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Impact of Phosphate Rock Impurities on the Manufacture of Phosacid and Granular Phosphates

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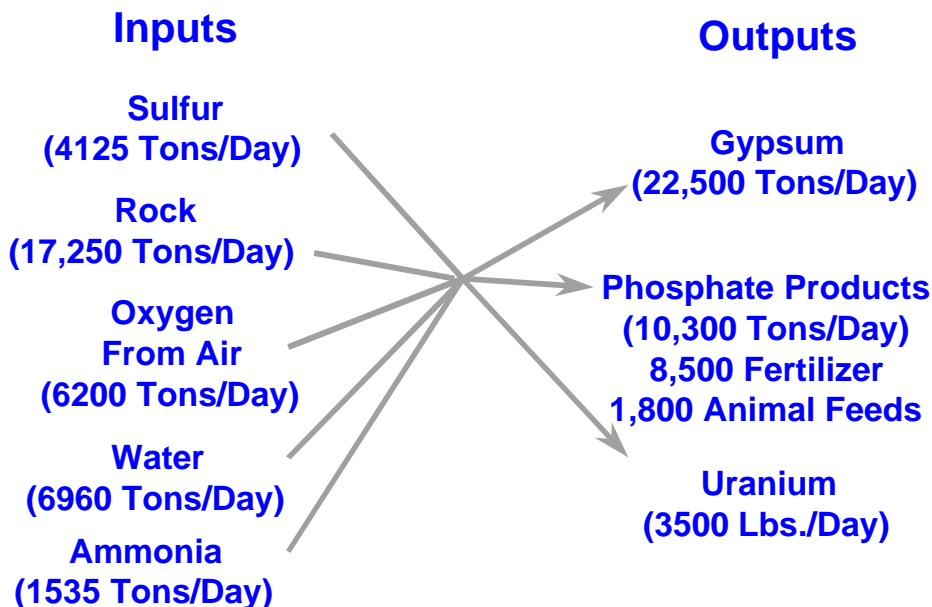
Introduction

In the past, when phosphate rock quality was good, few paid attention to any of the impurities or other qualities associated with phosphate rock. In general, they had little or no effect on the ability to make the phosphate products for the market. However, as phosphate rock quality declined, it was apparent to the rock consumers that the individual impurities had a significant impact on their processes.

FIPR (Florida Institute of Phosphate Research) is presently funding an analysis of operating plant data to determine the range of the effects of rock impurities on production plant performance. The study will not be completed until 2002. IMC has agreed to share some of the Information they had developed in the early 1990's.

All of the relationships that will be described were developed from operating data obtained at the IMC New Wales fertilizer plant. Figure 1 shows the scale of this "Pilot Plant".

Figure 1 NEW WALES FLOW SHEET



Finally the impact of automatic controls on the operation of the plant will be described.

Rock Impurities

The rock impurities (and other qualities) that will be discussed in this paper include, BPL, CaO, MgO, Fe₂O₃, Al₂O₃, Minor Element Ratio (MER), Moisture, Uranium, Cadmium, Insol, Sulfate, Carbonate, variability, and size.

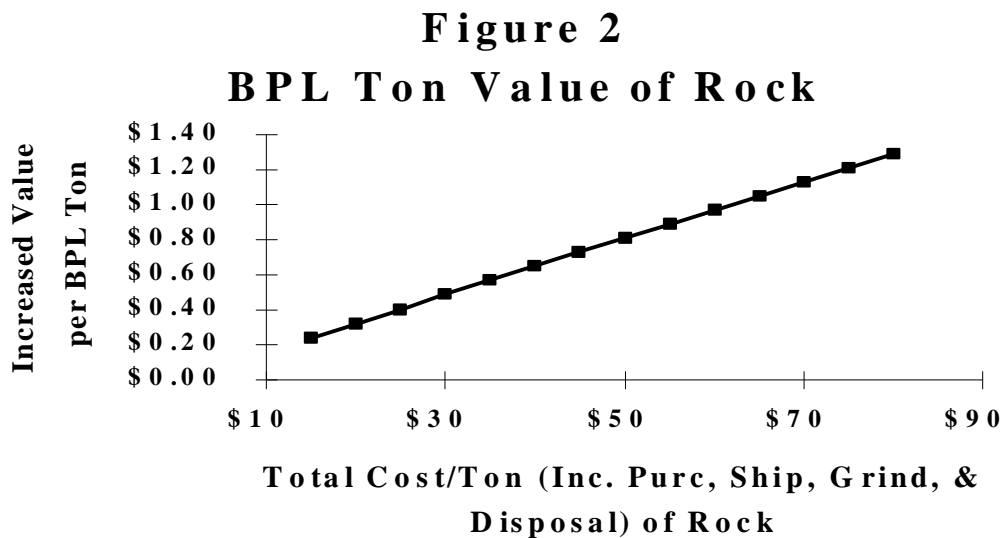
BPL

While strictly speaking, BPL is not an impurity; it certainly affects both the rock quality and does have an impact on the manufacturing process. Since higher BPL means less room for other impurities in the rock, it also means less insoluble material that must be removed in the rock digestion/filtration process. Since there is less filter cake, it means less potential for filter cake P₂O₅ losses. In general an improvement of about 0.2%/BPL improvement in recovery is observed.

In the cases where plant production is limited by rock grinding, rock handling, or filter cake handling, the BPL of the rock can also limit the production rate of the plant.

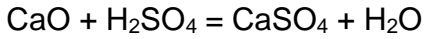
The BPL of the rock certainly affects the tons of rock required to produce a ton of P₂O₅, and therefore the cost of rock, shipping cost, grinding cost and cost of disposal of filter cake.

Figure 2 shows the value of a one BPL increment for rock vs. the total cost of the rock, including shipping, grinding and disposal.



CaO

The main importance of CaO is that it consumes sulfuric acid by the following reaction.



It is best to look at the ratio of $\text{CaO}/\text{P}_2\text{O}_5$ rather than just the CaO content itself when looking at the effect of CaO. For the case of a 1,000,000 ton per year P_2O_5 plant, an increase of 0.01 in the $\text{CaO}/\text{P}_2\text{O}_5$ ratio would mean that an additional 17,500 tons of sulfuric acid would be required each year at a cost of \$440,000 for sulfuric acid at a cost of \$25/ton.

CaO is typically not measured in the rock as it is mined. However, CaO is related to the BPL, Al_2O_3 and MgO of the rock. Figure 3 shows the relationship between the $\text{CaO}/\text{P}_2\text{O}_5$ and the BPL of the rock for over 1000 samples of rock received at New Wales in 1992.

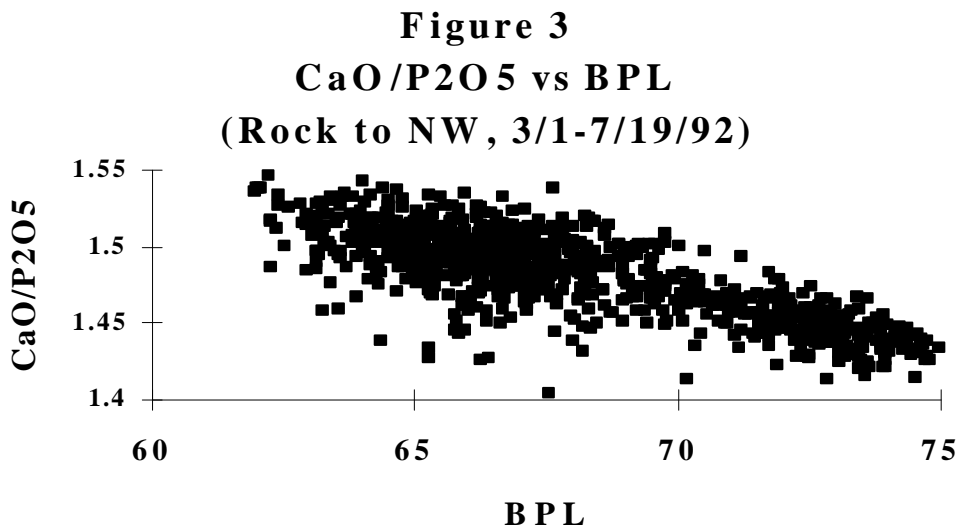
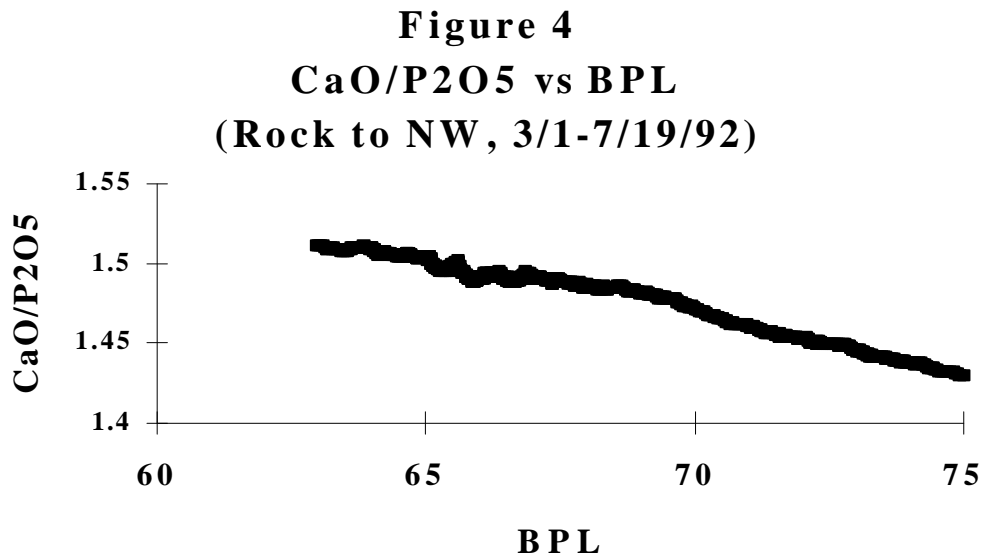


Figure 4 shows the same data with a 100 pt rolling average of the data.



Similar results are shown in Figures 5 and 6 for $\text{CaO}/\text{P}_2\text{O}_5$ and Al_2O_3 .

Figure 5
 $\text{CaO}/\text{P}_2\text{O}_5$ vs Al_2O_3
(Rock to NW, 3/1-7/19/92)

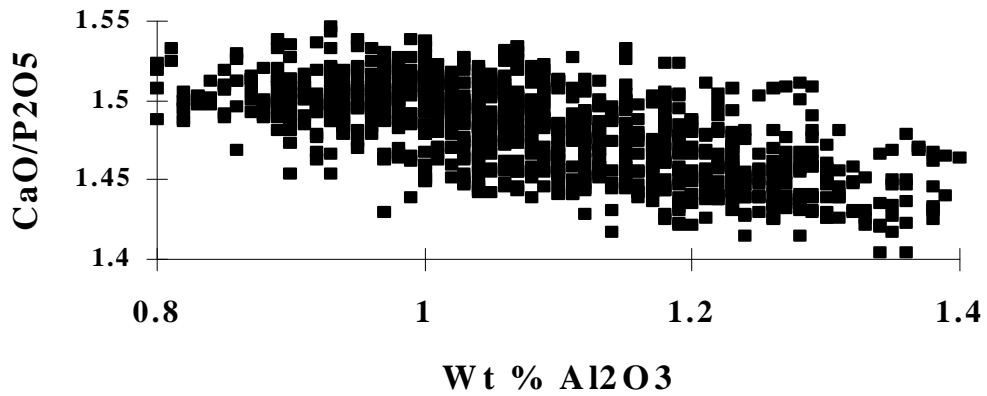
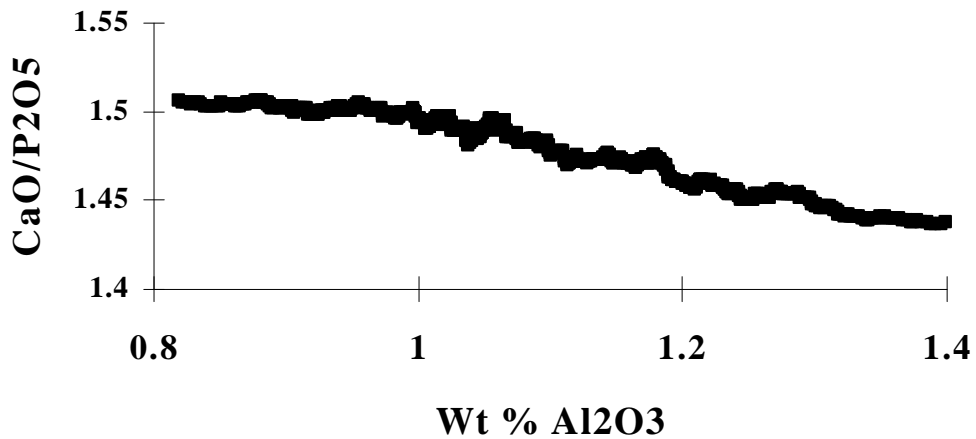


Figure 6
 $\text{CaO}/\text{P}_2\text{O}_5$ vs Al_2O_3
(Rock to NW, 3/1-7/19/92)



Similar results are shown in Figures 7 and 8 for $\text{CaO}/\text{P}_2\text{O}_5$ and MgO .

Figure 7
CaO/P₂O₅ vs MgO
(Rock to NW, 3/1-7/19/92)

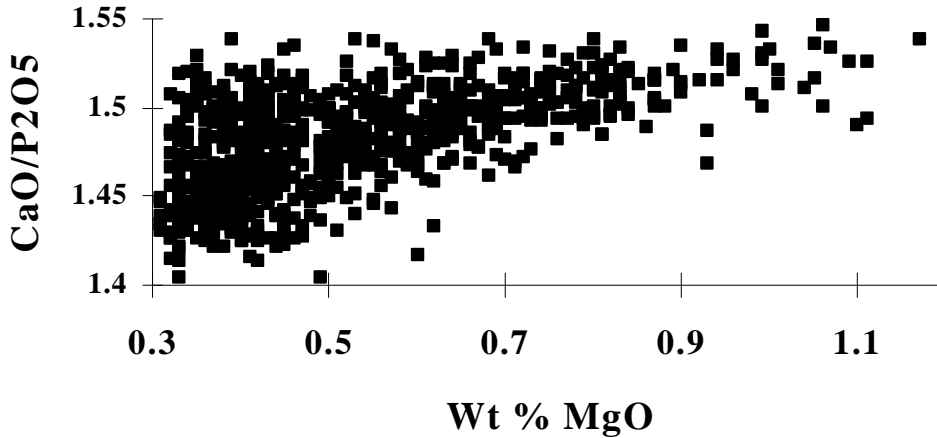
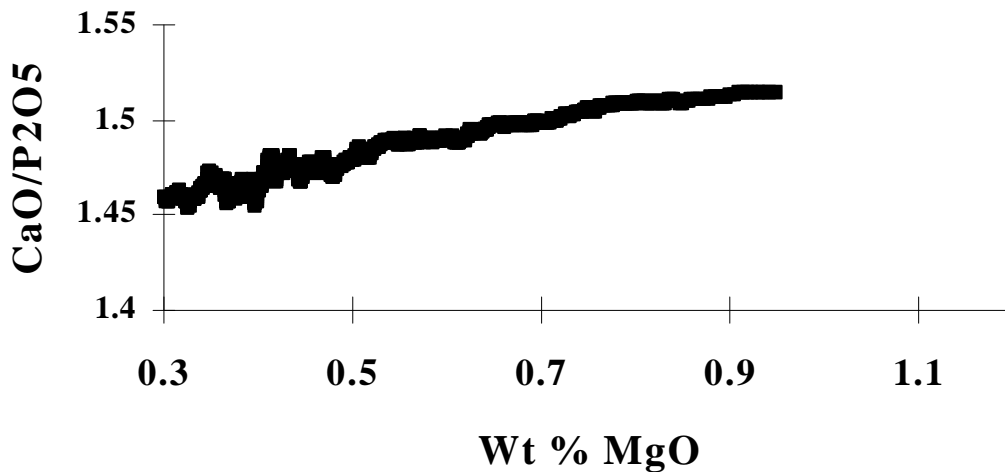


Figure 8
CaO/P₂O₅ vs MgO
(Rock to NW, 3/1-7/19/92)



As can be seen, there are clear relationships between the CaO/P₂O₅ and the BPL, Aluminum and MgO content of the rock. The CaO/P₂O₅ can be reduced by 0.05 by an increase of 9 units of BPL, a decrease of 0.40% MgO or an increase of 0.25% Al₂O₃.

It is not necessary to analyze for CaO in the rock if the BPL (P_2O_5), Al_2O_3 and MgO of the rock are known. A regression of 952 data sets for CaO/ P_2O_5 shows the following:

Regression Statistics

Multiple R	0.972
R Square	0.946
Standard Error	0.398
Observations	952

	<u>Coefficients</u>	<u>t Statistic</u>	<u>P-value</u>
Intercept	0.000		
P2O5	1.902	78.832	0
P2O5^2	-0.0121	-16.586	1.8256E-54
Al2O3	-1.643	-19.972	2.1696E-74
MgO-ACT	-0.013	-0.062	0.95063483
MgO-CS CT	-0.071	-0.290	0.77200733
MgO-FBC	0.863	7.238	9.3444E-13
MgO-FCT	0.887	6.477	1.4986E-10
MgO-FPT	0.717	6.165	1.0409E-09
MgO-HPT	1.419	8.406	1.5386E-16
MgO-KCT	0.758	3.413	0.00066892
MgO-KPT	0.680	2.628	0.0087321
MgO-NCT	0.622	1.652	0.09893612
MgO-NPT	0.575	3.119	0.00187187
MgO-PPT	0.606	3.043	0.00240807

The regression shows that the calculated CaO/ P_2O_5 has a standard error of less than 0.4 compared to a standard deviation for CaO analyses of 0.4. The CaO/ P_2O_5 is dependant on the P_2O_5 , Al_2O_3 , and a MgO relationship that is mine dependant, but not always significant. The coefficient for Al_2O_3 is 1.643. Direct substitution Al_2O_3 for any CaO would give a ratio of 1.647 suggesting that all the Al_2O_3 is present as substitutes such as Wavellite.

MgO

MgO is present in the rock mainly as Dolomite (mixture of calcium and magnesium carbonate). Essentially all the MgO dissolves in the digestion of the rock. Since all the P_2O_5 in the rock does not dissolve, it is possible to have a higher ratio of MgO/ P_2O_5 in the digestion acid than in the rock.

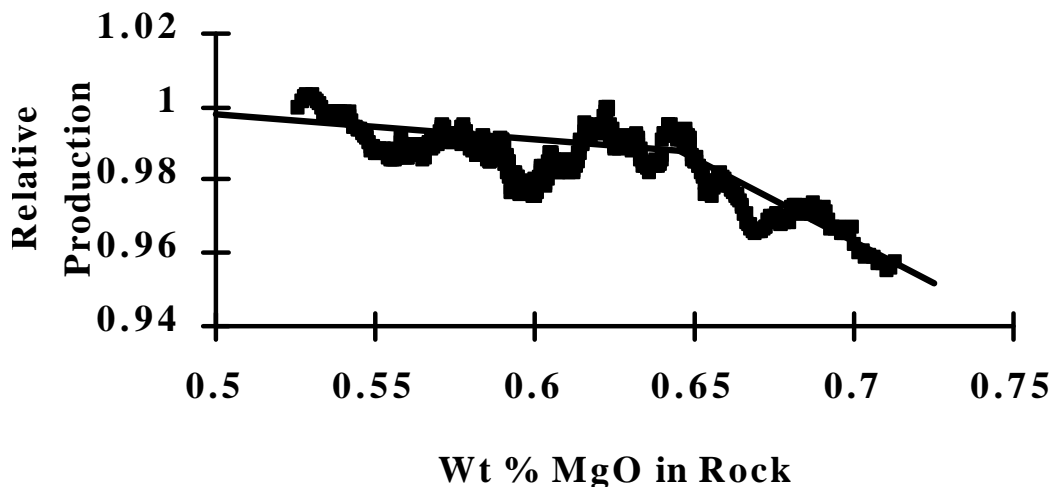
MgO is known to have a significant effect on P_2O_5 recovery in the acid digestion step. Based on operating data, an increase of 0.1% in MgO in the rock will decrease P_2O_5 recovery by at least 0.25%.

MgO can also affect the production rate. This effect is highly dependant on what is the limitation to production rate in a particular attack system i.e. filter, rock delivery rate, sulfuric addition rate

etc. Figure 9 shows how MgO content affected one production train at the IMC New Wales plant.

Performing a 10% rolling average on the data has smoothed the data. (If there were 1000 data points, the data was sorted on the X variable and a 100-point rolling average calculated for all the data.) The line represents one interpretation of the data. At the steepest part of the curve, there is a 4.3% reduction in rate for every 0.1% increase in MgO.

Figure 9
Relative Production vs Rock MgO
(2/15-9/30/91)



Since MgO also affects the $\text{CaO}/\text{P}_2\text{O}_5$, it affects the sulfuric consumption in the digestion of the rock.

Since there are no known compounds of MgO that give any significant precipitates without the use of additives, the ratio of MgO to P_2O_5 is little affected by the concentration of the phosphoric acid. As such, the ratio in the rock is little affected by any subsequent concentration and clarification steps and is essentially the same in most of the final end products.

MgO also affects the DAP grade. Before displaying this effect, we will give some general information of how rock quality affects DAP quality, the composition of DAP and ways to maintain DAP quality as rock quality declines.

Figure 10 shows the 5-week rolling average of the rock MER ($(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{MgO})/\text{P}_2\text{O}_5$) for a three and a half period for New Wales. As can be seen, there is a general trend upward with the MER increasing about 30% over the time period shown.

Figures 11 and 12 show the nitrogen content of the DAP produced for the two DAP plants at New Wales during this same time period. The nitrogen content is given as total N and ammoniacal N as non-ammonia additives were required as the rock MER increased.

Figure 10
New Wales Rock MER vs Time
5 Week Rolling Average



Figure 11
New Wales DAP 1 N vs Time
5 Week Rolling Average

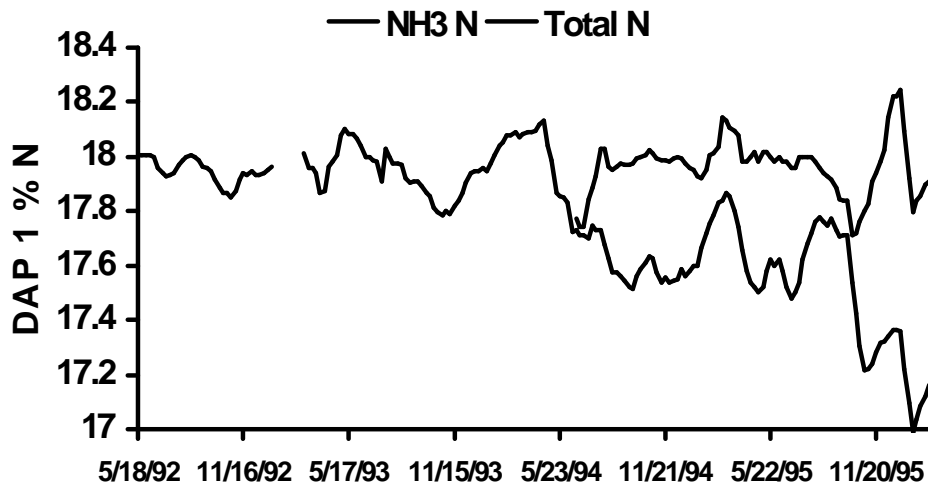
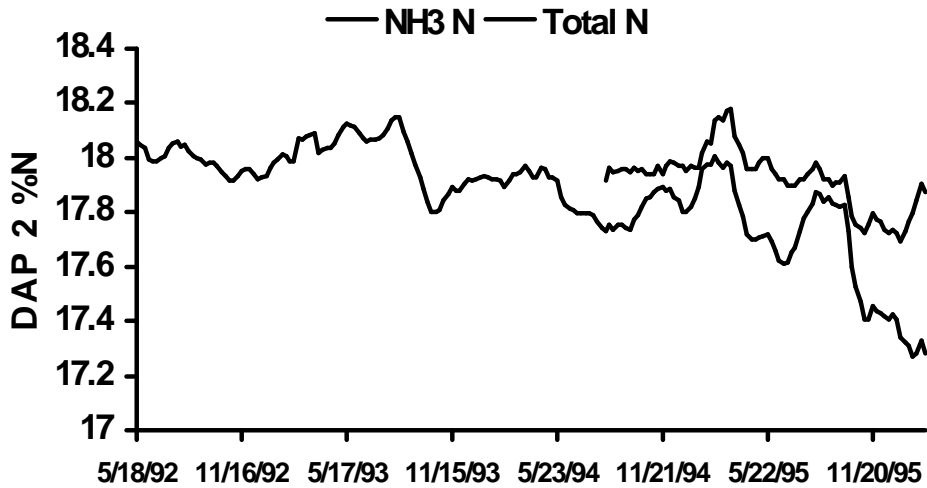


Figure 12
New Wales DAP 2 N vs Time
5 Week Rolling Average



Now it doesn't take a rocket scientist to see that the inverted rock MER data given in Figure 10 roughly corresponds with the total N plots given in Figures 11 and 12. Figures 13 and 14 show the MER plotted on the same graph as the DAP N data.

Figure 13
New Wales DAP 1 N vs Time
5 Week Rolling Average

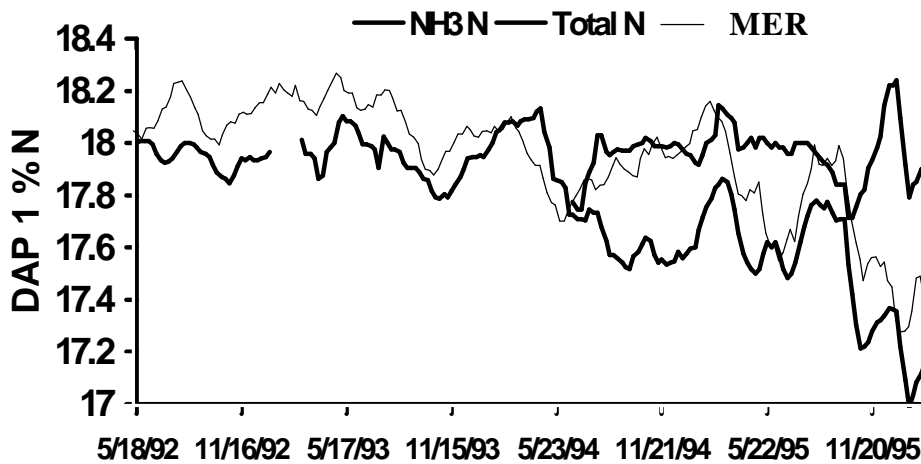


Figure 14
New Wales DAP 2 N vs Time
5 Week Rolling Average

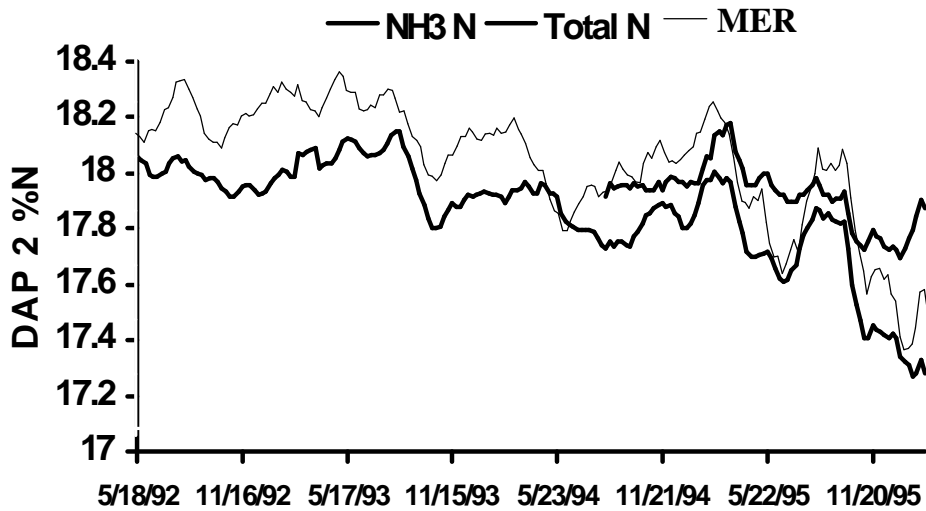
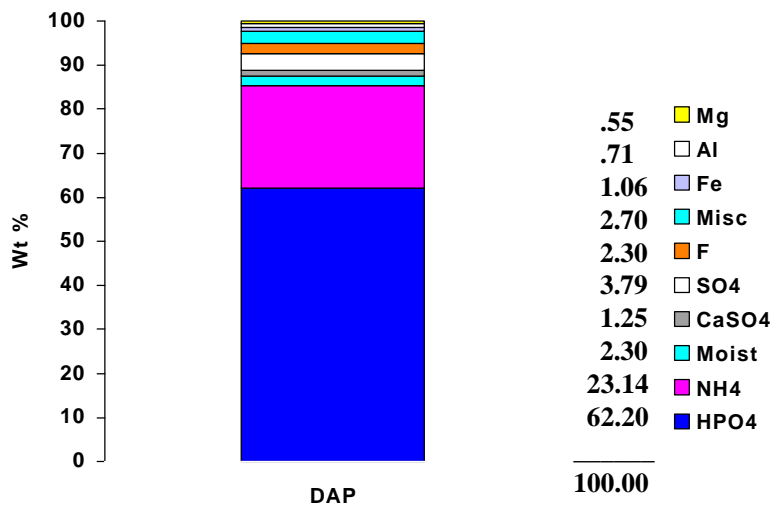


Figure 15 gives the typical composition of DAP over this time period.

Figure 15
Composition of New Wales DAP

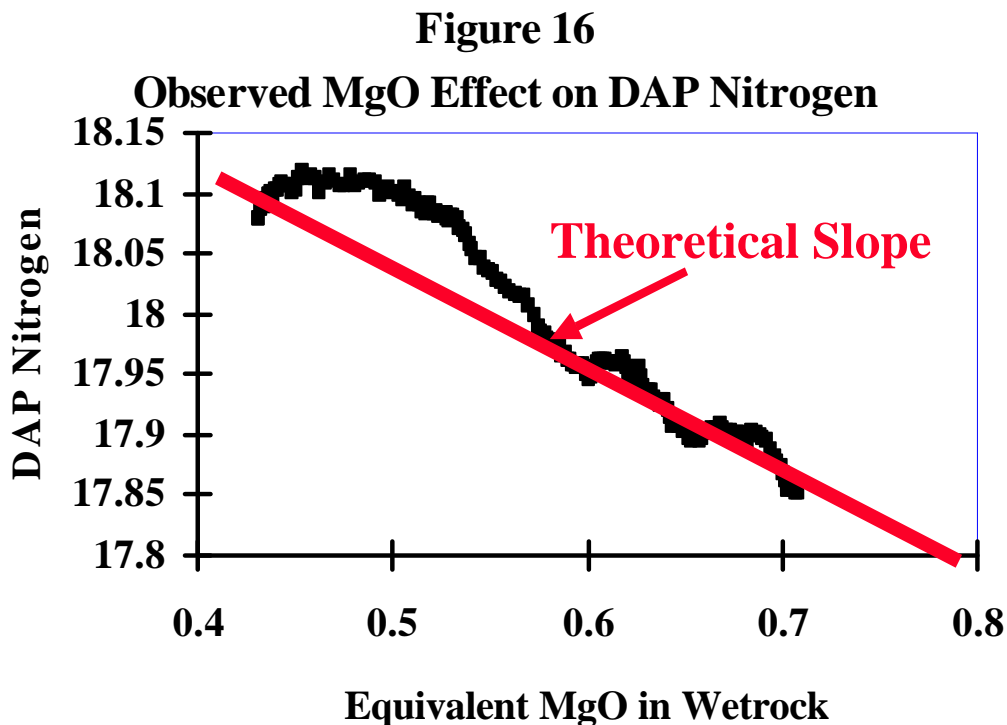


As can be seen, any increase on rock impurities will decrease the room available for nitrogen or phosphate.

It should also be noted that there must be a cation and anion balance in DAP. All the metals form compounds with sulfate, fluorides or phosphates. An increase in iron, aluminum or phosphate generally requires an increase in sulfate in the DAP.

If the magnesium increases in DAP, it replaces ammonia. Magnesium replaces 2 ammonia's. The molecular weight ratio of $MgO/2NH_3$ is 40/36.

Figure 16 shows the slope of data from New Wales, using a 10% rolling average of the data. The slope of the data is essentially the same as the 40/36 ratio.



There are several ways to maintain grade as rock quality declines. They include removing diluents and using additives with a higher packing density for nutrients.

Perhaps the easiest diluent to remove is $CaSO_4$. Calcium sulfate can be removed by increasing the sulfate content, though the added sulfate can be a larger diluent if it is not needed. Calcium sulfate can also be removed by clarification at the 30 and 40% P_2O_5 concentrations. Removal can be enhanced by cooling of the acid and by adding flocculants.

Fluorine (mainly fluorosilicates) can be removed by using acid that has been evaporated to a higher P_2O_5 strength. Evaporating the acid, particularly to 54% P_2O_5 will drive off a significant quantity of the fluorine. Some fluorine is removed in the attack tank, which can be enhanced by

using the high heat of dilution of the sulfuric acid addition. However, most of the fluorine that is removed has to be replaced with sulfate or nitrate to keep the anion/cation balance.

Water is also a diluent in DAP that can be removed. However, decreasing the water content to below 1% generally drives off a significant quantity of nitrogen, so grade may actually go down. Drying under vacuum at a lower temperature or increasing the residence time of the DAP in the dryer are effective, but both significantly increase the production cost of DAP.

Iron can also be removed from the phosphoric acid. It precipitates when the acid is evaporated to 54% P_2O_5 . The precipitated iron can be removed by centrifugation or clarification. However, the iron precipitates as complex iron phosphates so it is economically desirable to utilize them in other fertilizer products. Generally the solids can be used in the production of 10-50-0 or GTSP.

As rock quality has declined, cleaning up the acid has not been enough to maintain DAP quality. Nitrogen additives are now being used with a "higher packing density". These additives include ammonium nitrate and urea. Ammonia nitrate contains 35% N compared to 21% N for ammonia sulfate. Urea contains 46.7% N. However not everyone gives credit for either nitrate nitrogen or urea nitrogen. Additionally, some of the urea breaks down to ammonia in the dryer, reducing its effectiveness.

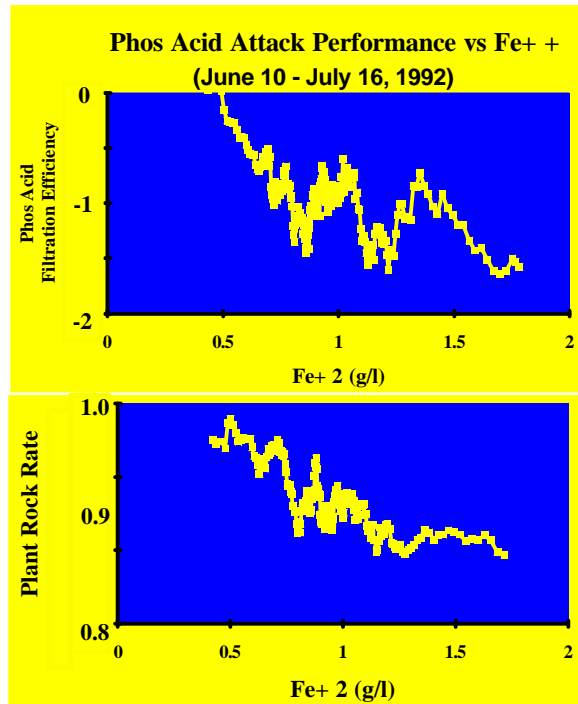
Fe₂O₃

Fe₂O₃ in the rock is determined by first digesting the rock in an acid. The amount of Fe₂O₃ found in the rock depends on the digestion acid used. In general, aqua regia digestion will give higher Fe₂O₃ assays than hydrochloric acid digestion, anywhere from 0-40% more iron. However, the hydrochloric acid digested iron most closely matches the iron that dissolves in the production plant.

While all the hydrochloric acid soluble iron does dissolve in the production plant, some may precipitate if there is a high (>0.2%) ammonia concentration in the pond water used to wash the gypsum cake. The iron precipitates as an iron ammonium phosphate compound.

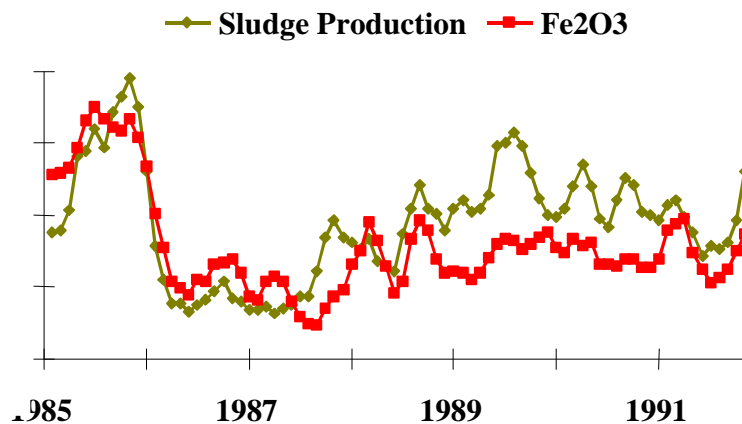
Analysis of plant operating data shows no significant impact of Fe₂O₃ on the P₂O₅ recovery in the acid digestion step. However, there does seem to be a relationship between the iron plus two (reduced state) and both the P₂O₅ recovery and the production rate. (Figure 17) This would suggest that oxidation of the rock leads to easier and more complete digestion of the rock. This of course suggests that better plant performance could be achieved by either using more oxidized rocks or by promoting oxidation of the rock during storage.

Figure 17



Unlike MgO, which does not significantly precipitate upon concentration of the acid, essentially all iron above 0.9% in the rock will precipitate as the acid is concentrated to 54% P₂O₅. The iron precipitates as iron (ammonium, or potassium, or sodium) phosphates. These complex phosphates precipitate at any concentration of phosphoric acid, but much faster at the higher phosphoric acid concentrations. Figure 18 shows how closely the sludge (precipitates that occur in 54% acid) production tracks the iron concentration in the rock over a 6-year time period.

Figure 18
Rock Fe₂O₃ and Sludge Production



If this precipitated iron sludge is removed from the acid, then iron has the smallest effect on the ability to make DAP grade. If it is not removed, then its effect is similar to that of aluminum, which will be discussed next.

Al₂O₃

Essentially all the Al₂O₃ in the rock dissolves in the acid during the rock digestion step. However, an increased Al₂O₃ in the rock will give an improved P₂O₅ recovery. From plant production data, there is a 0.12% improvement in P₂O₅ recovery for every 0.1% increase in Al₂O₃ content in the rock. Most, if not all of this improvement, is explained by the lower quantity of gypsum that is generated (as stated earlier, more Al₂O₃ means less CaO and therefore less gypsum). This also means that higher Al₂O₃ also requires less sulfuric acid to digest the rock.

Unlike Fe₂O₃, only a small amount of the Al₂O₃ precipitates as the phosphoric acid is concentrated. As a result, higher Al₂O₃ significantly affects the ability to make DAP grade. The relationship is about two thirds of that shown in Figure 16 for MgO.

High Al₂O₃ also affects the ability to defluorinate the acid. This is because the fluorine is present at AlF₃ and it must first be converted to a fluorosilicate by the addition of silica, which is a very slow reaction.

MER

For most of the history of phosphate rock mining "I+A" (iron plus aluminum) was considered the indicator of the quality of the rock. With the higher MgO that is now being mined, a new term "MER" (miner element ratio) has been developed. MER is (Iron + Aluminum + Magnesium)/P₂O₅.

In general the higher the MER, the more difficult it is to make on grade DAP. However, this only applies when sludge is not removed from the 54% P₂O₅ acid used to make DAP. Also since MgO has a more significant effect on DAP grade than either iron or aluminum, perhaps a better calculated MER would be (Iron + Aluminum +1.5 Magnesium)/P₂O₅ would be a better estimate of the effects of the impurities on DAP grade.

When the 54% P₂O₅ sludge is removed, the effect of Iron is diminished. In this case a properly calculated MER might be (0.5 Iron + aluminum + 1.5 Magnesium)/P₂O₅. If the total cost for making DAP is considered the MER could be calculated as (0.5 Iron – 2.8 Aluminum + Aluminum Squared +1.5 Magnesium)/P₂O₅. The important point is that the original method for indicating impurities (I+A) no longer applies.

Moisture

The moisture of well-drained Florida phosphate rocks varies from 5 to 20%. No relationships have been developed between the moisture and the BPL etc that are typically measured. High moisture rocks increase the cost of shipping the rock as well as possibly reducing the quantity of pond or process water than can be consumed by the acid production plant.

U₃O₈

Phosphate rock also contains a small quantity of uranium. The quantity is so small (about 1 pound per ton of P₂O₅ for Florida rock, generally less for other phosphate rocks) that it has an insignificant impact on the ability to make product grade. When uranium was recovered from phosphoric acid (there presently are no plants operating), it was important to use rock containing the highest quantity of uranium. Since phosphate pebble always contains more (typically 50+% more) uranium than concentrate from the same mine, pebble rock was used to the maximum extent possible. Also relationships were developed between the uranium content of the phosphate rock and the BPL etc. so that it was not necessary to analyze all the rock for uranium.

Cadmium

Since cadmium is a heavy metal, it is a major concern in Europe and some other areas of the world. This is because cadmium is taken up by some plants and passed through the food chain. While many of the world's phosphate rocks contain 10's of PPM of cadmium, the Florida phosphate rocks generally have less than 10 PPM of cadmium, which is less than the level of concern.

SO₄

All phosphates contain some sulfate. This represents "free" sulfate and is a credit when calculating the sulfuric acid required to digest the phosphate rock. However, it is relatively constant at about 0.8% in Florida phosphate rocks.

CO₃

Carbonate is contained in all Florida phosphate rocks. It is present mainly as limestone or dolomite. High carbonate causes excess foaming in the rock digestion process and can cause increased phosphate losses due to the foaming. Generally the foaming is controlled by the use of a defoaming agent.

The quantity of carbonate in Florida phosphate rocks correlates well with the MgO content of the rock. Of course, it would be nice if both were lower!

Insol

Insol is the material remaining after a laboratory digestion of the rock. However, since this digestion media is not the same as that used in the production plant reactor, it does not actually relate to the real insoluble rock fractions that the plant sees. In general the laboratory digestion leaves mostly the silica as the insol. In the plant, a significant portion of the silica dissolves in the acid forming fluorosilicic acid. On the other hand some species such as iron pyrites are soluble in the laboratory digestion but are not in the plant digestion. However, in general, lowering the insol in the rock is generally a good thing to do by the mine beneficiation process.

High insol in the rock increases the transportation cost of the rock. Also since it ends up on the gypsum stack, it affects the disposal cost. While there has been no correlation found between

insol and phosphate extraction efficiency, it is likely that high insol's increase the phosphate losses because of the greater quantity of filter cake that is generated.

Variability

While rock variability is not a rock impurity, it is an important attribute of the rock. Variability in the rock significantly affects the ability to efficiently digest the rock in the production plant. The most significant variables are the CaO, MgO, Fe₂O₃ and Al₂O₃. While BPL variability does not in itself affect the ability to control the digestion process, it does correlate with the other variables and can be used as an indicator of rock variability.

Figure 19 shows the variability in CaO for rock received at IMC New Wales for an 18-month period.

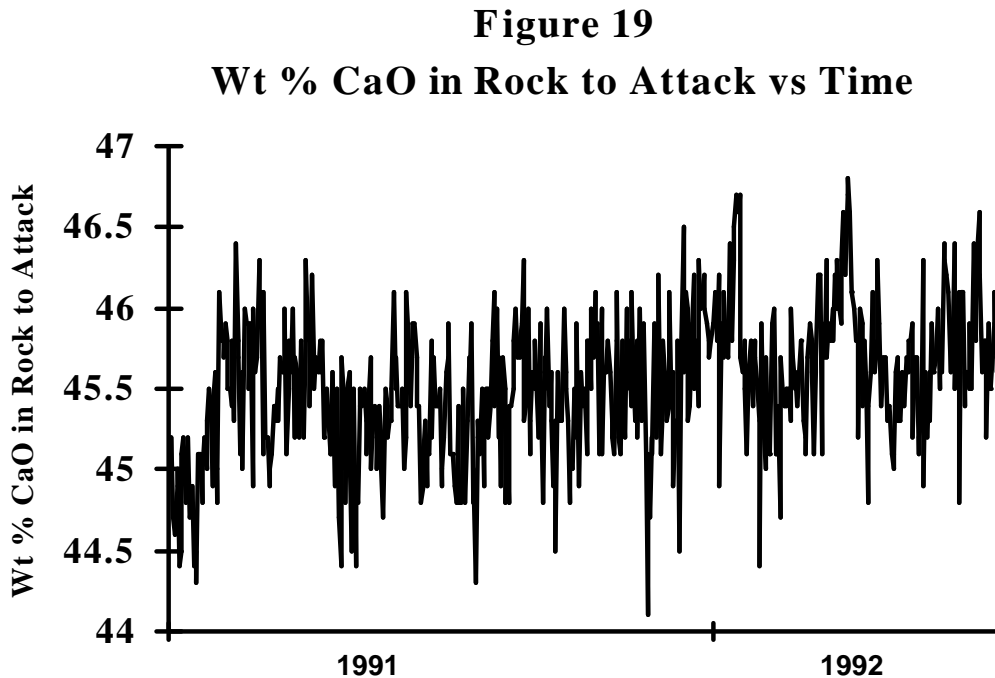
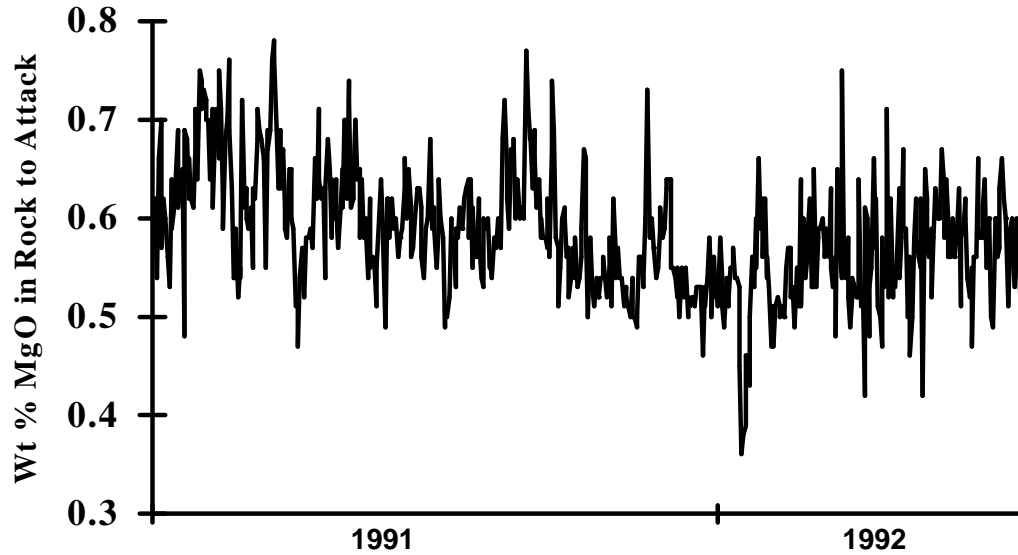


Figure 20 shows the variability in MgO for the same time period.

Figure 20**Wt % MgO in Rock to Attack vs Time**

Figures 21 and 22 show what we would like the variability to be.

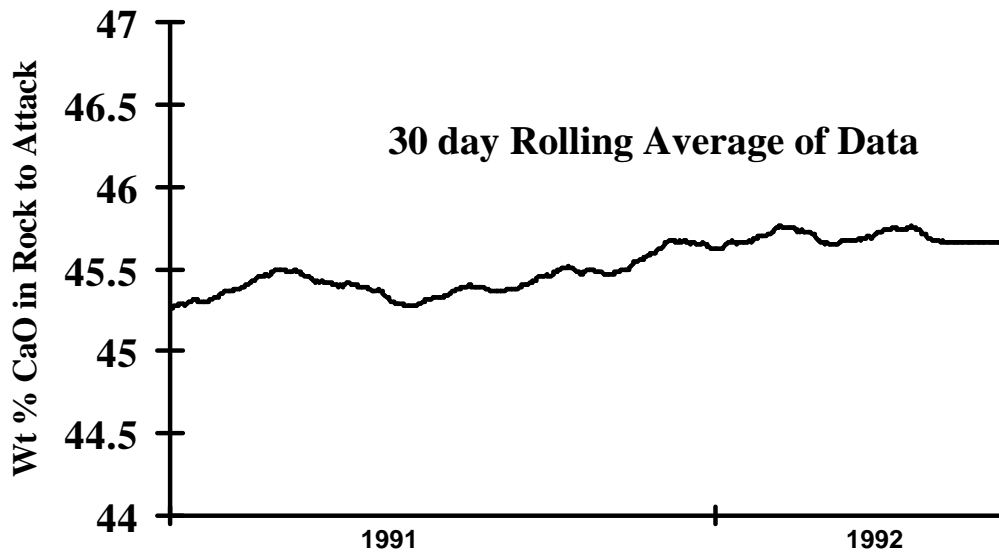
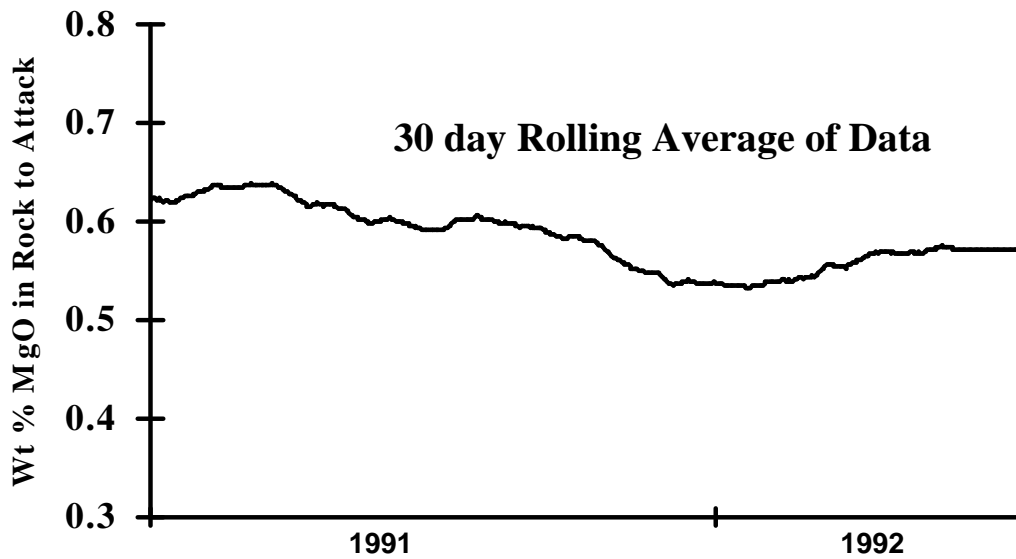
Figure 21**Wt % CaO in Rock to Attack vs Time**

Figure 22**Wt % MgO in Rock to Attack vs Time**

Of course, even if we did blend the rock in a 30-day blender, due to analytical error, the results would look like Figures 23 and 24.

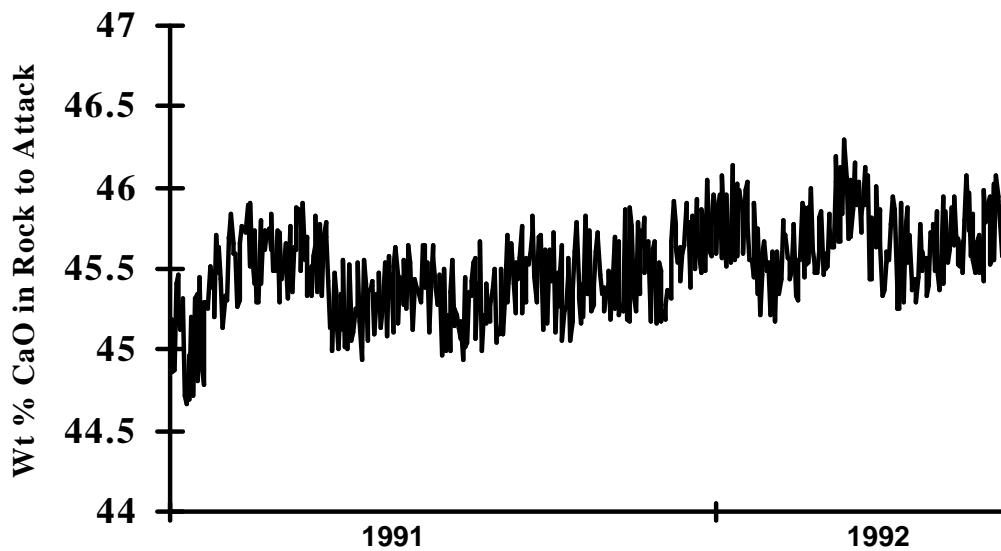
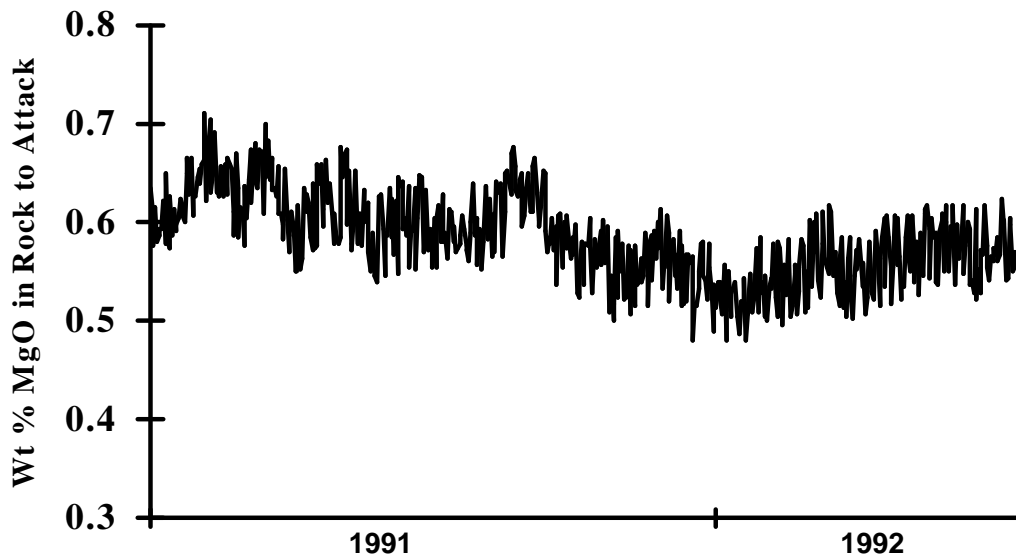
Figure 23**Wt % CaO in Rock to Attack vs Time**

Figure 24**Wt % MgO in Rock to Attack vs Time**

While such improved variability would be nice, it is difficult to achieve. It is impractical to build a pile of rock that would hold 30 days supply of rock and then constantly mix it. However, there are other ways that the variability of rock can be improved.

The first method of improving variability would be to continuously analyze the rock received by the production plant and then stack it in places on the pile with similar composition. Then rock could be retrieved from the pile by pulling from various places on the pile to hold the overall composition relatively constant. While this would significantly improve the variability, it will only become practical when a continuous analyzer becomes available that can accurately and quickly provide the several analyses required on the rock as received (without sample preparation). To date, the closest device we have that can possibly provide this kind of information is the LIBS (Laser Induced Breakdown Spectroscopy) system being developed by UF and others or LIL (Laser Induced Luminescence) system being developed by OUI/FIPR/IMC.

The second method to improve rock variability is termed the customer pile program. It can only be used where at least two customers are being supplied dissimilar rock from the same mine. In this method, a rock pile is maintained for each customer. During the mining and processing of the rock, it is normally sent to bins to drain excess water prior to dumping on the rock pile. During this time, a sample of the rock going to the bin is typically analyzed. Based on this analysis, a decision is made as to which pile to send the rock. This is made based on both the "closeness of fit" of the rock to each customer's rock quality and the need of the pile for additional rock. While this type of program is being used by IMC, it works best when there are many customers or plants involved. The biggest problems in its use are typically the occasional bad samples, bad or late analyses, or mechanical problems associated with stacking the rock.

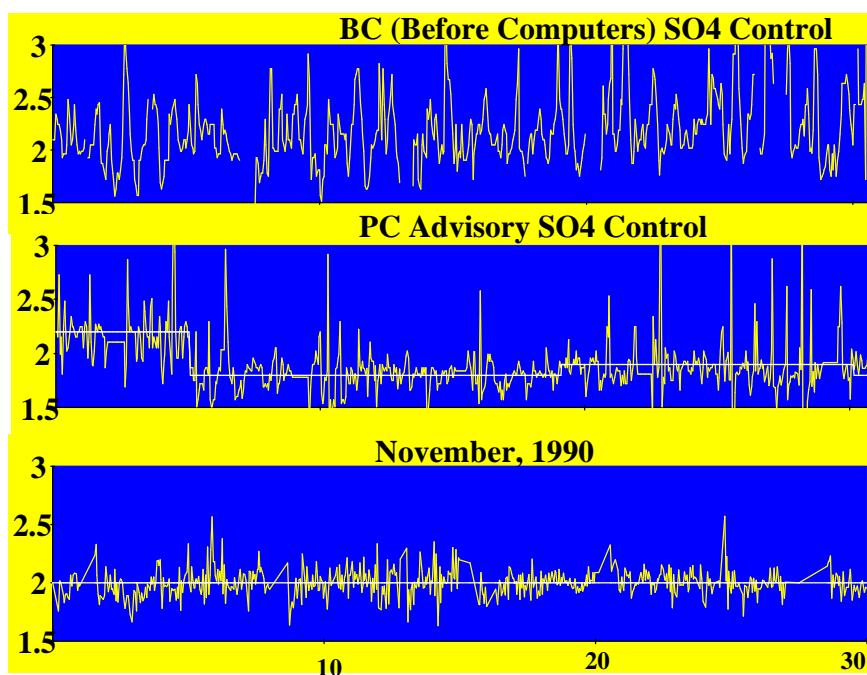
Size

Normally phosphate rock size varies from plus 1 inch to 16 or 20 mesh for pebble and 16 or 20 mesh to 150 mesh for concentrate. Since at least some of the rock must be ground to efficiently digest it, the size of the rock does matter. Typically it takes 3-4 Kilowatts/ton to grind pebble down to the same size a concentrate. In addition, grinding balls are consumed. This makes pebble somewhat more expensive than concentrate to process for the production plant.

Advanced Process Control

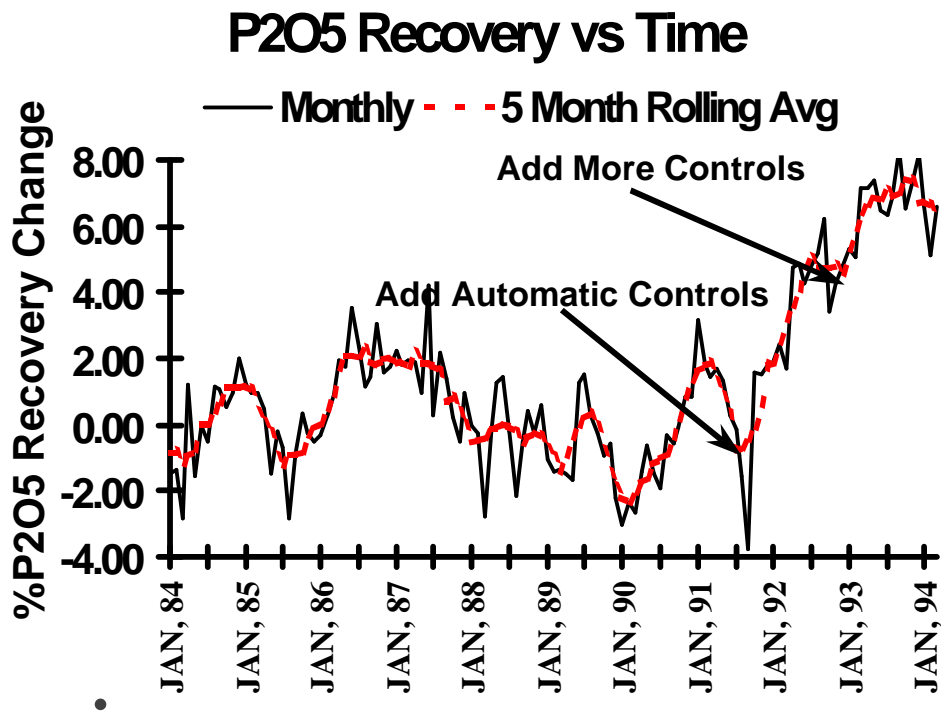
Finally, a word about advanced process control and how it affects operations. Figure 25 shows how sulfate control was improved over a very short period of time as the control of the phosphoric acid reactor went from operator control to computer advised control and finally on-line computer control.

Figure 25



Similar improvements were made in the control of attack P_2O_5 strength and operating rate. Figure 26 shows how these improvements affected the phosphate recovery of the complex during the same time period.

Figure 26



Conclusion

In the past few years, phosphate rock quality has become much more complex than just BPL and I+A. When we now talk about phosphate rock quality, it may mean as much as 10 different aspects of the rock, all of which may have significant impact on the value of the rock to a particular rock consumer.