

Monocal Chemistry and Phosphogypsum Radioactivity©

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Summary

In any instance of the monocal process for wet process phosphoric acid production some soluble sulfate will be present throughout the circuit. This is true of recycled weak filter acids or recycled slurries, even with supplemental phosphate rock added for desulfonation.

This small amount of sulfate will be ample to insure that most of the radium is present as insoluble radium sulfate or other solid forms such as radium fluoride. Because of the extremely low solubilities this material is sub-micron or colloidal in size.

Any process that attempts to partition radium radioactively in phosphogypsum must therefore approach the problem from a mechanical as well as a chemical standpoint.

Introduction

The variants of the wet process for phosphoric acid production termed “monocal” have been the subject of much research over this century. This paper does not try to be a reference for that interest. Instead it focuses primarily on the rather narrow subject of radiation partitioning and only discusses features of monocal processes that affect that area.

Most readers will have a vague and personal concept of what the monocal process is. Some will have first hand experience with an actual attempt to commercialize one flowsheet or another in that area. As the authors researched this technology we were astounded how many different variations existed, both for phosphoric acid production, and for DiCal production.

We hope someday, before the tribal memory fades, a kind soul will record our many and varied experiences. Texas City, IMC-Bonny, Stauffer's, U.S. Gypsum, Pennzoil. The names bring back memories of the early days...just a few short years ago.

For our purposes we will define the monocal process as the dissolution of phosphate rock in a solution of mono-calcium phosphate with soluble calcium as CaO in the 1.0 to 3.5% range, followed by appropriate steps to yield an improved phosphoric acid product.

Several researchers report trying to filter the digest prior to adding sulfuric acid in order to remove undesirable I&A and possible silica prior to further sulfuric addition. This is a classic monocal process goal. It's a shame no one has ever be able to make it work efficiently.

And no one has successfully added the next step: we take our filtered monocal solution and add only a small amount of sulfuric acid. We hope that the very insoluble radium sulfate is the first material to come down. We filter the slightly turbid solution to reduce radioactivity in our final gypsum.

This doesn't work either. The radium is already *down*.

Why Partition?

In 1995 the Florida Institute of Phosphate Research (FIPR) put out a RFP (request for proposal) to partition radioactivity. From their Web-site:

“64. FL Institute of Phosphate Research - RFP

The Florida Institute of Phosphate Research (FIPR) would [like] to receive proposals to carry out a two-part study of a monocalcium phosphate process to produce two different kinds of phosphogypsum by-products: a relatively pure gypsum exhibiting less than 10 pCi/gm of radium which can be used in agriculture and an impure, radium-enriched gypsum which would remain in the stack.

The first part of the study would consist of bench-scale tests to develop crude process parameters (temperatures, impurity levels, reactant ratios, etc.); the second part would be an approximation of process investments/costs (plus or minus 25%). Monocalcium phosphate technology has been extensively researched and is the subject of numerous literature and patent citations. As a slightly different wrinkle on this well-defined technology, FIPR would like to see de-slimed matrix used as the feedstock.

Researchers should submit proposals before JANUARY 1, 1996. “

There were takers. As far as we can tell, they assumed that our ideal process in the Introduction would work just fine. They drew a blank.

Most of the work in this area is proprietary. No one wants to talk about their failures. And when they are probed, one gets the opinion that they hope their special process can yet be made commercial.

To avoid claims of violation of confidentiality, we will confine our discussion to work completed this Spring in the Alan Cole Metallurgical Laboratory at FIPR and to a specific series of patents.

The participants in the study at FIPR were Arthur N. Baumann, retired IMC-New Wales Development Manager, who did all the work, and George (Jim) Hebbard, who wrote this paper.

Research First, Literature Survey Later

We first began work based on some comments from the distant past. As early as the '60's some researchers had noticed that some of the radiation in PhosAcid could be filtered out, albeit with difficulty.

We had in the back of our minds the hope that a hot 30% P_2O_5 slurry with 2% free CaO would have some dissolved radium present. First we filter out the recycled gypsum and gangue. Then, in line with our ideal process, we would add a small increment of sulfuric acid. A solid phase would form which would be newly formed gypsum and radioactive particles. This in turn would be filtered out and the balance of the monocal solution would be used to form almost pure gypsum.

To obtain our monocal solution we first filtered the recycle gypsum from a rock dissolving compartment operating at about 2.5% CaO. This is a very negative free acid condition with less than 0.1% dissolved sulfate. We filtered 25 milliliters of raw slurry through a cellulose medium with a 4 micron retention rating.

Art Baumann had set up the FIPR Ludlum 2200 Scalar Ratemeter gamma counter in the shielded lab at the back of the Alan Cole Metallurgical Lab. This involved running numerous background counts to develop averages for correction. Even 'hot' gypsum usually has a lower radiation count than the background. One takes a sample reading, a background reading, a second sample reading, and checks to see if the background has shifted. It usually has.

If the background shifts are a significant portion of the total sample count, estimating the means of two sets of similar samples becomes problematic. We discovered various samples of radioactive material in drawers below or near the radioactivity test bench. Phosphate rock was stored nearby. The daily cycle of the air conditioning load had a bearing. We removed as much of this abnormal background material as we could.

Let's cut to the chase. Art's work is discussed below. He discovered that the original gypsum from the rock dissolving compartment had a relatively high sample count when filtered on the 4 micron paper. Since the slurry solids percent was normal for a recirculated plant, most of this gypsum was simply residence time product.

Art then filtered the filtrate on 2.7 micron media, and that filtrate on 0.7 micron. Some of the later final filtrates were evaporated to dryness and measured. The radioactivity per gram increased as the size decreased. The weights of the evaporated solids were too small to be measured, but that small mass contained 16 to 20 % of the total radioactivity.

In the first sample (Set 4) 86.3% of the total counts (corrected for background) came from the +4 micron portion, 11.9% from -4/+2.7 micron, and 1.8% from the minus 0.7 micron fraction. This set of samples measured 25.2 counts/gram/minute (C/g/min) for the +4 micron cake, 2176 C/g/min for the 240 milligrams -4/+2.7, and only 920 C/g/min for the -2.7/+0.7 fraction. (The -0.7 was not measured.)

In this case most of the radioactivity stayed with the bulk cake. The particles that passed through were much "hotter." In an actual operating plant with much coarser filtration these filtrate solids would be recirculated backwards over and over again until they finally leave in the product acid or the gypsum filter cake.

Conclusion

By now the astute reader has probably noticed that we have not talked much about the monocal process. The same measurements obtained from a monocal filter feed might well be obtained in similar samples from a normally operating Prayon plant. And that is exactly the point of this paper. Because of the low solubility of the radium compounds, we see no reason why any variant of the wet process for phosphoric acid production should be able, under normal circumstances, to predictably partition radium between two cuts of phosphogypsum. Rather, in nearly all cases, some form of mechanical separation is needed (e.g. Larson, US Patent 4,328,193, 1980).

Please note also that these tests were not exhaustive. We could have added additional sulfuric acid to any filtration. Then, after evaporating the final minus 0.7 micron filtrate to dryness, perhaps some of the radiation would be found to have moved to a coarser size.

We will leave this, and other tests to later researchers with finer tools.

Research Work - Tests Completed

As mentioned above, background counts were obtained with a Ludlum 2200 Scalar Ratemeter used for the radiation readings. This is a very unsophisticated method of estimating sample radium content. In fact, the gamma radioactivity capable of producing a "count" can come from any part of the ^{238}U decay chain, i.e. ^{226}Ra , ^{210}Pb and ^{210}Po . Only the fact that these elements are present in a relative equilibrium makes the results useful at all. Radon was not measured either because alpha radiation cannot penetrate into the gamma probe.

The rock that was the basis of this work was a 50:50 blend of Kingsford concentrate and pebble ground dry. It analyzed as follows:

P_2O_5	CaO	Fe_2O_3	AL ₂ O ₃	MgO	F	C/g/min*
31.35	45.08	1.14	1.53	0.53	3.05	41

*(Counts are gamma counts per 20 minutes divided by sample weight and 20, or C/g/min)

An initial 25 ml. sample was obtained by syringe from the rock dissolving compartment of a phosphoric acid pilot plant operating in a monocalcium phosphate mode. Since the operation of the pilot plant is the subject of a patent development, very little information can be shared about its operation. The operating targets during all sampling were 30% P_2O_5 acid, 38% suspended solids, 2.5 % dissolved CaO, and 77 - 82°C.

The sample was vacuum filtered through paper rated at 4 micron retention. The first cake was dried under a heat lamp until the weight loss ceased. It was weighed and its radiation measured. It is likely that a small portion of the first cake weight is residual moisture in the cake and also in the filter paper.

The following tables contain columns for ID, Sample (description), Weight (grams total dried

paper and cake less original filter media), Background (time proximal measured background counts), C/g (counts per gram background corrected), and C/g/min (counts per gram per minute). In most cases the counting time was 20 minutes.

First Sample

-----20 minutes-----						
ID	Sample Weight	Counts	Background	C/g	C/g/min	
4-A	+4 μ	12.2569	933 ^a	624	309	15
4-B	4 μ /2.7 μ	0.2403	1147	624	2179	109
4-C	2.7 μ /0.7 μ	0.0859	703	624	920	46
	used F. paper	0.0535	681	624	310	15.5

(a. Note that counts for cakes weighing over 1 gram are for a 1 gram portion).

After this first series the background was checked the next morning 12 times. The average count was 616 with a standard deviation of 21.8 counts. The sample differences can be seen to be significant, but the variation is discomfoting. The rock radiation, for example, measured 41 C/g/min at first and then 46 C/g/min after the background was reduced.

The +4 μ cake from above was repulped in acetone and re-filtered on 4 μ paper. One gram of the resultant cake and the filter media after cake removal measured as follows:

ID	Sample Weight	Counts	Background	C/g	C/g/min	
4-A.rp	re pulp	1.0000	922	624	310	15.5
	media	0.0331	685	624	1843	61

The smaller amount of material lodged in the repulp cake filter media was also much hotter than the material lodged in the original filtration media.

It was after this set of runs that the radiation laboratory housekeeping was improved.

No attempt was made to monitor the radiation in the -0.7 μ filtrate for the first few sets of samples. When the radiation balance was calculated for the above repulp operation, it was found that only 86.4% of the radiation in the repulped cake was accounted for in the cake and filter media. This lends credence to the difficulty of mechanically removing the radiation from the bulk gypsum by repulp or washing)..

Looking at the above samples 4-A, 4-B, and 4-C again, but still noting the absence of final filtrate radiation, we can see that 14% of the radiation was found in the 4 μ /0.7 μ cut which was only 2.6% of the mass:

ID	Sample Weight	% of Weight	C/g/min	Total Counts/min	
4-A	+4 μ	12.2569	97.4	15.0	183.9
4-B	4 μ /2.7 μ	0.2403	1.9	109	26.0
4-C	2.7 μ /0.7 μ ID	0.0859	.07	46.0	4.0
Totals		12.5829			214

These initial tests give clear evidence that some of the radiation present can both be moved mechanically and is likely a particulate. The 2.7 micron and 0.7 micron filter media were 47mm membranes held in a Millipore magnetic filter housing. Membrane filters provide little opportunity for adsorption and are often used for estimating particle sizes of dilute slurries.

Sample 4-B was digested with 50 ml of hot tap water for 5 minutes, gravity filtered and washed with 40 ml cold tap water. The washed 4-B residue was dried and counted as was the material retained on 0.7µ media. The resulting radiation (total counts) was 86.4% of the background-corrected counts for 4-B, above:

Filter Residue	Counts	Background	Total Sample Count
4-B	955	639	316
0.7µ Residue	775	639	136
Total 20 minute count			452

The original total count for 4-B was, from above, 1147 - 624 or 523. $452/523 = 86.4\%$. Even though we are looking at small differences between large numbers, this check indicates that the particulate material is relatively insoluble in water. The test also shows that repulping the cake found on a membrane filter does not destroy the size assumption hypothesis.

The first sample was repeated after certain changes to the phosphoric acid reactor conditions and housekeeping was improved in the radiation lab. The results are similar to the first set:

ID	Sample Weight	Counts	Background	C/g	C/g/min
8-A	+4µ	14.1872	977	639	338
8_B	4µ/2.7µ	0.0864	768	639	1493
8-C	2.7µ/0.7	0.0749	795	939	2083

Recall that the 14.1872 gram of sample 8-A was reduced to 1.000 grams for counting. Therefore the actual counts for the total radiation in the three cuts is more clearly represented as:

ID	Sample Weight	-----20 minute-----			Total	
		Counts	Background	Counts	% of Total	
8-A	+4µ	14.1872	977	639	4,795.3	94.4
8_B	4µ/2.7µ	0.0864	768	639	129	2.5
8-C	2.7µ/0.7	0.0749	795	639	156	3.1
Total					5,080.3	

There is an interesting consideration hereabouts. The radiation appears to have shifted to finer sizes in this sample set. The reactor changes among other things caused less precipitation of calcium sulfate during rock dissolution. In other words there was a net reduction in the amount of sulfuric acid entering the rock dissolving compartment. Since we did not evaporate the final filtrate to dryness we cannot estimate whether the total radiation shifted or the fine percentage increased. We also have no information on whether the change was related to less co-precipitation of gypsum and radium compounds or to less sulfate available to precipitate radium compounds.

Before discussing the sample set where we measured the -0.7μ radiation, we should note that measurements made on slurry from the filter feed compartment were easily distinguishable from the rock dissolution samples. There was a reduction in radiation in the finer fraction in the filter feed. Even with shifts in the background radiation, this difference may be considered significant.

ID	Sample	Weight	Counts	Background	C/g	C/g/min	
RD	+4 μ	13.7391	940	657	283	14.0	
RD	4 μ /0.7 μ	00.0276	1421	634	28,514	1425.7	
FF	+4 μ	13.5000	946	657	289	14.5	
FF	4 μ /0.7 μ	00.0583	1411	634	13,327	666.38	

For these sample sets the fines have become a great deal hotter. Recall, though, that the thirteen grams of main cake weigh some 325 times more than the hotter fines. Most of the radiation was still in the bulk cake. For the RD (rock dissolution) set, 83.2 % of the counts occurred in the 13,7391 grams of +4 μ cake.

For the last test, two samples were run from the rock dissolution compartment with the final filtrates evaporated to dryness. Only the first is reported here:

ID	Sample	Weight	Counts	Background	C/g	C/g/min	
12-A	+4 μ	16.7476	978	655	323	16.1	
12-1A	4 μ /0.7 μ	00.0434	709	639	1613	1425.7	
12-2A	Wash	not mea.	1683	614	-----	-----	

We ignored the calculations for counts/weight for the wash as various hydrated states were assumed to exist and the weight was very small. The radiation balance is as follows:

ID	Sample	Weight	Counts	Background	Total Counts	% of Total	
12-A	+4 μ	16.7476	978	655	5409.5	66.9	
12-1A	4 μ /0.7 μ	00.0434	709	639	1613	19.9	
12-2A	Wash	not mea.	1683	614	1069	13.2	
					Total	8091.5	100

Now that we include the radiation in the minus 0.7 μ fraction, we note that only two thirds of the radiation remains in the coarse cake.

We've presented the data in this order not to confuse our readers, but so they can experience more clearly the difficulties of trying to partition radiation. We know very little about the nature of the radiation in the final cut, only that it contains just over 13% of the total radioactivity. An XRD (X-Ray Diffraction scan of one of the -4 μ /+2.7 μ did show traces of RaF_3 .

The last two sets of data shown above may also tell us that the reactor conditions can be modified to change the radiation balance. If this is so, then it may be worth while experimenting with various reactor configurations and calcium-quench rates and modes to send the distribution in a favorable direction. This can be done while operating as a monocal process or as a conventional Prayon-style plant.

Literature Search Later

After the above work was begun, a short review of available literature was begun. Several references soon turned up describing the radioactivity as particulate. One patent (cited above, Larson, 4,328,193, 1982) specifically teaches centrifuging radium sulfate from a filtered monocal solution.

Dr. William Burnett, et al, Florida State University, completed a major study of radiation in phosphogypsum in 1995 (FIPR 05-035-115). He concluded that much of the radioactive material was present as fine particulates.

Yet recently I have spoken with several researchers who approach the question of partitioning as if it has a simple phase change solution. Perhaps if it is a simple radio-colloid, as suggested by Larson, referring to Kirk & Othmer, Encyclopedia of Chemical Technology, Ed. 1, Vol.11, page 469, a further precipitation can somehow be induced. No one, to our knowledge, has been successful yet.

If the radiation is primarily a separate particle, some form of hydraulic scrubbing and sizing should be capable of some separation. However, there is bound to be some co-crystallized radium in the bulk gypsum. Some of the rock radium dissolves in close proximity to the gypsum growth that occurs when newly dissolving rock quenches the sulfate in recycle streams. If so, monocal rock dissolving would seem to favor low co-crystallized radium. (The lower volume of recycled fluids carry less sulfate, and therefore cause less co-crystallization during rock dissolution *and* produce less gypsum volume with the gangue.) There is probably a ultimate lower limit for the wet process as we know it. The data is too varied to prove one way or another, but I'm sure it would be below 10 pCi/G.

The Larson patent is interesting in this regard. Obviously, if the gangue from rock dissolution and any gypsum recycled or formed from recycled liquors is filtered efficiently enough to produce a very pure monocalcium phosphate, a very pure gypsum can be produced. It's purity might even approach that of the billions of tons of gypsum laying around on the ground in the Western U.S. It's cost might be relatively low, but the filtration cost, phosphate losses and gangue disposal problems of the first cut might outweigh the savings from being able to sell the cleaner fraction into the Southeastern gypsum market.

At the moment the most efficient use of phosphogypsum averaging 26 pCi/gm is probably as an agricultural supplement and for roadbed material. The later use is the subject of an exemption request filed with EPA in 1997. Phosphogypsum, being porous—after all, “good” PG in our industry is by definition a good filtercake—makes an excellent construction material. It is not sticky like clay, dewateres rapidly after rains, and the irregular crystals our plants favor lock together eliminating the plastic flow expected of such small grains.

Recent risk modeling has looked at the lifetime risk of cancer from living near or traveling on a road built with phosphogypsum (PG) or living for a whole lifetime in a home built on PG-treated agricultural soil. At a recent FIPR Board meeting, it was noted that one of the attendees probably

contacted more additional radiation exposure flying in from Denver than if he had driven the whole distance on a road built of phosphogypsum. Even if one adds up the exposure of persons along the road, the added risk is still many times less than the risk from the normal radiation background. More tissue damage would probably occur from maintenance of Larson's centrifuges than from living near a gypsum road using an equivalent volume of PG. So why partition PG radioactivity at all?

Monocalcium Phosphate Routes to Valuable Products

There turned out to be quite a body of material published on mono-cal chemistry applied to wet process phosphoric acid. One patent (cited above, Larson, 4,328,193, 1982) even shows how radiation can be removed from PG by centrifugation.

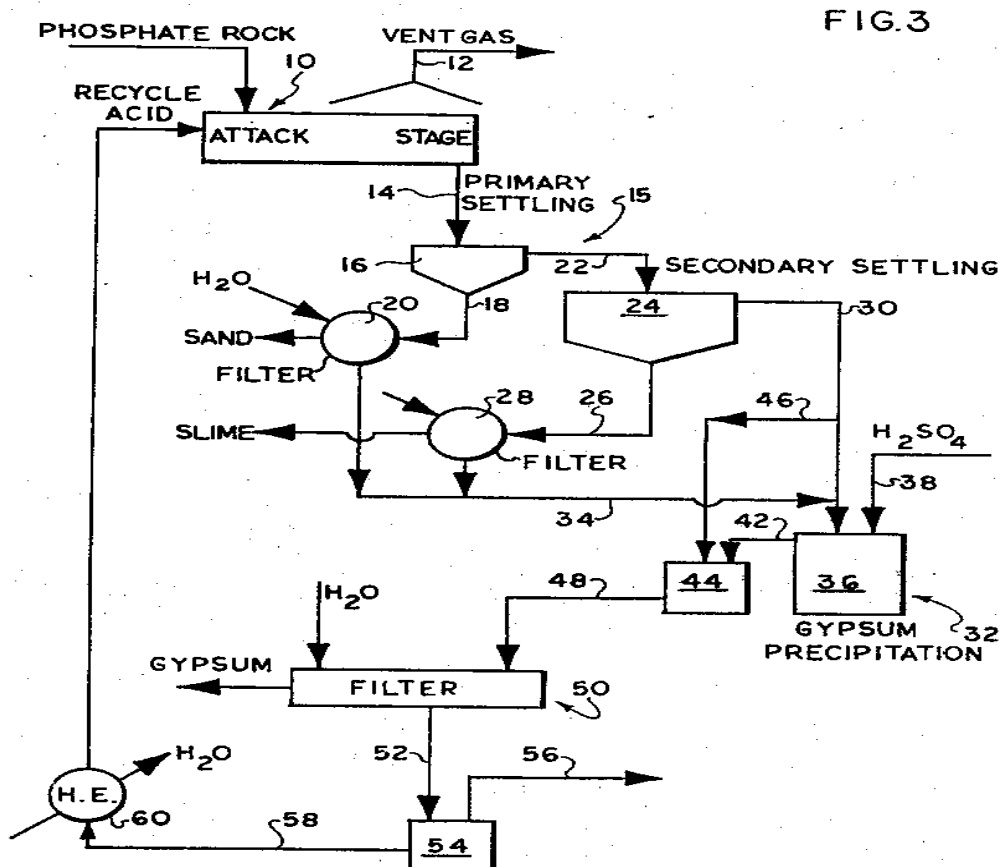
The rock dissolution conditions in a mono-calcium phosphate solution are extremely mild. It has even been proposed (Hauge, Case, Dreschel, et al) that some of the impurities in the rock might even remain as solids or, in the case of fluorine, re-precipitate as calcium fluoride.

Everett Case, in a patent filed in 1968, discusses means of producing monocalcium phosphate solutions in a phosphoric acid plant (PAP). He is particularly concerned with the recycle of a low-solids acid to rock dissolution to keep the original gangue filter volume down. Derald, et al describe in U.S. 4,828,811 a monocal process that accepts unbeneficiated ore as a feedstock.

Much of the early work with monocal chemistry involved the production of dicalcium phosphate. Hauge (U.S. Patent 4,088,738) 1978, added milk of lime to filtered monocal solutions to produce feed-grade Dical. Bridger (U.S. Patent 4,141,958) 1979, started with a monocalcium phosphate solution and used solvent extraction to produce phosphoric acid and fertilizer grade Dical. Olin at Texas City, Texas and IMC at the Bonny Plant extracted monocal solutions from green superphosphate. Why have all these processes been abandoned or died stillborn?

There are a lot of explanations. The most common is that the cheapest way to make DiCal is to add ground limestone to defluorinated acid. Phosphoric acid can easily be defluorinated by steam or air stripping a solution to which some form of soluble silica has been added. The vapour pressure of SiF_4 is reasonably high, and as long as one adds available silica and waits for the highly stable aluminum fluoride ligand to decompose, 100 P/F is easily reached.

On the next page is a image of the Case Patent, which is typical of some of the thinking about application of monocal chemistry to gypsum and acid improvement. This patent and many others is on file in the FIPR library for your later reference.



The Case patent is typical of some of the schemes for taking advantage of monocal chemistry. I have noted in experiments, however, that it is difficult to judge the amount of co-crystallized P_2O_5 that will form. Of course, depending on sulfur cost, the sulfur savings may outweigh the lower recover due to C.S P_2O_5 losses. The drawing above gives one a good taste of the complexity of most monocal processes. Either multiple filtration, or in this case sedimentation and filtration are required. A simpler process is needed that yields most of the advantages and few of the costs and disadvantages.

A recent process development may provide just that. It is currently subject to secrecy agreements and a patent application is being written. Further testing is expected to show greater than 5% sulfur savings, great overall recoveries, and rejection of some rock gangue. Although in common with most monocal flowsheets, it can run up to over 40% P_2O_5 , reasonable filtration rates are expected at 30% P_2O_5 . And who knows, we may even be able to improve the gyp!

NOTE: After this paper went to press, data errors were found in the radiation levels of the later samples. The conclusions are the same, but the higher radioactivity's of the fines are wrong.

