate Levels on CS (Citrate Soluble) P₂O₅ Losses

After many years and innumerable attempts to find a gypsum CS loss/reactor Sulfuric acid relationship, the solution is at hand. Unfortunately, it's proprietary. But don't despair--I can tell you what was wrong with the Fröchen-Becker analysis⁴ that led us to keep attack sulfates high for decades.

And in actual fact, high sulfates in crystallization set up a condition of artificially reduced rock reactivity that eliminate one of the causes of high CS losses with highly reactive rock. So it's been there all along and we just haven't seen it.

The paper "Crystallization and Co-crystallization In The Manufacture of Wet-Process Phosphoric Acid" given by J. Fröchen and P. Becker at the ISMA technical meeting in Stockholm in 1959 is a must-read for all Phos Acid process engineers. However, if you look closely, you will see the root of the Sulfate level-CS level controversy. In the section "1) Influence of sulfuric acid excess." the text begins:

"1) Influence of sulfuric acid excess.

This factor was mentioned by Waggamann (see Appdx I.) He stated that the sulfuric acid concentration affects the P₂O₅ content in the gypsum."

Fröchen and Becker go on to explain a series of tests in which they add rock to varying levels of sulfuric in phosphoric acid. Into four litres of pure phosphoric acid seeded with 0.5 g/litre of crystals, they add 50 grams of rock at a rate of 10 grams per minute. Four trials represent 0, 10, 20 and 30 grams per litre sulfuric acid. Since the phos acid was about 34 % P₂O₅, this represents a little less than 1, 2, and 3% total sulfate before rock addition is started.

Incidentally, I am taking license with their text by equating "10 grs/min." and "10 gr/lit." (op.cit) as grams, not grains, and "340 grs/l Phos. Acid conc." as 340 grams per liter P₂O₅. but it makes sense that way..

What also makes sense is that at these levels of sulfate, the rock solubility would be much lower for the 30 G/L case than for the lower sulfate levels. This variation in rate of solubilization might just, by itself, account for a differing degree of co-crystallization of HPO₄⁻ in the product gypsum.

I mention this not so much to poke holes in a very important work in the history of our industry as to point out the need for an open mind and on-going research.

Appendix II: Effect of Recirculation Rate on Sulfuric Acid Reactions

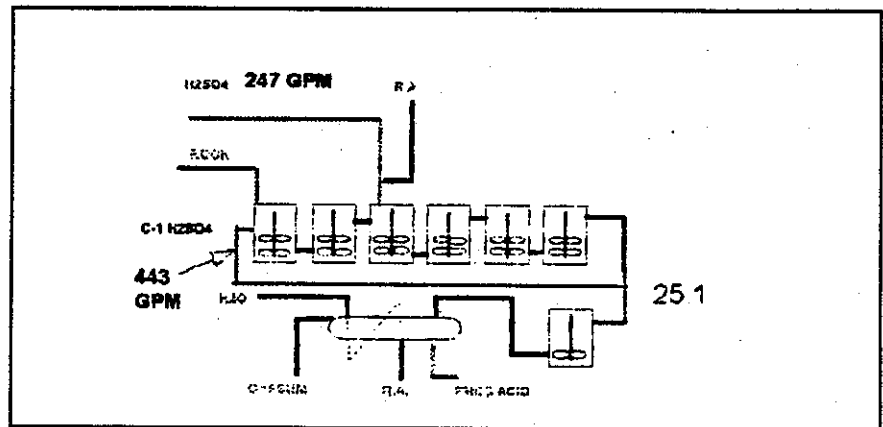
We normally tell people that our industry reacts sulfuric acid with phosphate rock to make phosphoric acid. This is shown in Figure II-1, with the width of the streams proportional to their mass flow.

In reality, we add the rock to a much larger flow of phosphoric acid and gypsum, and shortly thereafter add sulfuric acid to precipitate the new gypsum. The rock would be only sparingly soluble in sulfuric acid, a lot of fluorine would be driven off, and an attrition scrubber would be required to obtain any sort of efficiency if we added the rock to anything like a sulfuric acid stream.

This recirculating system is shown in Figure II-2. Note the raw material streams are quite small compared to even a 15:1 recirculation.

Figure II-3 is a typical multi-compartment reactor with inputs as shown. Note that there is a certain amount of residence volume between rock addition and sulfuric acid addition. With this physical relationship, let's consider the relative amount of dissolved sulfate (total H_2SO_4) entering the first rock dissolving compartment, Compartment 1 (C-1 for short).

At 1000 TPD product and a recirculation of 25:1, 2.5% total H_2SO_4 , with a sulfuric acid consumption of 2.6 T/T P_2O_5 , the sulfuric acid in the slurry H_2SO_4 in Compartment 6 entering C-1 is approximately 443 gallons per minute. Under the same conditions the sulfuric acid flow to C-3 is 247 gallons per minute.

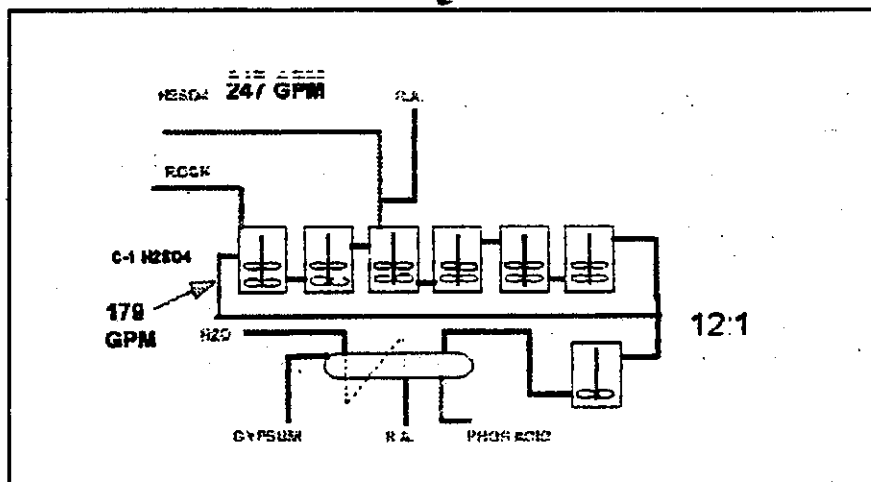
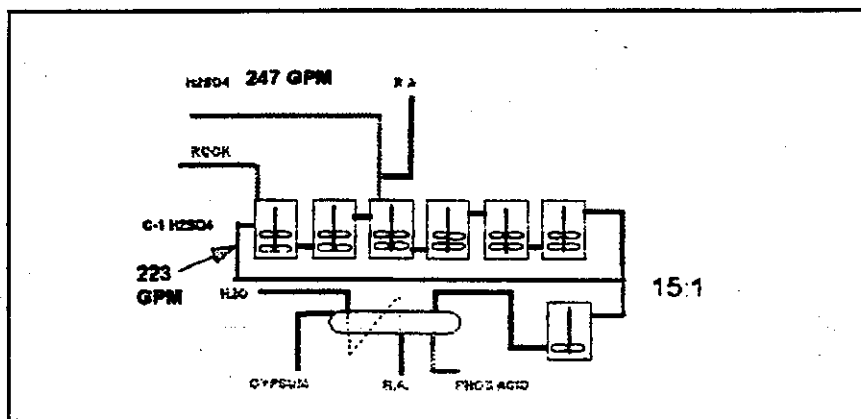


Compare this with the same plant but with a C-6 sulfate of 2.1% and a recirculation ratio of 15:1. The relative GPM of sulfuric are now 223 GPM to C-1 and 247 GPM to C-3.

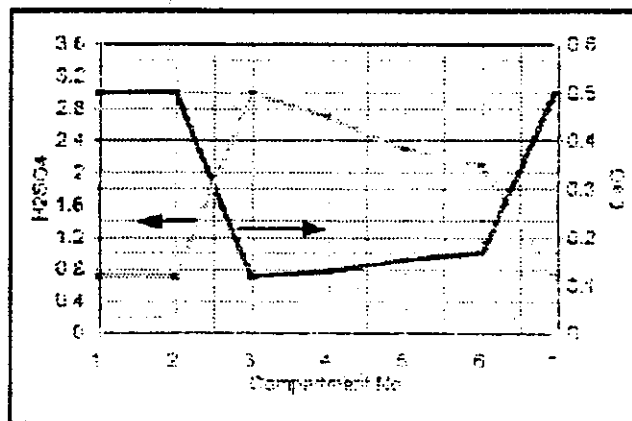
A reduction of recirculation to 12:1 at 2.1 % C-6 H_2SO_4 gives us a ratio of C-1 sulfuric input to C-3 sulfuric input of 0.7:1 (179 GPM to C-1, in C-6 recycle, 247 GPM. Of course these numbers vary with recovery, rock CaO/P_2O_5 ratio, and several other assumptions, but you should get the general idea. Running an attack with more sulfuric going to C-1 than to C-3 is not the way to handle South County rock.

At some point it is useful to measure the actual calcium and sulfate levels at various points around the attack circuit. We can use it to define a kind of solubility product to allow us to estimate the true (chemical) free acids from only the more common sulfate value.

It is impossible to calculate these ahead of time for a number of reasons. The most significant is that we are really measuring supersaturations, and these are not clear-cut functions of rate or volume. The solubility products vary with crystal habit, agitation, rock analysis, and, of course, the normal variables of rate, temperature and phosphoric acid concentration. I have seen numerous anomalies wherein plants with excellent filtration and large crystals were operating at solubility products in the 0.4 range, whereas plants suffering with excess nucleation and tiny crystals were operating at 0.14 $CaO \times H_2SO_4$. The implication is that the normal concept of supersaturation does not apply to WPPA plants. Perhaps the problem relates to the nucleation mechanism, in our case contact versus homogeneous.



While developing this interesting, if not immediately useful data, a graph like Figure II-4 can be drawn. Here we see the meat of the sulfuric interactions. Note that the sulfuric analysis entering rock dissolution plummets while the CaO level jumps upwards. Then, with the addition of more sulfuric acid in C-3, this calcium disappears and the sulfate reaches a peak. This peak slowly drops off to the sulfate value in C-6.



There is not sufficient time in this paper to discuss the reason I have shown the calcium values remaining somewhat constant while sulfate drops in C-4 through C-6. Suffice it to say that this happens during high production rates growing cluster crystals and has something to do with nuclei redissolution.

Where is all this leading us? Well, if the sulfate in the recirculation into C-1 largely disappears, where does it go? If the calcium from fresh rock addition plummets after the mixing tee, where does it go? The answer is obvious, "Into crystallization."

Whoa! Does this mean that the great majority of the crystal growth occurs in two compartments of a six compartment attack? This would mean that the crystal growth rate is enormous compared to our normal thinking. Without thinking at all, we might say that it takes three to four hours to grow a normal crystal to filterable size, say 70 microns across. If we could keep the crystals growing at top rate, all the time, the same attack volume might grow crystals greater than 200 microns across!

Our level of technology is not quite there yet, but it will happen. It will take a major deviation from current phosphoric acid technology and a fair amount of investigation. Unfortunately, our industry has reached the nadir of its R&D efforts just when raw materials and plant capacity cost the most. What a quandary!

Following up on the ratio of sulfuric entering C-1 from C-6 versus the base sulfuric feed rate, this is a good variable to track while considering crystal habit changes, CI (citrate insoluble P₂O₅) losses, and CS losses. At any given recirculation it has a rough relationship to free acid in C-1 and C-2 but brings in the quantity of sulfuric available to precipitate calcium in C-1. It is also the most important variable to consider when making recirculation rate changes.

REFERENCES and NOTES

1. Hebbard, George M., AIChE Central Florida February, 1994 Meeting, **Habits of Gypsum Crystal Growth**
2. This recommendation is only valid if the operators are skilled, they DO drop rates, and the residence time between mill and attack is less than an hour. Obviously reducing recirculation has a major effect on sulfate control, but the trade off in feed forward control is always concern with overreacting. Before the rock arrives at the attack, the attack sulfate will, in this scenario, start to drop, then rise with the lower reactivity.
3. Richard L. Gilbert and Edgard C. Moreno, **Dissolution of Phosphate Rock By Mixtures of Sulfuric and Phosphoric Acids**, page 368, I&EC Process Design and Development, Vol 4 No. 4, October, 1965 (FIPR has the original, thanks to IMCC.)
4. J. Fröchen and P. Becker, **Crystallization and Co-crystallization In The Manufacture of Wet-Process Phosphoric Acid**, J. Fröchen and P. Becker, International Superphosphate Manufactures' Association, Stockholm, 1959.
5. Harold B. Caldwell, **Process and Apparatus for Manufacturing Phosphoric Acid**, U.S. Patent 3,416,889, December 17, 1968. Assigned to Whiting Corporation.
6. V. N. Rudin, D. O. Ivanov, P.V. Klassen, and I.V. Melikov , **Increase of Efficiency and Phosphorus Yield in the Existing Processes of Phosphoric Acid Production in the Presence of the Seeding Crystals**, NIUF-NTI, Russia (FIPR File copy)

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