International Fertilizer Industry Association

IFA Technical Conference

The Hague, The Netherlands
6-8 October 1992

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

UTILIZATION OF PHOSPHATE ROCK FROM THE SOUTHERN EXTENSION OF THE BONE VALLEY DEPOSITS

B. M. Blythe, S. M. Janikowski and D. W. Leyshon

Jacobs Engineering Group Inc., USA

INTRODUCTION

This paper is one of a series of papers by Jacobs dealing with the utilization of lower grade rock to make phosphoric acid. Jacobs other recent papers on this subject have dealt with problems related to rock from Venezuela, China and Montana (1)(3).

This paper will deal with the use of Florida rock from the Southern extension of the Bone Valley deposits. The area involved is shown in the MAP, Figure 1.

The area to the North has been the source of most of the rock mined in Florida. The area to the south roughly bounded on the north by the Hillsborough/Polk County lines is somewhat different in geology. The gen[illegible]ed geological section of the Central Florida area is shown in Figure 2. A similar sketch for the South Florida area is shown in Figure 3. The layer of deep, well defined phosphate is missing from this profile and the phosphate is somewhat older, less weathered and is interspersed with dolomite.

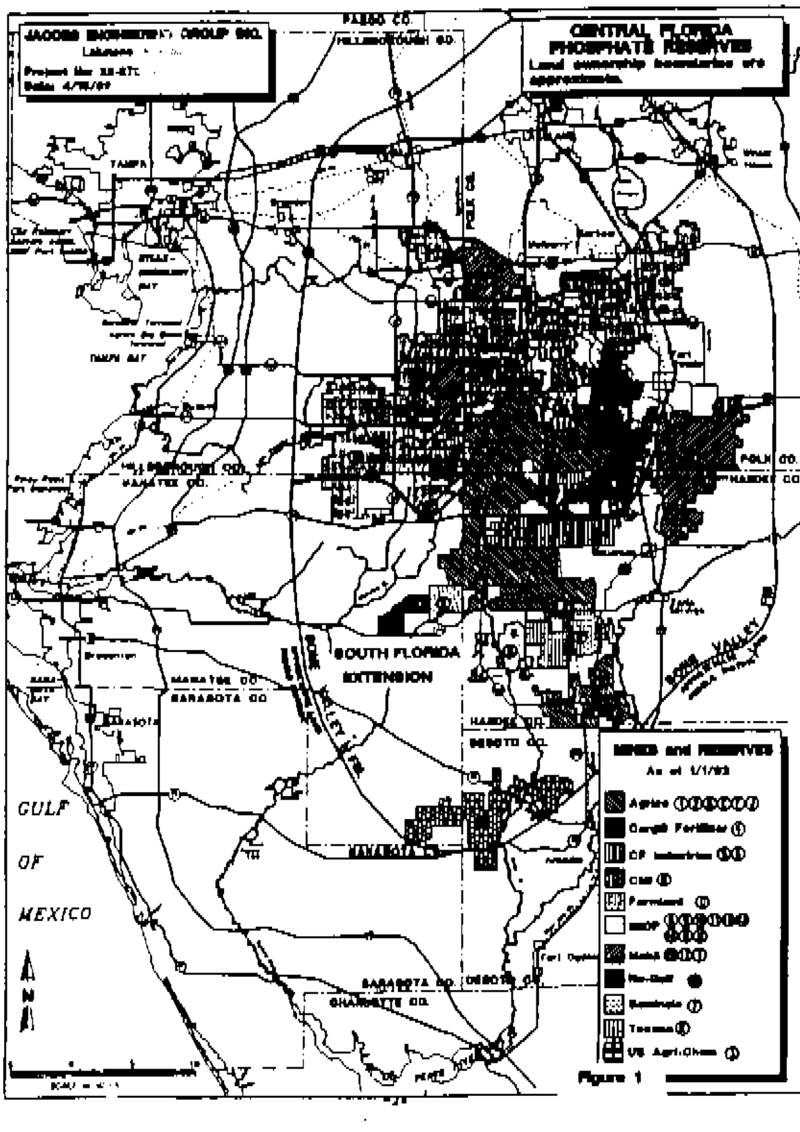

Figure 1

GENERALIZED GEOLOGIC SECTION IN THE CENTRAL FLORIDA PHOSPHATE DISTRICT

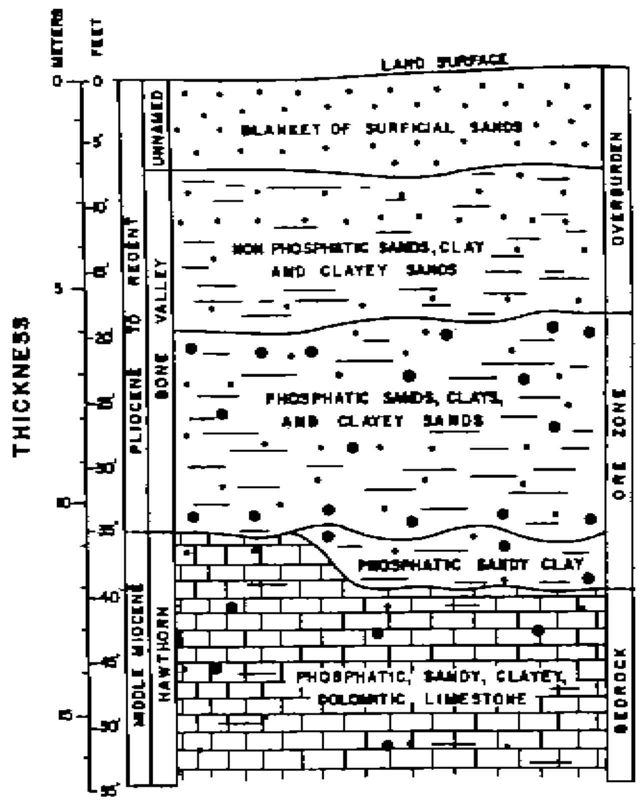

Figure 2

GENERALIZED GEOLOGIC SECTION IN THE SOUTH FLORIDA AND THE NORTH FLORIDA/SOUTH CENTRAL GEORGIA AREAS

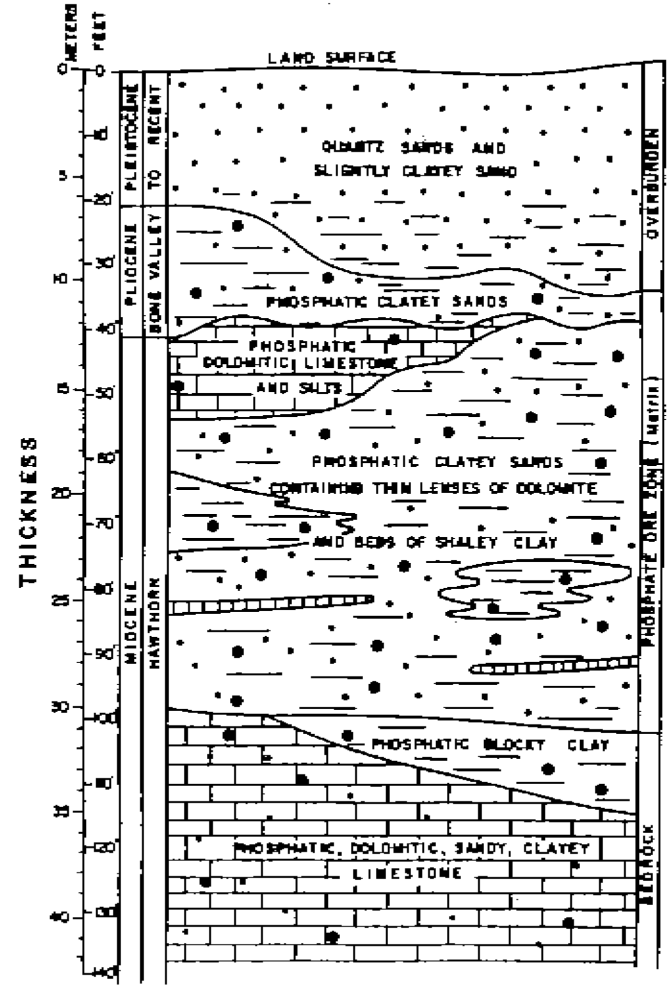

Figure 3

The work reported here is an evaluation by Jacobs of the rock of one company, referred to here as Company "X". A comprehensive multi producer study has been undertaken by the Florida Institute of Phosphate Research entitled "Characterization of Future Florida Phosphate Resources". This work is currently in its early phase of geological and mineralogical study. The program is being done in-house by FIPR with initial findings due out in 1993.

Beginning in the early 1980's, many Florida producers began to treat rock containing more impurities, particularly silica and Mg0 and began to become concerned with future even lower grade rock.

Bauman (2) described the work by IMC in 1978 to evaluate the effect of higher magnesium on both the phosphoric acid plant and the granulation plant.

Present Florida rock, in general, is known to be easily handled in making phosphoric acid, producing a very filterable gypsum, a relatively strong P_2O_5 acid, relatively high yields and an acid that granulates well. It produces conditions of low corrosivity when making acid and is moderate in sulfuric acid consumption.

This paper will deal with pilot plant tests done on 4 rock samples. These are:

Central Florida Commercial Plant Feed
A more or less typical Florida rock currently processed by Company "X".

Central Florida Low Grade Pebble
A rock which could be available in the future by mining into the Hawthorne layer. Known to be high in magnesium.

South Florida Pebble
Comprises about 45% of this deposit's product. It might need to be treated by itself in the future.

South Florida Blend
A mixture of 46% pebble, 54% concentrate - this is run-of-mine.

The fact that the pebble is as high as 45% of the total indicates this rock is not truly like the deposit geology shown in Figure 3, which runs much lower in pebble. Therefore, we can say that not all South Florida phosphate rock will be significantly different compared to the past Central Florida material. Much of the export rock probably will be similar to current supplies, at least over the next decade and more like the present Florida rock than any other. It is expected to maintain the better qualities, good gypsum filtration rate, etc., that Central Florida rock is known for, as cited above. The world rock market is declining; rock P_2O_5 is being replaced by phosphoric acid and DAP. Therefore, it is expected that Florida will be able to maintain its quality for the 8.0 to 10.0 million tons of rock shipped out, but the local producers will be called upon to consume larger quantities of "garbage".

As we will see in these tests, some of the rock to be mined by Company "X" over the next 10 years will not be all that bad.

Evaluation Program

To explore the characteristics of Company "X's" South Florida future rock, Jacobs did a rather substantial study incorporating commercial in-plant tests and pilot plant tests for comparison of current performance with expected future performance.

The program used as control, the present performance of a large Prayon phosphoric acid plant, and compared this with pilot plant tests using the same rock and similar operating conditions as run during the commercial plant study.

Jacobs and Dorrco earlier have, over the years, done other similar formal and informal studies to compare pilot plant performance with commercial plant performance. The tests reported here add to that data base.

Rock Preparation

The Central Florida commercial plant rock was received dry and ground as it was being fed to the commercial plant. It was a composite of rock samples taken over the period of time the filter leaf tests were taken in the plant, about 56 hours.

The Central Florida low grade pebble was received as 4,100 pounds (3,270 lb dry) of matrix as drill cores. The cores were sampled and processed through a Jacobs pilot plant core washer. The deslimed sample was then oven dried and rod mill ground.

The South Florida matrix core samples totalled 7,340 pounds wet (5,970 pounds dry) and were processed through the Jacobs pilot plant core washer and split into washed pebble and flotation feed. The flotation feed was then put through Jacobs' float pilot plant which used the two stage fatty acid/amine process to make a concentrate. Two samples were then produced for acidulation tests. One consisted of pebble only, the other was a blend of pebble and concentrate, about 46% pebble, 54% concentrate. The two samples were also rod mill ground so that all phosphoric acid pilot plant feeds were ground as nearly the same as we could make them. See Table 1 for the size analyses. As the pilot plant tests progressed, head samples were taken and the chemical analyses of the feed are reported in Table 2.

Filtration Tests on the Commercial Plant

Twelve filtration tests were carried out alongside the commercial plant phosphoric acid plant filter to provide a basis for comparison between the production plant and the pilot plant. Such a comparison makes possible the interpretation of pilot plant results in terms of production plant performance.

The filtration test procedure used was similar to that used in the pilot plant. The filtration tests were carried out in a test filter of 3.0" diameter, using a polypropylene 250 cfm filter cloth (N227-047-25 National Filter Media) and 20" vacuum. The feed slurry and the washes were taken from the filter feeds and were used at the plant temperatures. Three weights of slurry were used to provide a range of cake thicknesses. The resulting feed conditions were:

Slurry Weight, g	600	750	900
Wash Acid:			
Volume, mL	134	168	201
Specific Gravity		1.050 to 1.096	
Temperature		61 to 69°C	
Pond Water:			
Volume, mL	164	205	246
Specific Gravity		1.017 to 1.028	
Temperature		60 to 69°C	

The filtered cakes were repulped in clean water, refiltered and washed to extract the water soluble P_2O_5. The cakes were then washed with methyl alcohol and oven dried. The wash liquors and the dried cakes were sent to Jacobs laboratory in Lakeland for analysis. This method of analysis gives true citrate soluble and water soluble losses because no significant amount of gypsum dissolves. Plant conditions during the filter tests are noted in Table 3.

Table 1

SIZE ANALYSES OF THE PILOT PLANT FEEDS

Tyler Screen No.	Company "X" Central FL Commercial Plant Feed	Company "X" Central FL Low Grade Pebble	Company "X" South Florida Pebble	Company "X" South Florida Blend
	%	%	%	%
14	.02	.01	0	0
20	.11	.07	.03	0
28	.37	.47	.28	.02
35	1.91	3.02	2.45	.36
48	6.24	8.78	7.97	2.77
65	13.82	16.59	16.22	9.51
100	28.29	29.88	30.11	26.51
150	39.08	39.52	40.18	38.51
200	48.25	48.61	49.61	47.80
-200	51.75	51.39	50.39	52.20
TOTAL	100.0%	100.0%	100.0%	100.0%

Notes

(1) -200 fraction obtained by wet screening of a 200 g sample.
All other fractions by dry Ro-tap of the remainder.

(2) All feeds were screened through a 14 mesh screen before sampling and feeding to the plant.

The oversize was 0.5% to 0.7% of the total. It was rejected in order to avoid mechanical problems with the rock feed system.

Table 2

CHEMICAL ANALYSES OF THE PHOSPHATES

	Company "X" Central FL Commercial Plant Feed	Company "X" Central FL Low Grade Pebble	Company "X" South Florida	
			Pebble	Blend
	%	%	%	%
BPL	69.21	63.12	60.87	64.94
P_2O_5	31.68	28.89	27.86	29.72
CaO	44.92	46.21	42.01	43.86
MgO	0.37	1.92	0.41	0.49
Fe_2O_3	1.07	0.93	0.84	0.92
Al_2O_3	1.11	1.09	0.98	1.00
Na_2O	0.49	0.55	0.62	0.63
K_2O	0.09	0.10	0.11	0.11
F	3.90	3.09	3.04	3.22
Cl	0.04	0.02	0.03	0.03
SO_3	0.83	1.07	1.10	1.18
CO_2	3.61	7.75	4.09	4.22
Organic C	0.19	0.24	0.30	0.31
Other Volatiles(1)	2.09	2.41	2.26	2.41
Soluble SiO_2	0.58	0.50	0.50	0.56
Acid Insoluble	9.98	7.59	15.85	10.97
TOTAL	100.95	102.34	100.00	99.63
Minus O = F + Cl(2)	1.65	1.30	1.28	1.35
% Accounted for	99.30	101.04	98.72	98.28
Total SiO_2	8.22	7.57	13.95	9.84
Acid Insoluble SiO_2	7.674	7.07	13.45	9.29
Moisture (3)	1.63	0.96	0.79	0.96
LOI 1000°C	5.89	10.40	6.62	6.94
CaO/P_2O_5	1.42	1.60	1.51	1.48
$I\&A/P_2O_5$	0.069	0.070	0.065	0.065
$(MgO + I\&A)/P_2O_5$	0.080	0.136	0.080	0.081
F/SiO_2 (Acid Soluble)(4)	6.74	6.12	6.08	5.85
F/SiO_2 (Total)(4)	0.47	0.41	0.22	0.33

NOTES

(1) Other volatiles = LOI - CO_2 - Organic C

Phosphoric Acid Pilot Plant Tests

The pilot plant used for the digestion and filtration tests is shown diagrammatically in the illustration on the next page. A single stirred tank reactor made of 316L stainless steel was used. The liquid volume in the reactor was approximately 9 liters. The reactor was fed with 80% sulfuric acid, phosphate rock and return acid. Liquid feeds were by means of peristaltic pumps. The rock was preweighed, fed by screw feeder and dispersed into the reactor slurry by means of the smaller agitator which is used for measuring corrosion/erosion.

Filtration of the slurry for the production of product acid and return acid was done using a Buchner filter which was moved from vacuum flask to vacuum flask so as to simulate qualitatively the operation of a full scale phosphoric acid plant filter. The filtration rate data reported was derived from the same filter test procedure used in the commercial plant tests. The conditions of the filter tests are described below.

Operating conditions, filtration rates and P_2O_5 losses were plotted on a graphical chronological log of the tests. An example is shown in Figure 5.

Test Run Conditions

The test runs were carried out under the following conditions:

Rock Feed:	
Commercial Plant Feed	900 g/h
Central Florida Pebble	995 g/h
South Florida Pebble	1040 g/h
South Florida Blend	960 g/h

The rock feed rates were calculated in each case to give approximately the same feed rate of P_2O_5 to the reactor.

Sulfuric acid feed:	80% H_2SO_4 at room temperature
Reactor temperature:	75 - 77°C (167 - 171°F)

The other controlled variables were shown on the graphical data logs for each run.

The conditions of the filtration tests were standardized as follows: -

Test filter:	3.03" diameter, 1/20th of a ft^2 area
Vacuum:	20" of mercury
Weight of Slurry:	750 g
Wash Acid:	
Volume	190 mL
Specific gravity	1.05
Temperature	60°C
Wash water (tap water)	
Volume	190 mL
Specific gravity	1.00
Temperature	60°C
Drying intervals between washes:	5 seconds
Drying time after last wash:	20 seconds

The graphical data log for the Central Florida Low Grade Pebble is shown on Figure 5. Two effects of high magnesium can be seen on the plots:

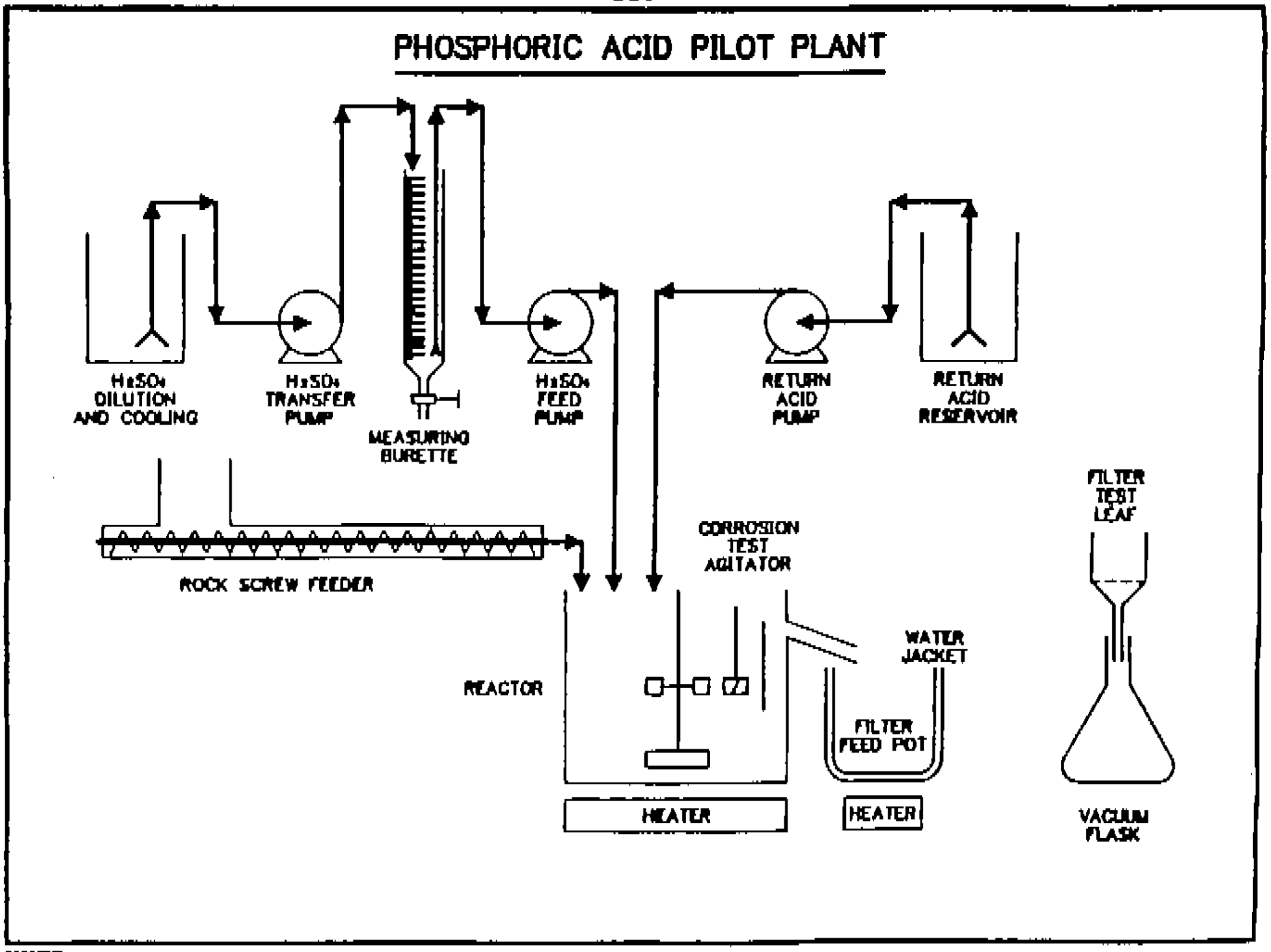

Figure 4

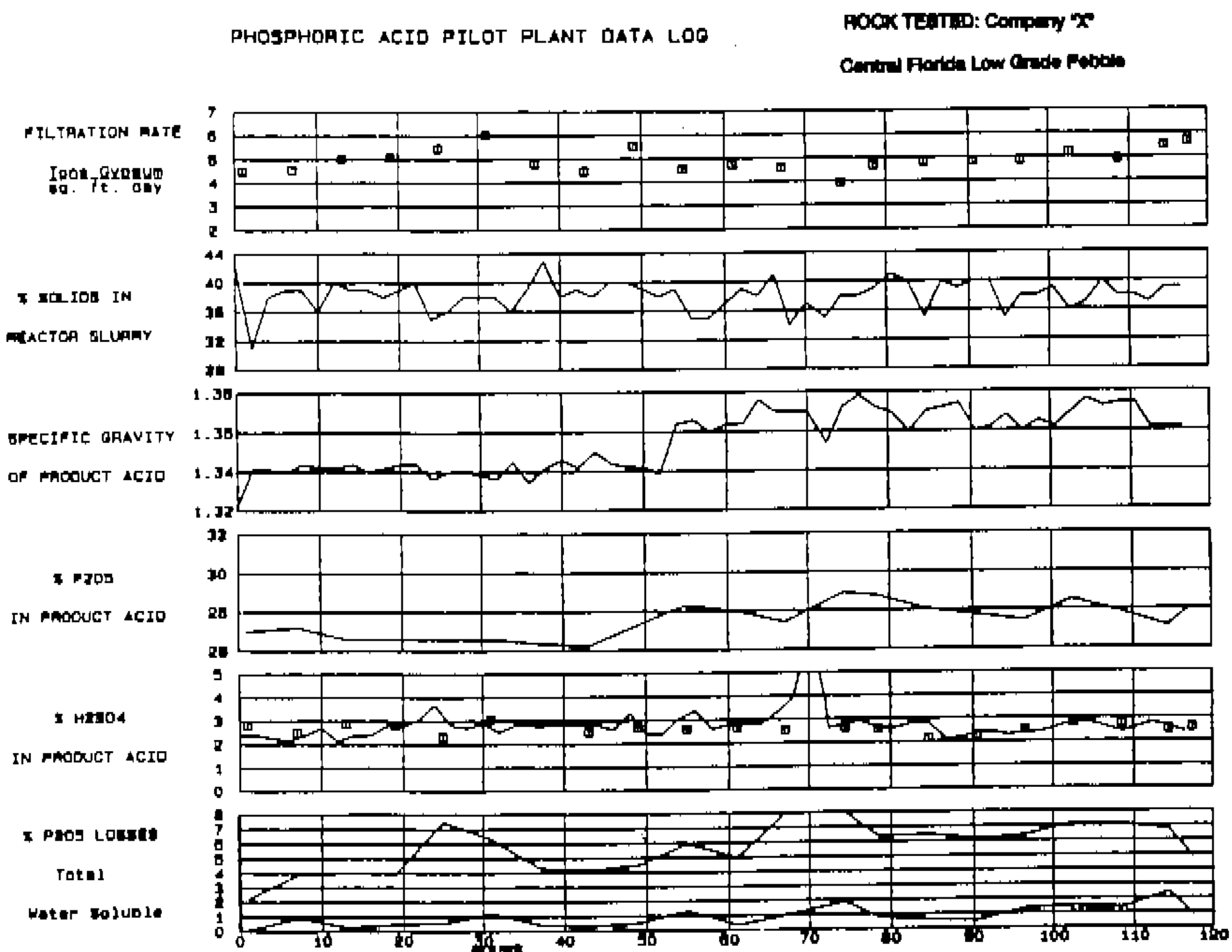

Figure 5

- The plant was operated at first with an acid specific gravity corresponding to 28% P_2O_5 when using normal Central Florida rock. Actual P_2O_5 analyses, received some 50 hours into the run, showed a P_2O_5 content below 27% at this specific gravity. The target specific gravity was then adjusted to give 28% P_2O_5. The higher specific gravity was caused by the higher impurity level.

- At this higher impurity level in the acid, the control of sulfate in the acid becomes more difficult, and 68 hours into the run sulfate control was lost. A reduction in the target sulfate level remedied this problem for the last 40 hours of the run.

Tests Results

Tables 3 and 4 are a summary of test run averages and results. One result that stands out is that the gypsum filtration rates for all rocks were relatively similar. There is logic to this as will be discussed below. However, it is worth mentioning here that although these tests were very close on the basis of tons of gypsum/m^2/day, we have seen variations in previous tests on other rocks of as much as 2:1 in filtration results.

It is necessary to discuss some of the factors related to the losses shown in Tables 3 and 4.

The normal citrate soluble loss for pilot plant tests is about 2.5% of the P_2O_5 fed due to the configuration of the reactor vessel. The Prayon commercial plant configuration is such that citrate soluble losses are about 3.5%. The tests indicate that the South Florida pebble and Sough Florida blend give a similar C.S. loss when compared to Central Florida rock. The high magnesium Central Florida low grade pebble, however, gave very high C.S. losses. This seems to be a characteristic of high magnesium rock and is similar to results obtained by Bauman (2).

The high magnesium rock also shows abnormally high citrate insoluble loss. Normal water soluble losses for pilot plant tests are about 0.3% to 0.5% of the P_2O_5 fed. Because of the inefficiencies of a commercial plant filter compared to the test leaf, plant losses would be about 1.5% P_2O_5 or higher on the basis of repulped slurry samples. Cake samples from commercial filters always understate true water soluble losses by at least 1%. Therefore, it is likely that the commercial plant losses for the Central Florida low grade pebble would be about 4% or possibly more above current plant levels. 1.0% is increased insoluble P_2O_5 (c.s. + c.i.) and 2.0% is predicted as extra water soluble loss.

For this particular owner, the bulk of future rock supplies will come from the South Florida reserves that compares favorably with their previous Central Florida rock.

Table 3

Run Averages

	Company "X" Central Florida Commercial Plant Feed		Company "X" Central FL Low Grade Pebble	Company "X" South Florida	
	Plant Site	Pilot Plant		Pebble	Blend
Duration of Run		95 hrs	118 hrs	98 hrs	94 hrs
Period Averaged	2 days	13-95	80-117.5 hrs	50-98 hrs	50-94 hrs
% P_2O_5 in Rock	31.68	31.68	28.89	27.86	29.72
Operating Conditions					
Retention, hrs.	3.5[(1)]	4.2	3.6	3.7	4.0
Reaction Volume cu. m/mtpd P_2O_5	1.30[(1)]	1.52	1.55	1.49	1.51
Plant Analyses:					
% H_2SO_4	2.5	2.50	2.62	2.79	2.55
Acid s.g.	1.34	1.326	1.368	1.351	1.340
% Solids in slurry	40	39	38	39	38
Lab Analyses:					
% H_2SO_4	2.5	2.38	2.51	2.39	2.00
% P_2O_5	27.75	27.49	27.82	29.15	28.18
Filter Tests					
% Solids in slurry	35.5	37.1	35.9	35.6	35.6
% Solids in cake	76.3	79.4	75.4	77.0	75.2
S Tons Gypsum/ft^2/day (mt/m^2/day)	5.26(51.5)	4.98(48.7)	5.11(50.0)	5.12(50.1)	5.08(49.7)
S Tons P_2O_5/ft^2/day (mt/m^2/day)	1.06(10.4)	1.02(10.0)	0.90(8.80)	0.93(9.1)	1.03(10.1)

NOTE [(1)]

The retention time and the reaction volume per ton of P_2O_5 shown for the commercial plant are based on a production rate of 850 stpd P_2O_5. The rock feed rate to the plant varied during the test period. This variation was equivalent to instantaneous production rates of about 700 to 900 stpd P_2O_5.

REFERENCES:

(1) Enriquez, J. M., Leon, V. E., Leyshon, D. W.
"The Use of Lower Grade Phosphate Rock in Phosphoric Acid Production",
American Chemical Society, Washington, D.C., August 1992.

(2) Bauman, A. N., Nielson, F. T., Surber, J. H., Yarnell, J. J.
"Process Improvements in Manufacture of Wet Process Acid from Florida Phosphate Rock of Various Compositions"
IFA (ISMA) Orlando, Florida, October 1978.

(3) Enriquez, J. M., Leon, V. E., Leyshon D. W.
"Treatment of Lower Grade Phosphate Rock During Phosphoric acid Production, British Sulphur Latin America Fertilizer Conference, Palm Beach, Florida, April. 1992.