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BENCH-SCALE STUDIES OF UTILIZATION OF PROBLEM ROCKS IN WET-PROCESS PHOSPHORIC ACID PRODUCTION

by

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Introduction

The International Fertilizer Development Center (IFDC) has been concerned with the use of indigenous phosphate rocks since its inception in 1974. IFDC's program regarding phosphate rocks was introduced at the last ISMA Technical Conference (1). That paper discussed the usage of several types of phosphate rocks representing potential sources of indigenous phosphate supplies for developing countries. In particular, it dealt with the difficulties in physical or chemical beneficiation or processing associated with phosphate rocks of different chemical and mineral compositions. For example, it was pointed out that certain high-silica rocks might be more economically processed directly into phosphoric acid without physical beneficiation. Other rocks discussed included those high in iron and aluminum oxides and/or hydroxides, organic matter, carbonate, and chloride.

At the heart of IFDC's phosphate rock program is a characterization program which falls into two parts. When a new phosphate rock is received for study, a thorough chemical and mineralogical study of a representative sample is first made. Up to now, IFDC has contracted these studies to the Tennessee Valley Authority (TVA). These studies evaluate the potential of the rock for different fertilizer uses and identify physical or chemical factors which may affect utilization.

When further processing is recommended, it is generally necessary to verify the behavior of the phosphate rock in beneficiation and acidulation processes. The evaluation of the recommendations of the characterization study constitutes the main effort of the second part of these studies.

One phase of this study is to determine the behavior of various phosphate rocks in phosphoric acid manufacture. IFDC constructed a bench-scale unit for this purpose. This paper describes some of the results obtained in this unit during the past year. The rocks described are: (1) Pesca (Colombia), (2) Hazara (Pakistan), (3) Araxa (Brazil), and (4) uncalcined North Carolina (United States).

Other phases of evaluation include beneficiation, production of thermal phosphates, and use as direct application phosphate sources; however, none of this work is described in this paper.

Description of Process and Equipment

To serve the purposes of IFDC's characterization program, a bench-scale wet-process phosphoric acid unit was designed according to specifications particular to IFDC's requirements. An important specification was that the unit must be small to allow the characterization with a minimum quantity of rock. The shipment of large quantities of rock is a disadvantage of larger units. Another important specification was that industrial-scale operations be simulated as closely as possible, in order to obtain meaningful data. The unit was to operate according to the dihydrate process, as this is the most conventional process in industry.

The bench-scale unit (figure 1) was designed according to the above specifications. It has a single tank reactor without compartments, coupled with a batch filtration system. This is complemented with clarification and concentration equipment. A single-tank reactor is ideal for a small-scale operation, as it avoids the complications of stages, compartments, and slurry recirculation. When slurry recirculation is high, the conditions in a reactor with compartments approach those of a single-tank reactor without compartments as there are essentially no concentration or temperature gradients in either system.

The slurry is not pumped at all in the bench-scale unit (the slurry is withdrawn from the reactor by a vacuum suction device). Avoiding slurry pumping on a small scale is important, as the gypsum crystals could be damaged otherwise.

The reaction mixture does not contact any metal, glass, or ceramic material, which would disturb the metal, fluorine, or silica balances in the system.

In the reactor, phosphate rock reacts with sulfuric acid in a 30% P_2O_5 phosphoric acid medium. The sulfate ion concentration is usually around 2% in the reaction slurry and the solids content may vary from 30%-40%, depending on the feeding and evaporation rates and the rock composition. In addition, the reactor temperature is controlled at 72°C and the residence time of slurry in the reactor is 5-6 hours. The reactor will hold up to 10 liters of slurry.

The batch filter is operated to simulate a three-wash tilting pan filter. The filtration data obtained are empirically corrected to correspond to an industrial-scale filter. It has been demonstrated industrially that with some rocks, a two-wash system can improve filtration rates without incurring greater water-soluble P_2O_5 losses. IFDC has adopted the more conservative three-wash system in view of the many unusual rocks it is likely to be testing.

The unit is operated in such a way as to enable important parameters to be assessed. Some of the technically and economically important characteristics of rocks evaluated for phosphoric acid production include the following: P_2O_5 recoveries, sulfuric acid consumption, filtration rates, quality of the acid, quality of the byproduct filter cake, process corrosiveness, foaming properties, and mass balances on important impurities. Because of the size of the unit, there are certain characteristics which may not be similar to those obtained in an industrial-scale plant. These are mainly associated with the geometrical limitations of the reactor and are the related evaporation rate, fluorine and silica balances, defoamer consumption, and effect of erosion. Other than these factors, data collected in this bench-scale unit for the major parameters are consistent with industrial experience. In the discussion of test results, the effects of geometrical factors in the reactor design on defluorination, etc., are considered. Geometrical limitations also affect impeller tip speeds, Reynolds number, and power inputs by unit volume in small and large reactors (table 1). The theoretical implications are that contacting of the rock with acid is better and erosion of impellers is higher in a large plant.

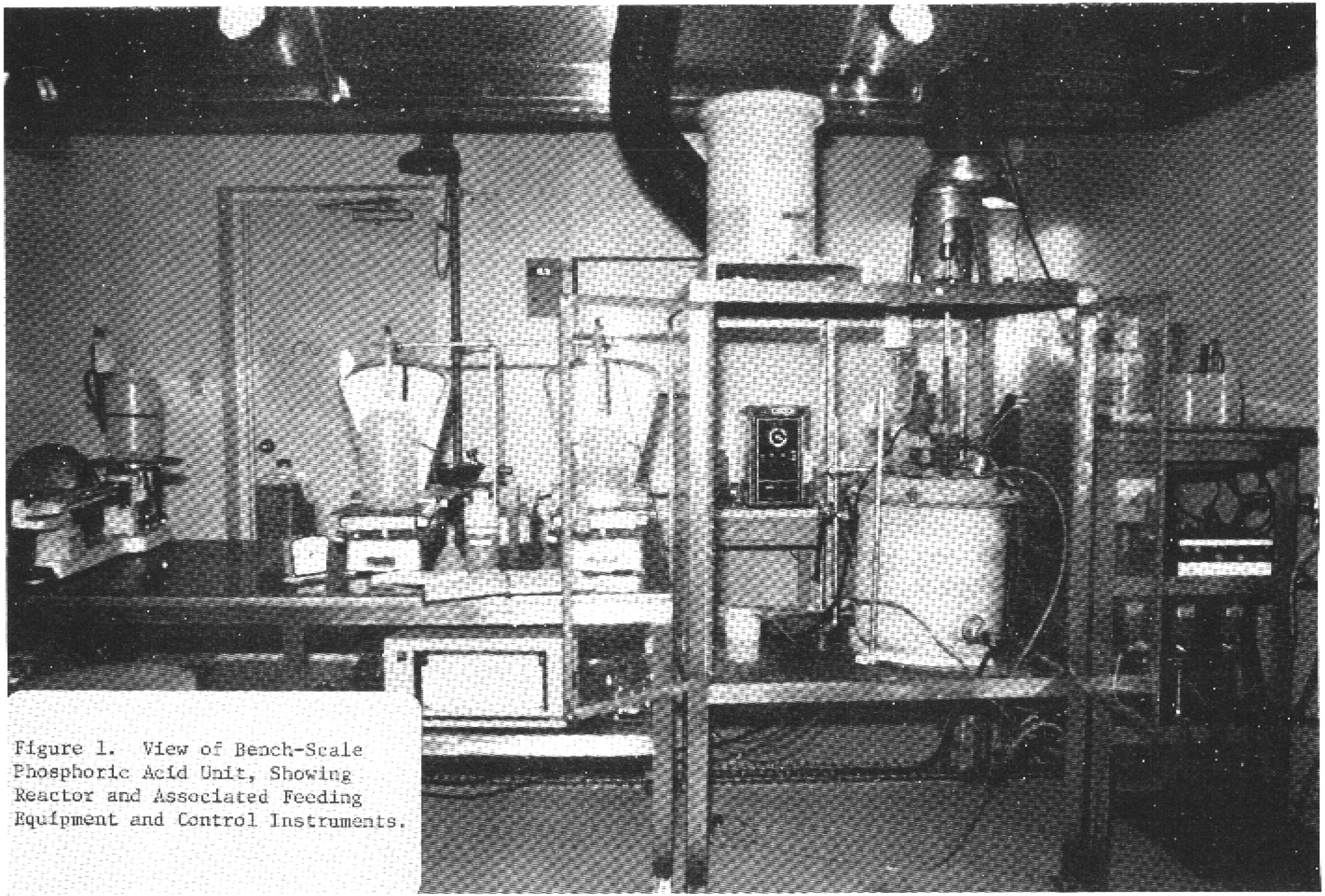

Figure 1. View of Bench-Scale Phosphoric Acid Unit, Showing Reactor and Associated Feeding Equipment and Control Instruments.

Table 1. Comparative Agitation Parameters in the Bench-Scale Unit and in an Industrial-Scale Phosphoric Acid Plant

	Bench-Scale Unit	Industrial-Scale Plant		
Filter acid production rate	0.5 liter/hour	156,000 liter/hour		
Agitation	Central	Fast	Medium	Slow
Impeller tip speed	1.7 m/s	6.3 m/s	3.9 m/s	1.6 m/s
Reynolds number	7,700	64,000	40,000	16,000
Power input, kW/m^3 slurry	4	1	1/2	1/4

The capacity of the unit is 100-150 g/hour of P_2O_5, or approximately 0.5 liter of 30% P_2O_5 phosphoric acid/hour. A preliminary characterization test lasts up to 100 hours. Thus, about 50 kg of rock are required for such a test. It is, of course, essential that such a sample be representative of the deposit of interest and that it be well homogenized before testing.

Operation of the unit may be intermittent, being comprised of an 8- to 16-hour feeding shift and a complementary night shift in which the reaction temperature and slurry contents and concentrations are kept constant. In this mode of operation, defluorination is higher and reaction efficiencies may be slightly higher than with a continuous operation. Other material balances, filtration rates, and gypsum morphology are not, in our experience, affected in the intermittent operation mode.

When starting a test with a new rock, it is necessary to operate for some time before the new chemical and gypsum crystal equilibria are reached. Because the initial slurry and recycle acids were obtained in previous tests, usually with different phosphate rocks, the first 30 hours of operation are taken as the transition period. It can be demonstrated that this transition time is adequate to replace 98% of the original slurry and that the chemical composition of the slurry reaches the new equilibrium. Microscopic observations are used to check whether gypsum crystal growth has reached steady state in the transition time. Specific surface area measurements (made by the BET method) also are used as an indication that equilibrium has been attained. Data are considered characteristic of the new rock when chemical and crystal equilibria are reached.

The analytical methods for process control are fast plant control methods. For the chemical characterization of the product acid and byproduct gypsum, quality control methods are used. Furthermore, the phosphoric acid unit has the support of various analytical and instrument laboratories to provide specialized capabilities as needed.

The resistance of various common stainless steels to corrosion and erosion in the reactor is studied carefully. The alloys which were studied in this work are AISI 316, AISI 317L, Carpenter 20 Cb-3, and Jessop 700; these steels were selected as being typical of stainless steels used in phosphoric acid plant design. The composition of these steels and other steels commonly found in phosphoric acid plants are given in table 2. Jessop 700 is seen to be similar in composition to several other steels found in phosphoric acid plants (with the exception of copper content), but which were not tested in the present studies. AISI 316 serves as a useful comparison between different rocks, as it is very sensitive to the corrosiveness of a phosphoric acid slurry.

The reactor agitator shaft is made of plastic and is fitted with stainless steel blades which serve as corrosion specimens and which may be removed for ease of study. Different alloys are used simultaneously on the agitator. These corrosion tests can be amplified in IFDC's specialized corrosion laboratory.

Following filter acid production, clarification of filter acid, concentration to about 54% P_2O_5, and clarification of the concentrated acid are studied. Typical problems studied include post-precipitation after desaturation and defluorination. The clarification test for filter acid consists of material balances on the clarified acid and sludge fractions after standing 24 hours at 60°C. The concentration of the acid from 30% P_2O_5 to 54% P_2O_5 is done batchwise, under vacuum. The clarification test of the 54% P_2O_5 acid consists of material balances on the clarified acid and sludge fraction formed during storage for 3 and 7 days at 55°-60°C. Longer periods of storage at ambient temperatures should be studied if it is expected that the product will be exported.

It is necessary to note that the behavior of every rock described here was characterized under closely similar conditions, but no optimization study was conducted. This means that the results obtained are typical of each rock but not optimal. Optimization work and choice of the best process and process conditions for a particular rock are within the scope of IFDC's work but constitute a separate problem which is not dealt with in this paper.

Table 2. Typical Compositions of Some Stainless Steels Commonly Used in Phosphoric Acid Plant Design

Steel	Cr	Ni	Mo	Cu	C_{max}	Important Minor Constituents
AISI 316	18	11	2.5	-	0.08	-
AISI 317L	20	14	3.5	-	0.03	-
Ferralium	25	5	2	3	0.06	-
Carpenter 20 Cb-3	20	34	2.5	3.3	0.07	Nb + Ta
Jessop 700	21	25	4.5	-	0.03	Nb
Henricot HV-9A	20	25	4.5	1.5	0.04	Nb
Uddeholm 904L	20	25	4.5	1.2	0.02	Nb
Uranus B6	20	25	4.5	1.5	0.02	-

Description of Rocks Tested

IFDC has a bank of phosphate rocks from which the four described in this paper were selected. The problem rocks described here were ones which were considered amenable to sulfuric acid acidulation in a conventional dihydrate process. Pesca and Hazara rocks were selected as typical examples of rocks high in silica content. Araxa was selected as an unusual igneous rock. The uncalcined North Carolina rock was selected to investigate the generally well-known effects of high carbonate and high organic matter.

As shown in tables 3 and 4, Pesca phosphate is a high-silica rock, containing little other gangue. The petrographic study of this rock revealed that the phosphate is imbedded in the silica and that liberation sizes required for upgrading by flotation would cause high P_2O_5 losses in the fines fraction. Chemical beneficiation or direct acidulation seemed to be the appropriate route to follow in processing this rock. IFDC has carried out beneficiation studies; these studies confirmed that the beneficiation route would result in high P_2O_5 losses.

Table 3. Chemical Analyses of Phosphate Rocks Studied
(Figures in Weight %, Dry Basis)

Component	Pesca	Hazara	Araxa	North Carolina
P_2O_5	20.5	28.4	35.5	29.7
CaO	29.0	41.9	47.3	47.4
SiO_2	39.2	23.0	0.41	1.73
F	2.0^a	2.92	2.54	3.53
CO_2	3.0^a	1.1^a	1.7	4.18
Al_2O_3	1.1^a	1.0	0.32	0.53
Fe_2O_3	0.8^a	1.85	2.42	0.79
MgO	0.09^a	0.13	0.07^a	0.79
Na_2O	0.14^a	0.16	0.03^a	0.98
K_2O	0.14^a	0.31	0.10^a	0.17
Organic C	0.3^a	0.18	$<0.1^a$	1.38
Total S	0.1^a	0.18 (sulfide)	1.52 (sulfate)	1.1^a
Cl	0.001	0.03^a	0.001	0.015
BaO	ND	ND	7.17	ND
TiO_2	ND	ND	0.50	ND
SrO	ND	ND	1.0^a	ND

a. Complementary analyses from similar samples.
ND = not determined.

The Hazara phosphate deposits have been found to include both high silica- and high dolomite-containing ore bodies. Characterization studies of samples of both types are available to IFDC. Work is being carried out in Pakistan to assess the suitability of exploiting these deposits for local fertilizer manufacture. The main conclusions of the characterization study of the high-silica rock was that the silica could not be removed from the phosphate particles by physical beneficiation because of the tight bonding between phosphate and silica. Even after grinding, portions of the chert matrix are tightly bonded to the phosphate. Further grinding to release the silica results in large P_2O_5 losses as slimes. Direct extraction of the P_2O_5 in a phosphoric acid production process was indicated as a possible means of processing the rock. The presence of sulfides, which could pose corrosion difficulties, was noted in the chemical analysis of the rock.

Araxa phosphate is an igneous rock which is mined and beneficiated commercially. Mineralogical and chemical characterization of the concentrate indicated that further upgrading using heavy media separation to reduce the barite and ilmenite content could be feasible (table 4). Some of the concentrate is used currently for the production of single and triple superphosphate. There are reports that it also has been used for direct application and in fused phosphates (2). In the production of phosphoric

Table 4. Comparative Geology and Mineralogy of Rocks Studied

Description of Rock Deposit	Pesca	Hazara	Araxa	North Carolina
Deposit origin	Sedimentary	Sedimentary	Igneous	Sedimentary
Approximate grade of deposit (% P_2O_5)	20	20-30[a]	12-35	18
Estimated reserves (million tons)	53	20[a]	91 [6 million tons-- high P_2O_5 (>20% P_2O_5) low Fe_2O_3 (<5% Fe_2O_3)]	1,000-2,000
Mining operations	Deposit being considered for commercial development	Deposit being considered for commercial development	Commercial open pit mine	Commercial open pit mine
Beneficiation	--	--	Several stages, including crushing, grinding, flotation to 35% P_2O_5 grade	Washing, screening, flotation to 30% P_2O_5 grade
Apatite type	Francolite	Francolite	Hydroxy-fluorapatite	Francolite
Mineralogy of Sample Studied				
Apatite, %	52	75	87[b]	87[b]
Gangue materials in approx. order of concentration	Chert (∿20%) Quartz (∿20%) Clays Magnetite Goethite-limonite	Quartz) Chert)—∿20% Chalcedony) Clays Limonite Sulfide	Barite (∿10%) Goethite Ilmenite Dolomite Amorphous silicates	Organic C (∿1.5%) Quartz Illite clay Sulfide Calcite Dolomite Nonsulfide S Amorphous iron oxide

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a. Best estimate available.

b. Beneficiated sample.

acid it was expected that the barite would be inert in the process and would not interfere substantially with filtration. The main problems foreseen were that the silica-fluorine ratio is low, and corrosive conditions could be expected to prevail, primarily depending on the role of the aluminum. Also, it was thought that if the R_2O_3-bearing minerals were solubilized, the content of these was sufficiently high to cause sludge problems. This concentrate has been tested in phosphoric acid pilot plants in Brazil and Europe, as well as in a full-scale plant in Brazil (3). IFDC has received partial results of these tests. Published data, however, do not appear to exist.

Calcined North Carolina concentrate has been used for years in phosphoric acid manufacture without major difficulties. The elimination of carbon dioxide and organic matter makes the use of defoamers unnecessary in the process and the product is a clear, green acid. However, because calcination is not always feasible or practical, IFDC elected to work with uncalcined North Carolina concentrate in order to gain experience in characterizing a typical rock high in carbonates and organic matter.

Results and Discussion

Pesca Rock

Despite the fact that Pesca rock contains only 20% P_2O_5, it was found to be possible to produce a 30% P_2O_5 filter acid under conventional dihydrate process conditions. The high silica content of the rock did not interfere adversely with the process. The main problems experienced in operating with this rock were in maintaining a constant level of $SO_4^=$ ion in the filter acid (a level between 1.5% and 2.5% was found to be necessary). In table 5A it is seen that the standard deviation of this value was much higher in this test than in the other tests. This was partly attributed to equipment limitations which have since been overcome. The relatively uneven operating conditions experienced in this test impaired the crystal size distribution and thus the filtration rate. When reasonably constant conditions were achieved, good gypsum crystals resulted (figure 2). After the initial period when elongated crystals were observed, crystals with a high width:length ratio were grown (table 7). It is reported in the literature that iron and aluminum favor the formation of such rhombic crystals (4). From table 6A the relatively high level of Al^{+++} in Pesca acid suggests that this may be one reason for the observed crystal morphology. Such crystals are generally associated with good filterability of the filter cake. However, the filtration rate in the Pesca test was relatively low (table 5A). This is explained by the high content (table 7) of quartz and chert in the filter cake, which reduced the cake porosity. The filtration rate obtained is in good agreement with that of another investigator (5).

Because of the uneven operating conditions, it was not possible to obtain accurate reaction efficiencies and material balances. However, approximate figures were obtained (table 5A) which indicate that a reasonably high reaction efficiency of 96% is achievable. A coarser sample of Pesca rock also was tested (28.9% minus 100-mesh), and the reaction efficiency was not significantly reduced.

The consumption of sulfuric acid/ton of P_2O_5 is relatively low with this rock, mainly because of its low carbonate content. Consumption of oleic acid as defoamer was quite variable. The figure quoted in table 5A

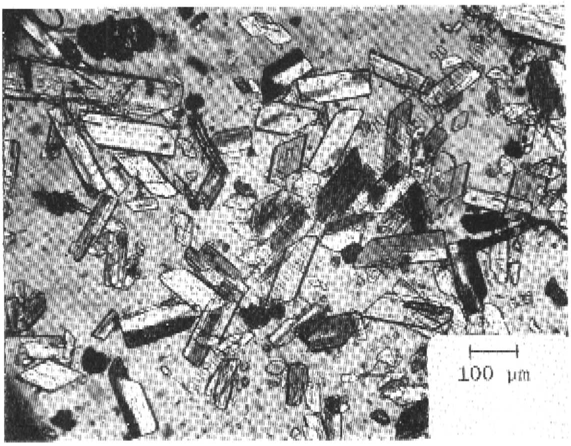

Figure 2. Filter Cake Crystals Typical of Operation with Pesca Phosphate Rock.

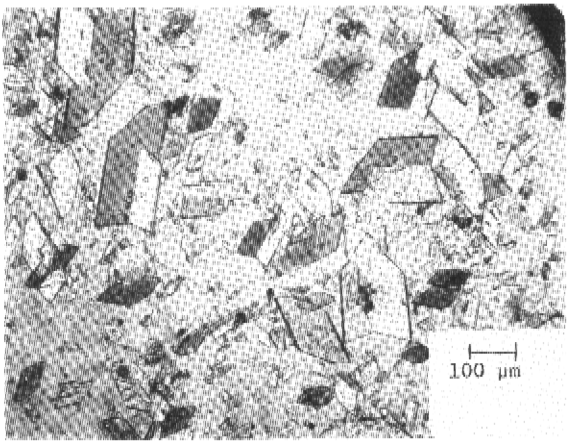

Figure 3. Filter Cake Crystals Typical of Operation with Hazara Phosphate Rock.

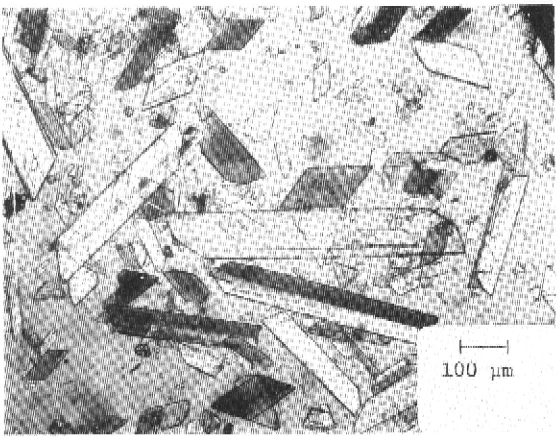

Figure 4. Filter Cake Crystals Typical of Operation with Araxa Phosphate Concentrate.

Table 5A. Summary of Results--Production of Filter-Grade Phosphoric Acid

Rock	Pesca	Hazara
Test time (incl. transition), hours	69	74.5
Feed particle size, Tyler mesh	56.4% -100 mesh	80.4% -100 mesh
Reaction temperature, °C	∿72	∿72
Residence time, hours	5-7	6
SO_4 content of filter acid, %		
Mean	2.0	1.9
Standard deviation	0.7	0.3
P_2O_5 content of filter acid, %		
Mean	33.8	29.1
Standard deviation	1.4	0.9
Solids content of slurry, %		
Mean	39.5	36.4
Standard deviation	3.0	2.2
Sulfuric acid consumption, tons 100% acid/ton P_2O_5 in rock	2.4	2.4
Oleic acid consumption as defoamer, kg/ton P_2O_5 in rock	0.4	None
Reaction efficiency,[a] %	96	98.5
P_2O_5 washing losses, %	2	2.0
P_2O_5 recovered in filter acid, %	94	96.5
Filtration rate, tons rock P_2O_5/day/m^2	4	4.5
Dynamic corrosion-erosion rates, mm/year		
Stainless steel:		
AISI 316	0.05	5.71
AISI 317L	0.03	0.03
Carpenter 20 Cb-3	0.03	0.04
Jessop 700	0.02	0.03
Byproduct solids, tons/ton rock P_2O_5 (dry basis)	6.3	5.0

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a. P_2O_5 in rock feed converted to water-soluble form.

(0.4 kg/ton P_2O_5) corresponds to the most carefully controlled use and was during operation with coarser feed.

The dynamic corrosion-erosion rates were very low. From the chemical analysis (table 3) the main contribution to corrosion-erosion was expected to be the erosive effect of the silica and corrosion from fluorine, depending on whether the dissolved fluoride would be complexed to less corrosive ionic species (such as $SiF_6^=$ and $AlF_6^=$). From table 6A, it can be seen that the fluoride level in Pesca acid is relatively high, hence the low corrosion can only be explained if it is assumed that the fluorine is present as a less corrosive species. The levels of Al_2O_3 and SiO_2 in the acid are consistent with the presence of the ionic species mentioned above. The percentage of fluorine evolved from the reactor is relatively high, but as explained earlier it is expected that this level would be lower on a larger scale. The slurry apparently was not very erosive despite its high content of silica. As pointed out earlier, the effect of erosion is expected to be greater in an industrial-scale plant.

The concentrated Pesca acid was more viscous than the other acids studied. This is attributed to the relatively high level of R_2O_3 in the acid. Some sludge formed after 3 days of clarification, but the total weight of water-insoluble solids was quite low.

Table 5B. Summary of Results--Production of Filter-Grade Phosphoric Acid

Rock	Araxa	North Carolina
Test time (incl. transition), hours	73.5	86.5[a]
Feed particle size, Tyler mesh	86.3% -100 mesh	75.7% -400 mesh
Reaction temperature, °C	∿72	∿72
Residence time, hours	5-6	5-6
$SO_4^=$ content of filter acid, %		
Mean	2.3	2.3
Standard deviation	0.3	0.2
P_2O_5 content of filter acid, %		
Mean	31.7	29.7
Standard deviation	1.3	1.5
Solids content of slurry, %		
Mean	33.1	30.7
Standard deviation	0.9	2.7
Sulfuric acid consumption, tons 100% acid/ton P_2O_5 in rock	2.3	2.9
Oleic acid consumption as defoamer, kg/ton P_2O_5 in rock	None	12
Reaction efficiency,[b] %	97.9	98.5
P_2O_5 washing losses, %	1.1	2.4
P_2O_5 recovered in filter acid, %	96.8	96.1
Filtration rate, tons rock P_2O_5/day/m^2	8.8	6[c]
Dynamic corrosion-erosion rates, mm/year		
Stainless steel:		
AISI 316	0.65	0.16
AISI 317L	0.16	0.04
Carpenter 20 Cb-3	0.18	0.04
Jessop 700	0.10	0.02
Byproduct solids, tons/ton rock P_2O_5 (dry basis)	4.3	5.0

a. Includes time of unsuccessful operation with coarser grind.

b. P_2O_5 in rock feed converted to water-soluble form.

c. Stable operation not achieved; conservative value quoted.

Hazara Rock

Despite the relatively high silica content of Hazara rock, no difficulties were experienced in producing a 30% P_2O_5 filter acid. A distinctly lime-green acid was produced. Good-sized, rhombic gypsum crystals which showed a tendency to form multiplanar twins (figure 3) were typical of the filter cake. As with Pesca rock, almost all the silica in the rock ended up in the filter cake. The small silica particles in the cake resulted in relatively low average filtration rate (4.5 tons P_2O_5/day/m^2).[1]

A fine grind (80.4% minus 100-mesh) was used because of the tight bonding between the silica and phosphate and the low reactivity of the rock. A relatively high reaction efficiency of 98.5% was obtained. It may be possible to achieve similarly high reaction efficiencies with a coarser grind. The water-soluble P_2O_5 losses, 2%, were typical of industrial operation with conventional rock.

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[1] Expressed in terms of P_2O_5 in rock feed to the system.

Table 6A. Properties of the Product Acids After Clarification

Rock	Pesca		Hazara	
Acid Grade	Filter	Concentrated	Filter	Concentrated
Analysis, Wt. %				
P_2O_5	31.1	55.9	27.8	50.7
SO_4	1.8	3.1	1.6	2.7
SiO_2	0.22	0.05	0.26	0.18
F	1.70	0.83	1.98	1.16
Al_2O_3	1.02	1.98	0.63	1.05
Fe_2O_3	0.98	1.87	1.69	3.04
MgO	0.08	0.12	0.08	0.03
Organic matter as C	ND	ND	ND	ND
Color	Light brown	Dark brown (opaque)	Lime green	Dark green
Density at 25°C, g/ml	1.36	1.78	1.34	1.70
Viscosity at 25°C, cP	7.8	164.0	8.2	62.0
at 50°C, cP	ND	56.5	ND	25.3
at 90°C, cP	ND	19.1	ND	12.1
Weight of sludge after clarification, kg/ton of crude acid:				
After 24 hours at 60°C	ND	ND	107	ND
After 3 days at 60°C	ND	83	ND	96
After 7 days at 60°C	ND	ND	ND	84
Water-insoluble solids in sludge, % by weight	ND	0.6	2.1	3 days 1% 7 days 2.9%

ND = not determined.

The corrosion-erosion rates for the stainless steels studied in Hazara acid were all relatively low, with the exception of AISI 316. The two samples of this steel were very badly corroded. It is not certain why this was so. If the corrosion was due to fluoride, it would be expected that all four steels would exhibit high corrosion rates (as with Araxa concentrate--see later). Some fluoride corrosion undoubtedly was occurring, as can be seen from the relative amounts of fluoride, silica and aluminum in the filter acid (table 6A) and the relatively low fluoride emission in the reactor off-gases (table 8) which tend to suggest the presence of a high proportion of free fluoride ions in the acid. It is suspected, however, that the high corrosion rate of the AISI 316 samples may be due to the chloride and sulfide content of the rock. The corrosion features of Hazara rock warrant further careful study.

No problem was experienced in concentrating the Hazara acid to 50% P_2O_5. There was not much post-precipitation at 60°C, but at ambient temperatures more sludge was formed.

Araxa Concentrate

Araxa concentrate did not pose any difficulties in the production of filter-grade phosphoric acid. The sample was finely ground (86.3% minus 100-mesh) as the characterization study indicated that it could be relatively unreactive. A very clear, yellow-colored acid was produced. Very

Table 6B. Properties of the Product Acids After Clarification

Rock	Araxa		North Carolina	
Acid Grade	Filter	Concentrated	Filter	Concentrated
Analysis, Wt. %				
P_2O_5	32.7	57.7	31.0	55.0
SO_4	2.4	3.4	2.3	3.8
SiO_2	0.06	0.04	0.11	0.05
F	0.47	0.12	1.11	0.32
Al_2O_3	0.008	0.09	0.28	0.52
Fe_2O_3	1.68	3.52	0.55	0.93
MgO	ND	ND	0.36	0.63
Organic matter as C	ND	ND	0.13	0.26
Color	Gold-yellow	Dark brown (opaque)	Dark brown	Dark brown (opaque)
Density at 25°C, g/ml	1.37	1.79	1.36	1.72
Viscosity at 25°C, cP	8.4	106.0	8.2	65.0
at 50°C, cP	ND	35.3	ND	25.4
at 90°C, cP	ND	16.8	ND	13.5
Weight of sludge after clarification, kg/ton of crude acid:				
After 24 hours at 60°C	35	ND	43	ND
After 3 days at 60°C	ND	218	ND	149
After 7 days at 60°C	ND	ND	ND	ND
Water-insoluble solids in sludge, % by weight	3.4	1.7	3.2	traces

ND = not determined.

good rhombic and elongated gypsum crystals were grown (figure 4). Some of these were very large, reaching 300-600 microns in length. From the rock analysis (table 3), Araxa concentrate contains a relatively high level of strontium. This may enhance good crystal growth, as reported in the literature (6). Relatively high filtration rates were achieved; an average value of 8.8 tons P_2O_5/day/m^2 was calculated. This was higher than values reported by other workers (3). This may either be explained by differences in process conditions or in the calculation procedure. The reaction efficiency was reasonably high (97.9%), and the wash losses of P_2O_5 were low (1.1%). The relatively high corrosion rates of all steels tested are attributed to fluoride corrosion. From table 6B, it can be seen that the SiO_2 and Al_2O_3 in the acid are both very low. The Al_2O_3 in the concentrate appears to be acid-insoluble, and the silica level is quite low thus causing there to be a high fluorine content in the acid as F^-. The filter cake analysis (table 7) shows a relatively high value of fluorine as well. The addition of reactive silica or aluminum oxide to the reactor would help to reduce the corrosion problem. This could be done either with additives or by blending the concentrate with another phosphate rock containing an excess of reactive silica or a reactive aluminum compound.

There was a relatively large volume of post-precipitation in the concentrated acid, which may be caused by the high Fe_2O_3 content of the acid. The amount is expected to be higher for longer periods at ambient temperatures. This would mean that this acid would best be used for fertilizer production at the site of manufacture, rather than be exported.

Table 7. Properties of the Filter Cakes
(Typical Values)

Rock	Pesca	Hazara	Araxa	North Carolina
Moisture Content, %	27.3	29.5	31.9	44.9
Important Impurities (Dry Basis), %				
Total P_2O_5	0.73	0.53	0.66	0.83
Water-soluble P_2O_5	0.26	0.33	0.22	0.56
SiO_2	31.9	15.4	0.32	0.87
F	0.09	0.08	0.82	0.53
Al_2O_3	0.10	0.07	0.24	ND
BaO	ND	ND	3.98	ND
Specific surface area, m^2/g	6.4	0.49	0.58	0.82
Gypsum crystal morphology				
Crystal type	Elongated, then rhombic plates	Rhombic, some twins	Rhombic and elongated crystals, some twins	Clusters of small rhombic crystals
Width:length ratio	1:3 to 1:10 at start, then 1:1 to 1:4	1:1 to 1:2	1:1.5 to 1:3.5	
Length (dominant range) (μm)	100-250	50-120	50-200 some 300-600	<30 100-150 (diameter of clusters)

ND = not determined.

Uncalcined North Carolina Concentrate

Because this concentrate is known to be very reactive, it was thought at first that coarse grinding (97.5% minus 20-mesh, 16.2% minus 100-mesh) would be sufficient for processing it into phosphoric acid. However, during operation it became evident that sulfuric acid was not reacting. Examination under an electron microscope showed that very small gypsum crystals were precipitating on the surface of the rock, covering the surface and blocking the reaction. Figures 5 and 6 show a partially blinded phosphate rock particle and a completely coated surface, respectively. Preliminary laboratory tests indicated that a two-stage attack system could circumvent the problem. However, in a single-tank reactor this problem had to be solved by very fine grinding to 75.7% minus 400-mesh. This fine grind was successfully processed, and no losses due to rock blinding by gypsum were observed. In fact, the gypsum crystallized in spherical agglomerates (figure 7) which filtered and washed very well. Filtration rates were in the order of 6 tons $P_2O_5/day/m^2$, and values of up to 9 were reached. The filter cake had a high moisture content (about

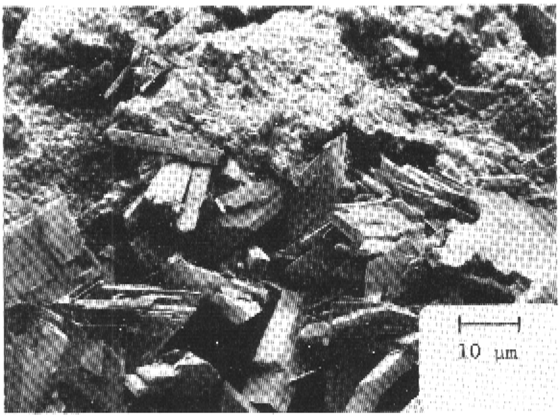

Figure 5. Gypsum Crystals Partially Coating a Particle of Uncalcined North Carolina Phosphate Concentrate.

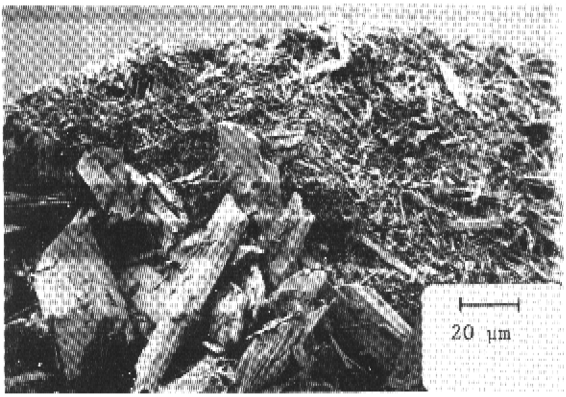

Figure 6. Gypsum Crystals Totally Coating a Particle of Uncalcined North Carolina Phosphate Concentrate.

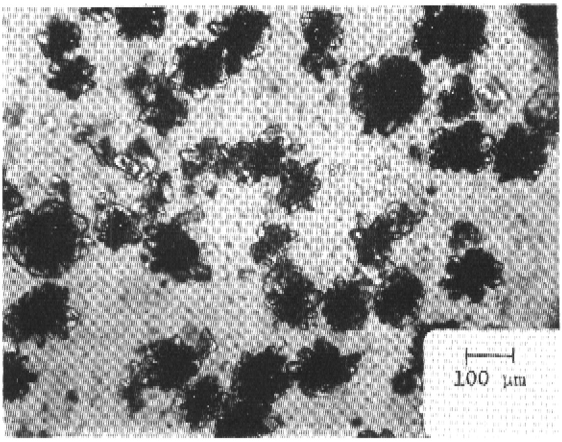

Figure 7. Filter Cake Crystals Typical of Operation with Uncalcined North Carolina Phosphate Concentrate.

40%). This value was lower when the highest filtration rates were achieved. Reaction and overall efficiencies were 98.5% and 96.1%, respectively. It must be noted that the filtration rate was very sensitive to evenness of sulfate ion concentrations, which, at 2.3% SO_4, resulted in an acid consumption of 2.9 tons H_2SO_4/ton P_2O_5 in the rock. This relatively high value is attributed to the high carbonate content of the rock. The filter acid had a dark appearance, containing 0.13% organic carbon. Solids precipitating upon desaturation in 24 hours at 60°C formed a sludge containing 3.2% by weight of water-insoluble solids. As expected, the magnesium content of the acid was relatively high (0.35% MgO). However, no problems were experienced in concentrating the acid to 55% P_2O_5. The high magnesium content would cause problems at superphosphoric acid concentrations. Defoamer consumption was high (12 kg/ton P_2O_5 of rock feed). This was expected because of the high organic content of the rock.

Table 8. Fluorine Distribution

Overall Distribution in Reactor System	Pesca	Hazara	Araxa	North Carolina
% in filter cake	10	3	43	20
% in reactor off-gases	40	30	36	50
% in filter acid	50	67	21	30
Distribution in Clarification and Concentration				
% in filter acid solids	ND	1	-	1
% evolved in concentration	∿35	45	18	24
% in concentrated acid	∿15	21	3	5

ND = not determined.

Further Work

The results described above are the initial findings of the characterization tests. It is necessary to carry out further work to optimize the conditions for processing the rocks. Optimization of important process variables such as reaction temperature, sulfate concentration in the acid, feed particle size and retention time can be carried out in the bench-scale unit. In addition, other common materials of construction should be evaluated for corrosion-erosion resistance including Uranus B6 and Ferralium. When optimum conditions of filtration rates and P_2O_5 recoveries are determined, it is then necessary to test the rock in a larger pilot plant. IFDC has constructed such a pilot plant, which processes about 10 kg/hour of rock, to be used to evaluate the optimum process and collect process data for process design and economic analysis. This unit forms part of a group of pilot plants including wet and dry beneficiation equipment and a granulation plant. The latter will allow the assessment of the phosphoric acid for granular fertilizer manufacture.

Ultimately, the results of the studies must be assessed in economic terms. When dealing with a rock deposit which has yet to be exploited, this can present some difficulties because no data on mining costs will be available. However, the costs of processing the run-of-mine product to phosphoric acid often can be assessed if some knowledge of local costs is available and if the relative sites of mine and factory are known.

Conclusions

Both high-silica rocks tested demonstrated that high reaction efficiencies can be obtained, despite tight bonding between the phosphate and silica particles. Silica in the filter cake reduces filtration rates but not to unacceptable levels. It is therefore of interest to consider direct acidulation of these and possibly other high-silica phosphate rocks as an alternative to beneficiation followed by acidulation. Direct acidulation may be the more economic route because of the high P_2O_5 losses likely to be sustained in beneficiation. Pesca rock did not exhibit any unusual properties in processing. Hazara rock, on the other hand, created highly corrosive conditions so far as AISI 316 is concerned and this will require additional study.

In the case of Araxa phosphate concentrate, if due consideration is given to corrosion and post-precipitation problems, this phosphate has been demonstrated to be suitable for phosphoric acid manufacture without further beneficiation.

In the case of uncalcined North Carolina concentrate, it is doubtful whether the economics of processing such a rock without calcination would ever be better than those of processing calcined rock. However, the work carried out demonstrated that it is possible to grow easily filterable gypsum crystals despite a high content of organic material. Thus, it may be possible to avoid calcination to remove organic matter in some problem rocks.

In the cases of Pesca and Hazara rocks, optimization work followed by pilot-plant testing is recommended. Full-scale operating experience with Araxa is available, so further bench-scale work is probably not warranted. As North Carolina rock is not indigenous to a developing country, it is doubtful whether IFDC will study it further.

The present work should be regarded as an encouragement to the development of indigenous phosphate sources which traditionally are considered to be difficult for use in phosphoric acid manufacture.

Acknowledgement

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