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# PROCESS IMPROVEMENTS IN MANUFACTURE OF WET PROCESS ACID FROM FLORIDA PHOSPHATE ROCK OF VARIOUS COMPOSITIONS

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World phosphate rock production is in excess of 115 million tons per annum. Although there is no shortage of phosphate rock, per se, the increased rate of production is bringing deposits onstream with a greater variation in the composition of the rock. Primary deposits have previously been mined selectively according to impurity levels.

The major impurities found in phosphate rock become solubilized in the phosphoric acid produced by the reaction of rock and sulfuric acid. Unless the level of these impurities can be decreased in the product acid, a dilution of the phosphate content of the end solid products result.

## ATTACK/FILTRATION

IMC, in the early 1960's, constructed a small pilot plant to investigate the performance of various phosphate rocks in the wet acid process. Through the years, equipment and technique changed as operating experience was acquired.

In the 1960's, most of the commercial plants being constructed recycled all the excess slurry not fed to the filter back to the first compartment where the rock is added. Pilot plant tankage, when arranged in this fashion, has the flowsheet shown in Figure 1.

In 1970, one of the more popular designs used the slurry flows shown in Figure 2. This basic design was used in constructing the New Wales Plant.

In this type of plant, it is possible to maintain two different levels of sulfate in the phosphoric acid slurry. In the attack system a low level is desired for dissolving coarse phosphate particles. In the digestor section, this level can be raised for maximum crystallization without fear of occluding undigested phosphate rock. This technique can be of value in processing various high impurity rocks, and was investigated as a means of utilizing high MgO phosphate rock for phosphoric acid manufacture. Comparative tests using the same rock or similar type were run without the sulfuric acid addition to the digestor.

The chemical analysis of the phosphate rocks used in the test series is given in Table I. In all of the pilot plant tests, a control test is made using a sample of rock commercially prepared for use in the New Wales plant. Thus, the rocks listed here include this type of commerically dried and ground rock as well as the experimental rock. The control rocks were used in Tests 61-A, 64-1 and 65-1.

The experimental rocks for tests 63-2, 66-1 and 66-2 come from areas south of present Florida phosphate rock operations. In the tests 66-1 and 66-2 the beneficiated rock was contaminated before grinding with phosphatized dolomitic rocks obtained from the same area as the feed. These tests simulated a ground rock product highly contaminated with natural minerals from the same geographical area.

The operating procedure used for these tests consists of the following steps:

- The ground phosphate rock and 70% sulfuric acid are metered continuously into the #1 attack compartment. For the two level sulfate operation, additional sulfuric acid is metered into the digestor.
- Defoamer is metered as needed into the #1 attack compartment.
- The recycled slurry and recycled 22% $P_2O_5$ filter wash flows are timed and controlled through the use of electronically operated valves. This allows a variability in the recycle/product ratio with a variation in feed rate. The 22% acid volume obtained from the counter-current filter washes is that a consistent percent solids in the slurry can be maintained.
- Filtration is done batch-wise every twenty minutes. The volume of the slurry in the digestor is allowed to vary in order to supply these periodic demands.
- Temperature is maintained at 175$^{o}$F by the heat of dilution supplied by the 70% $H_2SO_4$ feed with supplementary heat supplied electrically beneath the compartments.
- Sulfate levels in the attack compartment and the digestor are monitored every twenty minutes by instrumentation described first in 1964.(1) The digestor was monitored only in those tests when sulfuric acid was added.

Each test in this series was preceeded by a twelve-hour purge period. This purge period was followed by a twelve-hour test period which was comprised of three four-hour segments. A feed rock sample was composited over the twelve-hour period and its analysis used for calculating the recoveries listed.

The gypsum and filter product hourly samples were composited for each segment. These chemical analyses were then averaged for use in calculating the recoveries.

Results of the aforementioned tests are summarized in Table II. Fresh water was used for filter washings in all cases.

The difference in the acidulation conditions between these tests is the higher free sulfate levels in the digestor. With these conditions, Test 66-1 with a 1.99% MgO content had, for design purposes, marginally acceptable overall recovery of 94.6%.

Figure 3 shows photo-micrographs of the gypsum crystals obtained in Tests 65-1 segment 3, 66-2 segment 9 and 66-1 segment 12. The digestion and filtration efficiencies for these segments are also presented with the photographs. The deviations from the test averages decrease as the digestion efficiencies increase due to more stable conditions.

Since the segments chosen were the last for each test, the digestion slurry should have the highest percentage of the digestion products of the feed rock. The residual dilution of the previous rock's test slurry would be at its lowest.

In the case of test 65-1, assuming plug flow through the system, the retention time was 5.34 hours. The purge and test period together should have allowed about a 90% turnover of the beginning slurry.

Tests 66-1 and 66-2 both had combined purge and test periods of forty-eight hours to yield a 96% changeout of the beginning slurry.

Blinding of filter cloth attributed to magnesium compounds (2) was not evident in the tests described, perhaps for the following reasons:

a. The batch filtration procedure. In Test 66-1, the filtration cycle time was approximately 4.5 minutes or 13.5 minutes per hour of operation. This means, that for the four day period when the high MgO rock was being tested, the filter had the equivalent of 21.6 hours of operations. The problem of filter blinding would have had to be very rapid to become evident in this relatively short time.

b. The use of fresh water as process water. Since the compounds described also contain fluorine it is possible a higher slurry fluorine content from using pond water (recycled evaporator and flash cooler water) is needed to trigger their precipitation.

c. The aluminum content of the rock might have been insufficient to cause the compound to exceed its solubility limit.

The small scale tests described have demonstrated that high magnesium containing phosphate rock can be utilized for wet process acid production. Acceptable digestion and filtration efficiencies can be attained by raising the free sulfate content of the digestion slurry in filter feed stabilization compartments.

The free sulfate levels described have not been optimized. The target level was 2.0-2.5%. This range was reached as an average once in three tries. The individual segment filtration efficiencies were 99+ when a 2.3% free sulfate level was present in the digestor.

## CLARIFICATION

The principal reaction in the wet acid process results in the production of calcium sulfate and phosphoric acid. The separation of the calcium sulfate from the phosphoric acid has first priority before the rejection of other impurities can be considered.

The filter removes almost all of the calcium sulfate. However, calcium sulfate is slightly soluble in phosphoric acid. The solubility decreases with an increase in the free sulfuric acid level and the phosphoric acid concentration of the liquid phase.

Figures 4-6 show laboratory data for the solubility of CaO in phosphoric acid as a function of the free sulfuric acid concentration.

Figure 4 is the data for 30% $P_2O_5$ acid after equilibration for 96 hours. If we assume the free acid level in a Prayon system of 1.2% for Florida rock, the CaO in solution is o.32, at 71°C.

Figure 5 indicates that the former acid, concentrated to 42% $P_2O_5$ with a corresponding increase of free acid to 1.7% $H_2SO_4$, yields an acid with 0.16% CaO in solution.

Figure 6 indicates that the same acid concentrated to 52-55% $P_2O_5$ with a corresponding increase in free acid to 2.2% $H_2SO_4$, yields an acid with 0.06% CaO in solution.

With no rejection of calcium sulfate from the equilibrated acid, the concentrated acid would have a minimum sludge content of 1.9% by weight of anhydrite, due to precipitation of the dissolved calcium during concentration. On cooling, the amount would increase further.

Figure 7 is a summary of the preceding solubility charts as a function of $P_2O_5$ concentration in the 2.6 - 3.8% $H_2SO_4$ free acid level.

To increase filter capacities, producers are using filter cloths of higher porosity. The standard method for porosity determination measures the amount of air that will pass through a fabric at a differential pressure of one half inch of water. (ASTM method No. D737-75). Years ago, the cloth used had a porosity of 100 cfm (283 liters per min.), now the cloths used have porosities in the 150-250 cfm range (425 - 566 liters per min.). A high porosity cloth does not blind as soon as does a low porosity cloth, but it passes fine particles of calcium sulfate until its own filter mat is formed.

Therefore, filter product contains more calcium sulfate today than formerly. In addition, holes occur in the cloth passing calcium sulfate into the filter product.

Figure 8 indicates the decrease in solubility of sodium and potassium fluosilicates as phosphoric acid is concentrated.

So far, the data indicates that by manipulating $P_2O_5$ and $SO_4$ concentrations, a substantial amount of dissolved impurities can be precipitated for removal by either settling, centrifuging or filtration.

However, the literature abounds in data (3) that indicate a precipitation of iron and aluminum phosphate complexes as the $P_2O_5$ concentration of the acid exceeds 40 - 42%.

From heat balance considerations in evaporator design, it has become common practice in the U.S. to evaporate phosphoric acid in 3 steps. The first step is to concentrate from filter product up to 40% $P_2O_5$. The next step concentrates to 48% $P_2O_5$, while the last step concentrates to 54% $P_2O_5$.

Therefore, it became logical to use a 39 - 41% $P_2O_5$ concentration. We call this '40% clarification'.

In the U.S., the precipitated impurities in wet acid are called 'sludge'. This part of the paper will describe IMC practice in removing precipitated impurities as a sludge for transfer back to the attack system using 40% clarification. Although the data reported here concern a Prayon type dihydrate operation, they can be applied to other systems.

## PRESENT FULL SCALE OPERATION

IMC's New Wales plant contains 2-912 STPD $P_2O_5$ Prayon acid systems, each operating now at about 1400 STPD. The attack system consists of 8 compartments, the first six for the primary attack system, the last 2 may someday be used for the Prayon dihydrate-hemihydrate process. Now they act as filter feed compartments. The extra compartments have the advantage that they can be used to change the solubility characteristics of the attack slurry without affecting the gypsum crysals that have been formed in the first six compartments.

For example, Florida rock in a Prayon system generally forms the best filtering crystals at about 1.2% free sulfuric acid. At this free acid level, the soluble calcium level is high. At New Wales, extra sulfuric acid is added to the last two compartments to decrease calcium solubility without adversely affecting filtration. Filtration rates have been as high as 0.9 TPH $P_2O_5/ft^2$ on the 1810 $ft^2$ effective area of the Bird-Prayon 30-D filter.

The filter product passes into a raked surge tank. Initially, the underflow sludge from the 30% tank was sent back to attack. The sludge from the 40% clarifier was also sent back to attack. Since some phosphoric acid must be added to the sludge for ease in pumping, the two sludge recycle streams meant too much $P_2O_5$ recycle.

Now, as shown on Figure 9, the 30% underflow passes to the No. 1 evaporator. There is no overflow except on the East train where 30% overflow is transferred as needed to the DAP scrubbers.

The output of the evaporator passes into an aging tank where time and cooling permit crystal growth of solids that are removed in the underflow of the 40% clarifier.

The 40% clarifier product is used in the diammonium phosphate or slurry triple superphosphate plants or may be sent on to other evaporators for further concentration.

Table III, shows analytical data for the input and output streams of the 40% clarification system at New Wales as an average of five 8 hour composite analyses. The average analyses of the rock fed to the attack train during that period is shown also.

Using analytical and mass balance data, calculations indicate that impurities were removed in the clarifier in substantial quantities. For examples, two-thirds of the calcium, one-half of the sodium, one-third of the potassium and one-quarter of the fluorine are rejected in the underflow stream.

The suspended solids in the underflow (Table III) are less than those truly precipitated since the precipitated solids must be mixed with some acid to yield a slurry capable of being pumped back to the attack system. The 2% increase in the dry basis $P_2O_5$ content of the overflow is a real measure of impurity rejection.

The recycling of the underflow from the 40% clarifier has at least two disadvantages. (1) Since the underflow is typically 36-38% $P_2O_5$, recycle is a production loss of a corresponding quantity of $P_2O_5$. (2) The major disadvantage may be viewed from the point of view of energy conservation. The 40% clarifier underflow is diluted with water to attack strength-circa 28% $P_2O_5$. This water must be removed in first stage evaporation. At a first stage steam rate of 1.1 lb steam/lb $P_2O_5$, the additional energy consumption is of major consequence.

The 40% underflow solids are predominately gypsum, sodium and potassium fluosilicates. There is also a surprisingly high (1.6% D.B.) $Al_2O_3$ content. When these solids are recycled to the attack system, some become undesirable nuclei for gypsum crystals while some redissolve. This is judged to be detrimental to attack and filtration efficiencies.

These disadvantages caused New Wales to investigate the feasibility of filtering the 40% clarifier underflow to permit discarding the solids.

## PILOT FILTRATION OF 40% UNDERFLOW

Pilot studies were undertaken in the Spring of 1977. There were several process requirements to be met:

- All filtrate streams, both primary and wash filtrates, had to be at $P_2O_5$ concentrations that could be used readily in the existing plant without further processing. This meant minimum wash volumes.
- The cake was to contain less than 4% $P_2O_5$.
- The wt % suspended solids in the filtrates was to be less than 1%.

The pilot filter was a sliding pan type belt filter. The filtrate box on the filter was designed to provide three identical 1.6 $ft.^2$ sections. The filtrate flowed to the filtrate receivers through hoses. The various flow rates around the filter were measured with a graduated cylinder and stopwatch. All streams were sampled and analyzed for various chemical species.

Various wash configurations were tested. The final choice was a two-stage counter-current wash. While there was sufficient area for primary filtration, there was much more wash area than needed. It was possible to operate with the primary filtration section flooded, but the wash sections went surface dry almost immediately. The filtrate and wash areas could not be changed because the partitions in the filtrate box were immovable.

The 40% underflow fed to the filter averaged 17% S.S. by wt. The primary filtrate was nominally 40% $P_2O_5$ and about 0.7% S.S. by wt.

Pond water was fed onto the filter near the discharge end. The first pass through the cake yielded about 13% $P_2O_5$ liquor. (No. 3 filtrate) All of the No. 3 filtrate was pumped back onto the filter as first wash. This wash passed through the cake to result in the No. 2 filtrate which was recovered as 30% $P_2O_5$ acid containing about 0.6% S.S. by weight.

Table IV is a summary of the analytical data gathered during the pilot studies. Mass balances have been performed using those data. Table V shows the percent of each species discarded with the cake, based on the quantity of each species being fed to the 40% clarification system.

Of particular interest is the magnitude of the rejection of the $Al_2O_3$, MgO, F, and $K_2O$ streams. The rejection of $Al_2O_3$ and MgO is important because of their effect on acid viscosity as it is concentrated, as well as their adverse effects on DAP grade. By reducing the $K_2O$ level in the acid, the formation of $Fe_3KH_{14}(PO_4)_8 \cdot 4H_2O$ should be inhibited. (4) The fluorine removal is particularly significant to New Wales because part of the acid production is used to produce defluorinated animal feed ingredients. By removing part of the fluorine at the 40% U.F. filter, an increase in defluorination rate at the Animal Feed Ingredients Facility is expected.

Based on the above pilot plant data, New Wales has designed a full scale belt filter process. It is believed a 151 $ft^2$ belt filter will meet the process requirements mentioned earlier. The flowsheet, Figure 10, illustrates the process.

The proposed belt filter will have a fixed vacuum pan design. The filter cloth is carried by a heavy, rubber transport belt. The filtrate goes through the cloth, along flow channels in the transport belt surface to drain holes that permit flow to the vacuum box. The filtrates are separated by spade dampers in the vacuum box. Each filtrate section has its own receiver and seal tank.

The solids will be discharged into a hopper and will be sluiced by pond water to flow by gravity to the phosphoric acid plant waste gypsum stack. The solids are expected to contain about 3% $P_2O_5$, most of which are water soluble losses.

After the cake is discharged, the filter cloth and transport belt will separate. The cloth is to be washed on both sides, and the transport belt washed on the side that is in contact with the cloth. The cloth wash is very important to prevent cloth blinding.

When the 40% filter process is commercialized, it is expected that rock with high impurity levels will be processed with good efficiencies. Overall plant $P_2O_5$ losses in the filter cake should average about 0.25%. Production capacity as well as overall chemical efficiencies are expected to increase to levels providing an acceptable economic return.

## ACKNOWLEDGEMENTS

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FIGURE I

1960 SLURRY FLOWS

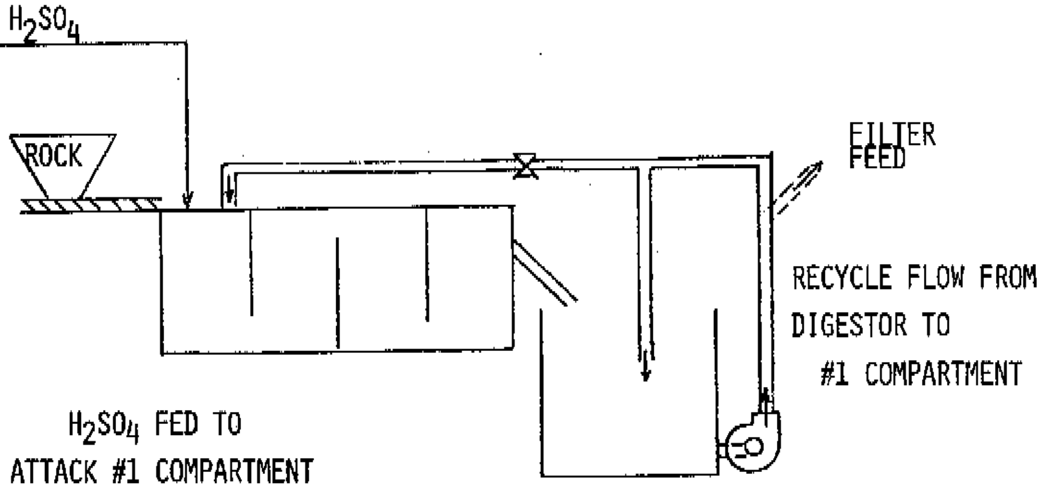
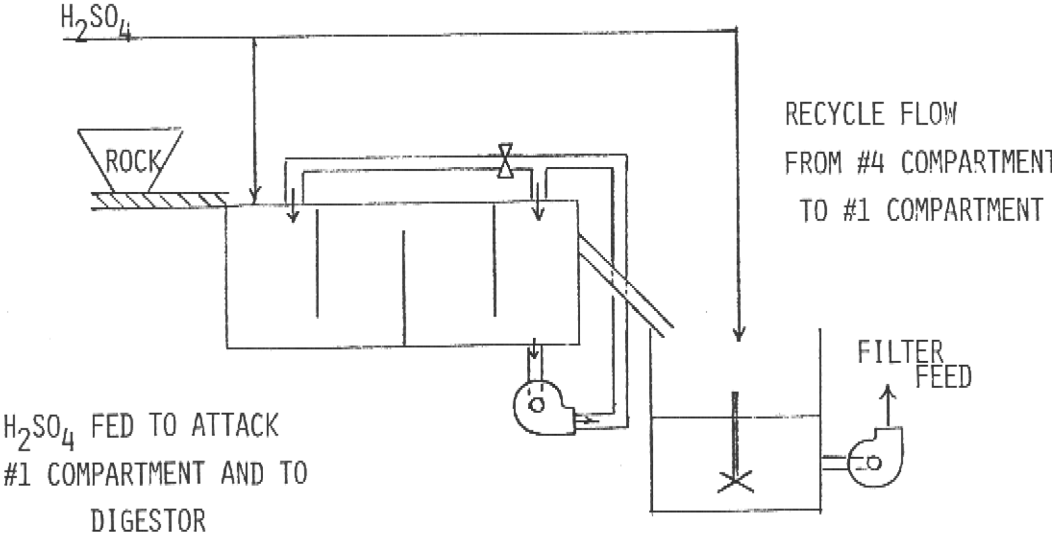
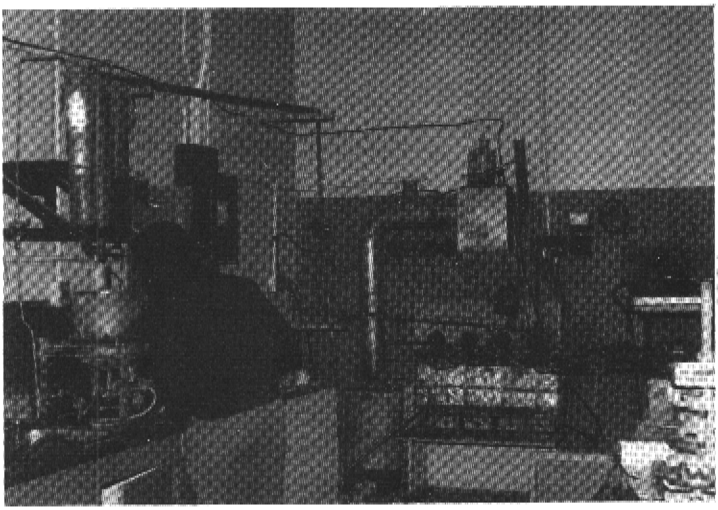


FIGURE II

1970 SLURRY FLOWS





## TABLE I

## TEST ROCK ANALYSIS

| TEST # | 63-2 | 61A & 64-1 | 65-1 | 66-1 | 66-2 |
|---|---|---|---|---|---|
| $P_2O_5$ | 30.0 | 30.0 | 30.4 | 26.6 | 27.3 |
| CaO | 47.5 | 47.0 | 46.5 | 44.1 | 45.0 |
| $Fe_2O_3$ | 2.18 | 1.57 | 1.31 | 2.41 | 2.64 |
| $Al_2O_3$ | 0.78 | 1.28 | 0.96 | 0.83 | 0.72 |
| MgO | 0.81 | 0.74 | 0.46 | 1.99 | 1.76 |
| INSOL | 2.79 | 8.8 | 8.15 | 7.57 | 6.80 |

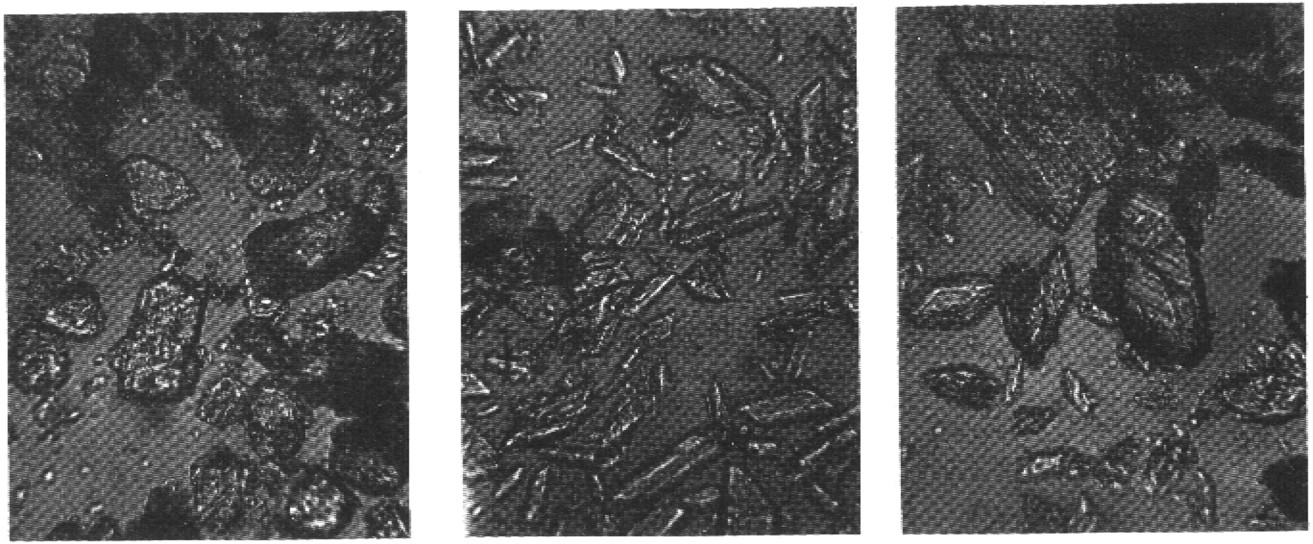
## TABLE II

## SUMMARY OF RESULTS

| | ROCK | EFFICIENCIES | | SULFATE* | |
|---|---|---|---|---|---|
| | MgO | DIGESTION | FILTRATION | ATTACK | DIGESTOR |
| 64-1 | 0.74 | 97.9 | 98.3 | 0.77 | 2.68 |
| 63-2 | 0.81 | 97.1 | 98.3 | 0.85 | 2.56 |
| 66-1 | 1.99 | 95.5 | 99.1 | 1.38 | 2.48 |
| 65-1 | 0.46 | 96.8 | 98.8 | 0.99 | 0.99 |
| 61-A | 0.71 | 96.4 | 97.9 | 0.5 | 0.5 |
| 66-2 | 1.76 | 93.2 | 95.4 | 1.34 | 1.34 |

* CORRECTED FOR SOLUBLE CaO

FIGURE 3



65-1
SEG. 3
MgO = 0.46

EFFICIENCIES

DIGESTION 96.9%
FILTRATION 98.7%

66-2
SEG. 9
MgO = 1.76

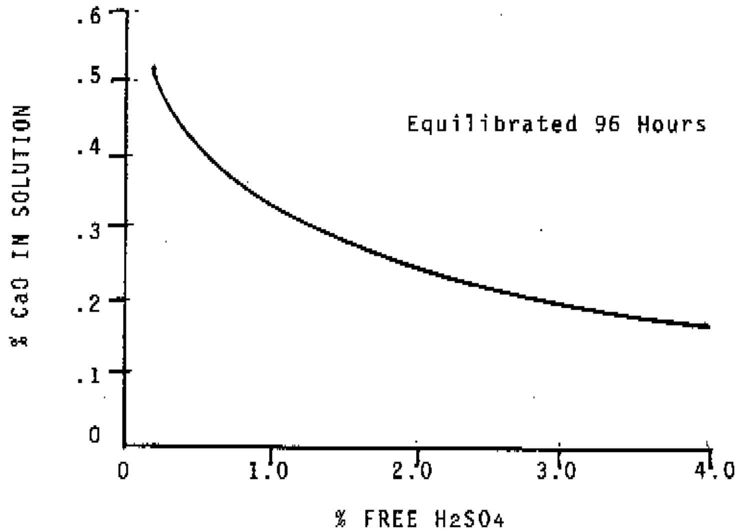
EFFICIENCIES

DIGESTION 91.5%
FILTRATION 93.7%

66-1
SEG. 12
MgO = 1.99

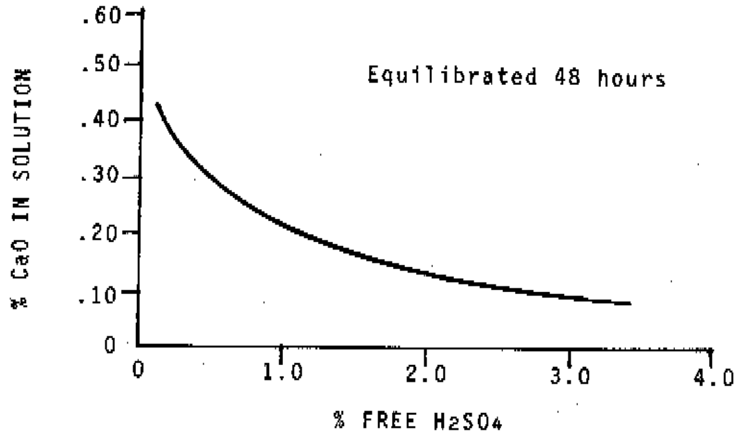
EFFICIENCIES

DIGESTION 95.8%
FILTRATION 98.8%



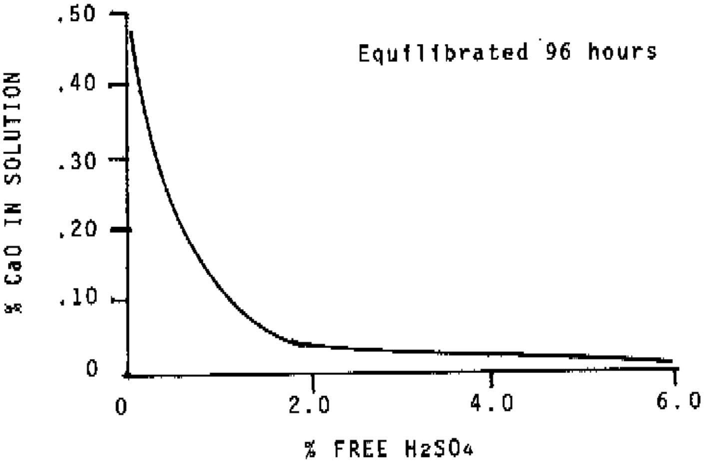
CaO SOLUBILITY IN 30% $P_2O_5$ ACID VS. FREE $H_2SO_4$ @ 71°C.

FIGURE 4



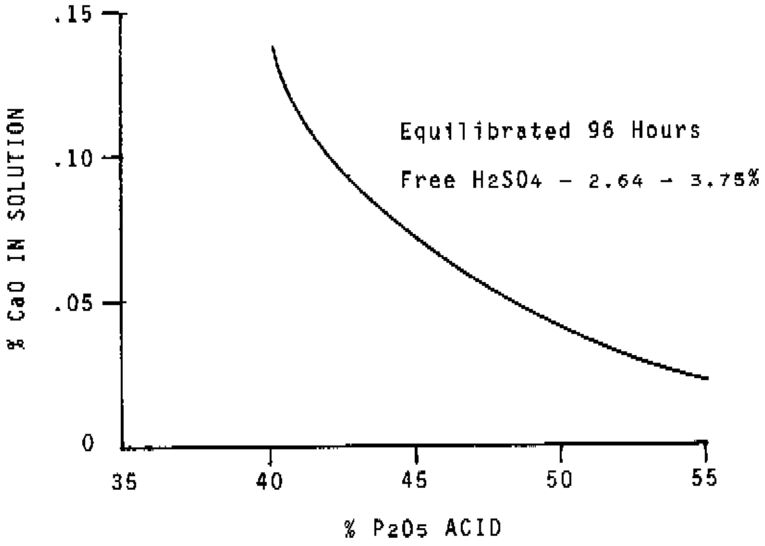
CaO SOLUBILITY IN 42% $P_2O_5$ ACID VS. FREE $H_2SO_4$ @ 82° C

FIGURE 5



CaO SOLUBILITY IN 54% $P_2O_5$ ACID VS. FREE $H_2SO_4$ @ 82° C

FIGURE 6



CaO SOLUBILITY VS. $P_2O_5$ CONCENTRATION @ 82° C

FIGURE 7

FIGURE 8

SOLUBILITY OF SODIUM AND POTASSIUM FLUOSILICATES

IN PHOSPHORIC ACID @ 73°C

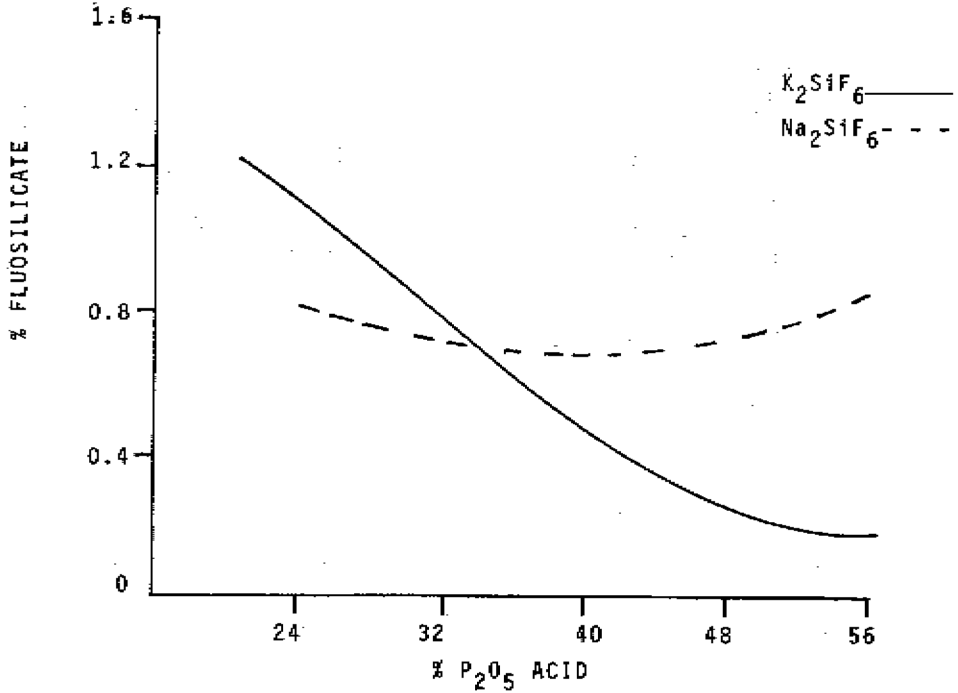
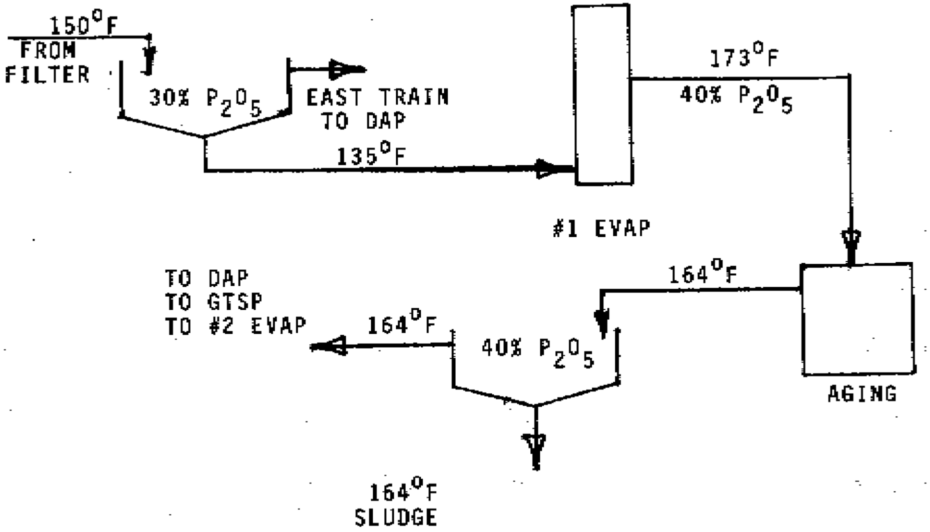


FIGURE 9

NEW WALES

40% CLARIFICATION CIRCUIT



## TABLE III

## CHEMICAL ANALYSES OF ROCK AND STREAM COMPONENTS

## IN 40% CLARIFICATION SYSTEM A

| | W.B. $P_2O_5$ | D.B. $P_2O_5$ | SS | CaO | $SO_3$ | $Fe_2O_3$ | $Al_2O_3$ | MgO | F | $Na_2O$ | $K_2O$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ROCK FEED TO ATTACK | 30.90 | 31.14 | -- | 45.77 | 2.60 | 1.59 | 1.23 | 0.50 | 3.66 | 0.60 | 0.07 | 0.78 |
| #1 EVAP. PRODUCT | 40.10 | 60.40 | 2.03 | 0.57 | 2.83 | 1.72 | 1.48 | 0.54 | 2.53 | 0.22 | 0.11 | 33.69 |
| #2 EVAP. FEED | 41.19 | 62.43 | 1.43 | 0.25 | 2.25 | 1.73 | 1.44 | 0.54 | 2.22 | 0.11 | 0.08 | 34.03 |
| 40% CLARIFIER U.F. | 37.42 | 52.46 | 11.64 | 2.37 | 5.01 | 1.56 | 1.57 | 0.64 | 4.25 | 0.60 | 0.52 | 28.68 |
| % REJECTION TO U.F. BY MASS BALANCE | 12.5 | -- | -- | 62.7 | 29.5 | 11.4 | 14.2 | 15.8 | 25.2 | 57.7 | 30.4 | |

A COMPOSITE OF EAST AND WEST TRAINS

# TABLE IV

## ANALYTICAL DATA

## PILOT FILTER TESTS - 1977

WT%

| | TOTAL $P_2O_5$ | WS $P_2O_5$ | S.S. | $Fe_2O_3$ | $Al_2O_3$ | $Na_2O$ | $K_2O$ | MgO | F | CaO | $SO_3$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FEED | 33.0 | X | 15.2 | 1.14 | 1.36 | 1.25 | 0.28 | 0.72 | 4.76 | 3.71 | 6.74 | X |
| PRIM. FILT. | 38.5 | X | 1.1 | 1.46 | 1.19 | 0.12 | 0.04 | 0.57 | 2.56 | 0.26 | 2.16 | X |
| WASH FILT. | 29.2 | X | 0.8 | 1.16 | 1.00 | 0.14 | 0.05 | X | 2.46 | X | 1.81 | X |
| CAKE | 3.4 | 2.8 | X | 0.07 | 1.39 | 5.53 | 1.71 | 1.07 | 12.74 | 15.64 | 21.7 | 27.5 |
| WASH WATER | 0.68 | X | X | 0.04 | 0.02 | 0.2 | X | 1.01 | | 0.04 | 0.39 | X |

THESE DATA REPRESENT AVERAGE ANALYSES FROM MANY TEST RUNS.

TEST DURATION RANGED FROM 6 HOURS TO 5 DAYS.

## TABLE V

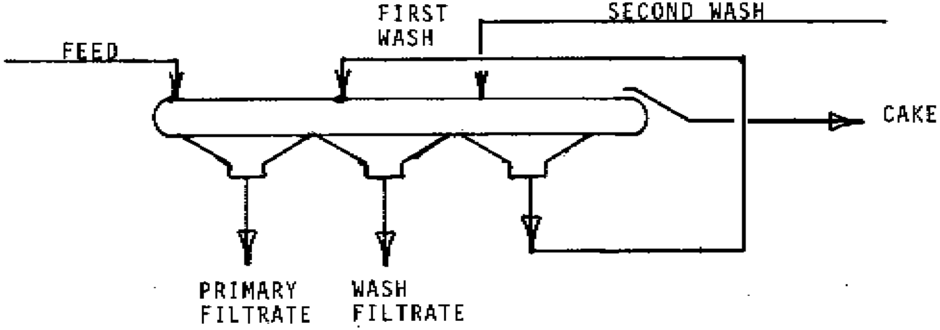
## PROJECTED SPECIE REJECTION IN CAKE AS % OF SPECIE FED TO 40% CLARIFICATION SYSTEM

| SPECIE | % REJECTED |
|---|---|
| $P_2O_5$ | 0.26 |
| CaO | 48.9 |
| $SO_3$ | 19.4 |
| $Fe_2O_3$ | 0.15 |
| $Al_2O_3$ | 2.9 |
| $Na_2O$ | 51.5 |
| $K_2O$ | 41.5 |
| MgO | 5.1 |
| F | 12.4 |

## FIGURE 10

## 40% UNDER FLOW FILTER

## PROCESS FLOWSHEET



| | FEED | PRIM.FILT. | 1st WASH | 2nd WASH | WASH FILT. | CAKE |
|---|---|---|---|---|---|---|
| gpm | 185 | 135 | 58 | 44 | 70 | - |
| ton/hr | 73.97 | 50.6 | 14.5 | 71 | 23.4 | 110 |
| %$P_2O_5$ | 35.8 | 38 | 13 | 0.6 | 30 | 3.5 |
| ton/h/$P_2O_5$ | 26.51 | 19.2 | 1.9 | 0.07 | 7.0 | 0.38 |