International
Fertilizer Industry
Association

ISMA* Technical Conference

Orlando, Florida, USA
23-27 October 1978

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

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

BENEFICIATION OF SOUTH FLORIDA HIGH CARBONATE PHOSPHORITES

By: James E. Lawver, Bernard L. Murowchick, Robert E. Snow

International Minerals & Chemical Corporation, U.S.A.

ABSTRACT

The ever increasing demands for phosphate rock and the concomitant expiration of high grade phosphate rock in Central Florida has triggered research and development efforts to develop a process for beneficiating the lean high-carbonate reserves of South Florida.

The South Florida matrix is lower grade, thicker, and will require deeper mining than the typical reserves in Central Florida. South Florida reserves contain little if any pebble that is salable simply by desliming and sizing;and the matrix also contains large quantities of dolomite, calcite and sometimes sea shell that must be removed by beneficiation in order to produce a salable product.

This paper describes the general geology and mineralogy of a typical South Florida deposit and presents a flow sheet now being tested at pilot plant level by International Minerals & Chemical Corporation. The process involves the use of a heavy media step to remove much of the carbonate minerals in the -3 +16 mesh size range followed by a rod mill grind of the heavy media sink and the -16 +28 mesh feed and three stages of froth flotation. The -28 +150 mesh fraction is subjected to a typical anionic phosphate float, de-oiling and a conventional cationic silica float, after which the two-stage concentrate is subjected to a final stage of flotation to remove carbonate minerals and produce a product containing about 64-66% BPL and 1% MgO.

U.S. DEMAND AND GRADE DISTRIBUTION

During 1977 the United States produced 47.2 million metric tons of phosphate rock products 1/. The state of Florida alone produced 38.2 X 10^6 tonnes or nearly 33% of the 115.8 X 10^6 tonne world production.

The time trend of major products from phosphate rock in the United States is shown in Figure 1 2/.

TRENDS IN PRODUCTION OF MAJOR PRODUCTS FROM PHOSPHATE ROCK - USA

1970 - 1977

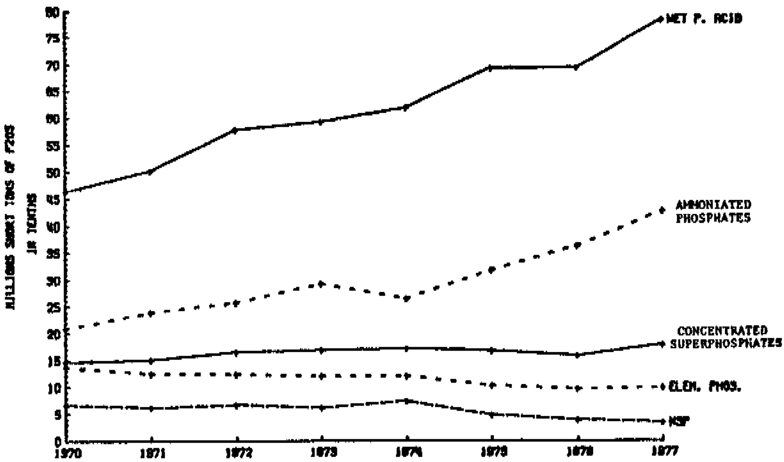
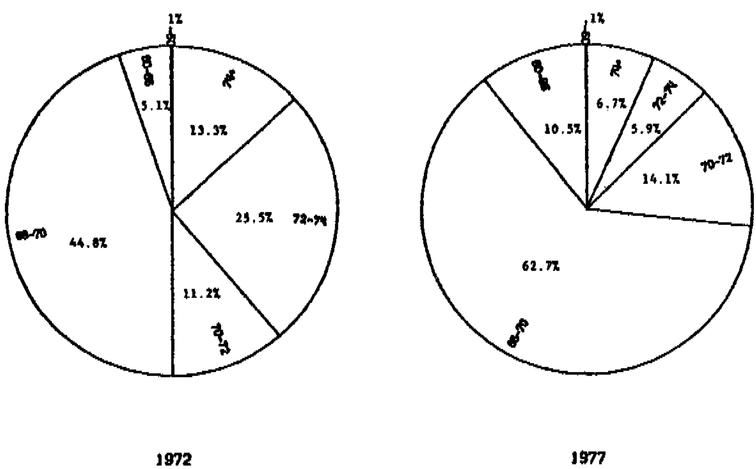


FIGURE 1

Figure 2 shows a comparison of the grade distribution of products produced in the United States in 1972 vs. 1977 3/.

% DISTRIBUTION OF DIFFERENT GRADES OF PHOSPHATE GRADE % BPL



SOURCE: W. F. Stowasser, U.S. Bureau of Mines

FIGURE 2

It is apparent that more and more of the U.S.A. production is being used and will continue to be used for wet-process acid and at the same time the grade of the products is steadily decreasing. In the state of Florida the reserves that have historically produced a salable pebble by simple sizing and desliming an easily beneficiated matrix are gradually but certainly becoming depleted. It appears, however, that there are enormous reserves in the South Florida extension of the Central Florida phosphate district provided that a mineral beneficiation method can be devised to process high carbonate ore from a matrix that contains essentially no salable pebble. The same general type of material is also found in the upper Hawthorne or the so-called "deep matrix" material of the existing Central Florida region. A successful beneficiation scheme thus also increases the potential reserves of Central Florida. See Figure 3 4/.

LOCATION OF THE MAJOR PHOSPHATE DEPOSITS
IN THE SOUTHEASTERN UNITED STATES

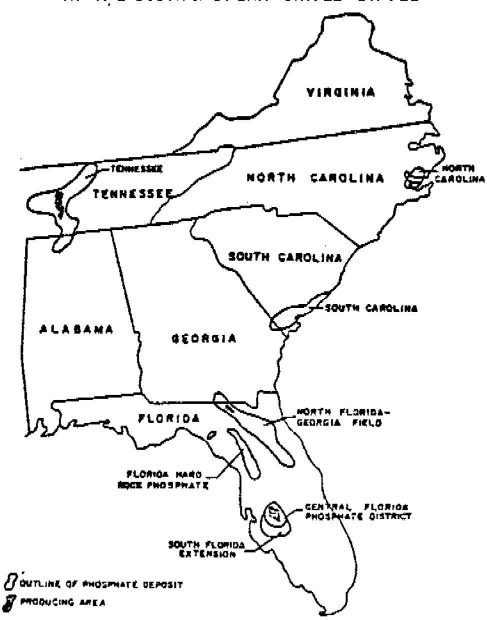


FIGURE 3

GEOLOGY OF THE CENTRAL AND SOUTH FLORIDA PHOSPHATE DISTRICT

The phosphate deposits of Central Florida and its southern extension are located in southwestern Polk, southeastern Hillsborough, Manatee, Hardee, and DeSoto counties. They occur as a relatively thin blanket of sediments covering an area of several thousand square miles.

The origin of the phosphate deposits is directly related to the Ocala uplift, which is a broad, anticlinal structure, that extends into Polk County. During Miocene time, the shallow marine environmental conditions surrounding the flank of the Ocala arch were ideal for the deposition of the Hawthorne Formation, which is a dolomitic limestone containing as much as 10% phosphatic pellets, fine sand, and interbedded clay. Repeated cycles of phosphate precipitation from sea water, compaction, and dessication, followed by fragmentation and transportation produced a wide range of phosphate particle sizes deposited over a very large area. Phosphatic gravel-rich sediments tended to be concentrated in central Polk and eastern Hillsborough counties, while southward and southwestward, the amount of pebble and gravel size decreased and sand size clastics increased.

This process of deposition, movement, and mechanical sorting continued through late Miocene time and into early Pliocene time when the Ocala uplift became more emergent, and erosional processes became more important in the central district. Cycles of marine transgression and regression resulted in extensive reworking and resorting of gravels, sands and clays, removing the finer materials to deeper parts of the topography and leaving the coarser fractions in shallower areas. As one goes west or south from the central district, these effects are less noticeable to absent.

In the area of land emergence, i.e., the central district, weathering of these phosphate beds began contemporaneously and has continued to the present time, resulting in supergene enrichment of the phosphate beds through removal of carbonates, removal of impurities in the phosphate particles, and local recrystallization of apatite. Continued weathering and alteration processes have resulted in an upper leached zone in much of the central district and especially the eastern portion, producing a kaolinitic sand rich in aluminum phosphate minerals.

In general, all of the Florida sedimentary phosphorites initially contained carbonate as dolomite and as substitutions within the apatite lattice, yielding a phosphate concentrate of inherent grade probably not greater than 66-68% BPL. Only through subsequent weathering has the carbonate been removed and the grade enhanced.

The phosphate matrix is variable in mineral composition, particle size distribution, aerial extent, and thickness. Mineralogically, it consists of a mixture of unconsolidated phosphate pellets and larger fragments, quartz, clays, and carbonates, predominantly dolomite. The phosphate is the apatite variety known as francolite or carbonate fluorapatite. The phosphate particles range from silt size to cobble size while the quartz is generally sandy and the clays (montmorillonite, attapulgite, illite, kaolinite) are extremely fine-grained, (finer than about .5μm).

Dolomite is usually minor or absent in the central part of the district where it has been removed by leaching. It increases in amount as one moves further south and southwest of the central area, and usually occurs as a marly clay although occasionally layers and lenses of harder rock are encountered.

This is evident from examination of the -150 mesh clay fraction from an area in Hardee County. Mineralogical analysis of numerous samples showed dolomite and the clay mineral montmorillonite as major components. By contrast, analysis of slimes from the central district showed only traces of dolomite and major amounts of montmorillonite.

Tables 1, 2, 3 and 4 illustrate typical mineral and chemical composition of -150 mesh phosphate slimes in Central Florida compared to the South Florida extension.

TABLE 1

TYPICAL MINERAL COMPOSITION
MINUS 150 MESH PHOSPHATE SLIMES

CENTRAL FLORIDA

MINERAL	WT-PCT	THEORETICAL COMPOSITION
Carbonate-Fluorapatite	20 - 25	$Ca_{10}(PO_4,CO_3)_6F_{2-3}$
Quartz	30 - 35	SiO_2
Montmorillonite	20 - 25	$(Fe,Al,Mg)_2(Al,Si)_4O_{10}(OH)_2(Ca,Na)$
Attapulgite	5 - 10	$(MG,Al,Fe)_5(Al,Si)_6O_{20}(OH)_2 8H_2O$
Wavellite	4 - 6	$Al_3(OH)_3(PO_4)_2 5H_2O$
Feldspar	2 - 3	$KAlSi_3O_8 + NaAlSi_3O_8$
Heavy Minerals	2 - 3	Zircon,Garnet,Ilmenite,Rutile
Dolomite	1 - 2	$CaMg(CO_3)_2$
Miscellaneous	0 - 1	Kaolinite,Crandallite,Hydrated Fe-Oxide, Organic

About 24 to 30% of the matrix is -150 mesh with as much as 70% of the -150 mesh material finer than 2 micrometers.

TABLE 2

TYPICAL MINERAL COMPOSITION
MINUS 150 MESH PHOSPHATE SLIMES

SOUTH FLORIDA

MINERAL	WT-PCT	THEORETICAL COMPOSITION
Carbonate-Fluorapatite	10 - 15	$Ca_{10}(PO_4,CO_3)_6F_{2-3}$
Quartz	15 - 20	SiO_2
Montmorillonite	15 - 20	$(Fe,Al,Mg)_2(Al,Si)_4O_{10}(OH)_2(Ca,Na)$
Attapulgite	10 - 15	$(Mg,Al,Fe)_5(Al,Si)_6O_{20}(OH)_2 8H_2O$
Calcite	Trace	$CaCO_3$
Feldspar	Trace	$KAlSi_3O_8 + NaAlSi_3O_8$
Heavy Minerals	Trace	Zircon,Garnet,Ilmenite,Rutile
Dolomite	40 - 50	$CaMg(CO_3)_2$
Miscellaneous	0 - 1	Kaolinite,Illite,Crandallite

About 30 to 40% of the matrix is -150 mesh and about 90% of the -150 mesh material is finer than 43 micrometers (325 mesh). The clay content (Montmorillonite and Attapulgite) of both Central and the South Florida Extension is essentially the same (about 35% wt. of the slimes). The clays are all finer than 2 micrometers.

TABLE 3

TYPICAL CHEMICAL COMPOSITION
MINUS 150 MESH PHOSPHATE SLIMES

CENTRAL FLORIDA

CONSTITUENT	ANALYSIS, PCT			
	TYPICAL		RANGE	
	Mesh Size		Mesh Size	
	150/325	-325	150/325	-325
P_2O_5	11.7	11.5	7 - 16	8 - 14
Insol	58.1	46.0	42 - 73	40 - 56
Fe_2O_3	2.0	2.3	1 - 2	2 - 4
Al_2O_3	4.7	10.3	4 - 6	9 - 12
MgO	0.5	1.3	.3 - .7	1 - 2

TABLE 4

TYPICAL CHEMICAL COMPOSITION
MINUS 150 MESH PHOSPHATE SLIMES

SOUTH FLORIDA

CONSTITUENT	ANALYSIS, PCT			
	TYPICAL		RANGE	
	Mesh Size		Mesh Size	
	150/325	-325	150/325	-325
P_2O_5	6.3	2.7	3 - 8	1 - 5
Insol	53.5	20.9	40 - 60	21 - 38
Fe_2O_3	1.1	1.8	1 - 2	1 - 2
Al_2O_3	1.0	3.4	Trace-1	3 - 5
CaO	17.1	20.0	14 - 22	17 - 23
MgO	5.3	11.6	3 - 7	8 - 15

Slimes disposal is a major and severe problem in both Central and South Florida. In South Florida about 2 1/2 tons of -150 mesh slimes are produced for each ton of product whereas in Central Florida the ratio is about one to one.

Despite the fact that from a geological point of view the only differences between the Central Florida deposit and its southern extension are those due to differences in enrichment, the method of beneficiation, the grade and impurity content of final products, and the overall economics associated with mining and processing the matrix is substantially different. The following table summarizes the major differences.

CHEMICAL & METALLURGICAL DIFFERENCES BETWEEN CENTRAL FLORIDA AND SOUTHERN EXTENSION MATRIX AND FINAL PRODUCTS

	CENTRAL DISTRICT	SOUTHERN EXTENSION
+16 Mesh "Pebble" in Matrix	10% of matrix 66% BPL (a salable product) Pebble content is higher due to reworking and cementation.	5% of matrix 40% BPL-requires beneficiation to produce a salable product
Grade of Phosphate Mineral	Higher due to development of weathering profile and leaching of impurities	Lower -- initial grade of original phosphate contains more carbonate as dolomite and in apatite lattice 64-68% BPL 1% MgO after beneficiation
Gangue	Primarily quartz and clay	Quartz and clay plus dolomite largely as marl but some cemented
Matrix Thickness	About 20 Feet	About 65 Feet
Matrix Grade	About 12% P_2O_5	About 7% P_2O_5
Overburden Thickness	About 25 Feet	About 35 Feet
Matrix Cubic Yds. Per Ton of Product	About 3-3 1/2	About 7
Total Cubic Yds. Per Ton of Product	6 to 10	9 to 12
-150 Mesh Slime	24 to 30%	30 to 40%
Tons Product/Acre Mined	10,000 Tons/Acre	15,000 Tons/Acre
Tons Product Per Acre Foot of Matrix	500	231
Tons Slimes / Ton Product	.9	2.4

CHEMICAL ANALYSIS OF WET-PROCESS ACID FEED ROCK

	CENTRAL DISTRICT	SOUTHERN EXTENSION
P_2O_5	29 - 32	29 - 31
CaO	44.0 - 48.0	45.0 - 47.5
Fe_2O_3	0.7 - 1.7	1.3 - 2.7
Al_2O_3	0.7 - 1.9	0.7 - 1.1
MgO	0.3 - 0.8	.3 - 1.3
F	3.3 - 3.7	3.2 - 3.6
Na_2O	.45 - .65	.65 - .80
K_2O	.08 - .11	.15 - .20

It is informative to compare the South Florida flow sheet, which appears on the following pages, with the typical (but efficient) Central Florida block flow diagram shown in Figure 4. 2/.

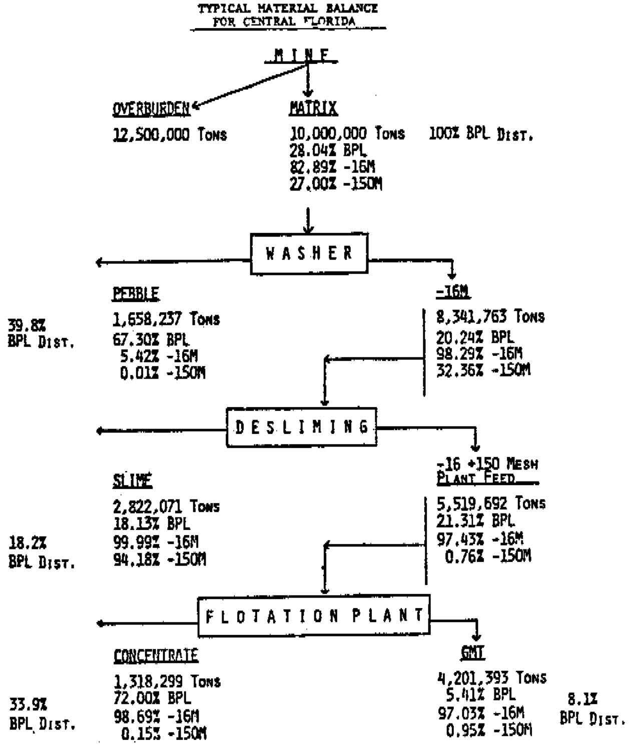


FIGURE 4

The South Florida conceptual flow sheet of a process designed to produce four million tons of product per 7500 hour year is shown on the following pages.

All of the major flows and the unit operations are shown. The details of reagent combinations and optimum levels of process variables have been withheld pending issuance of process patents.

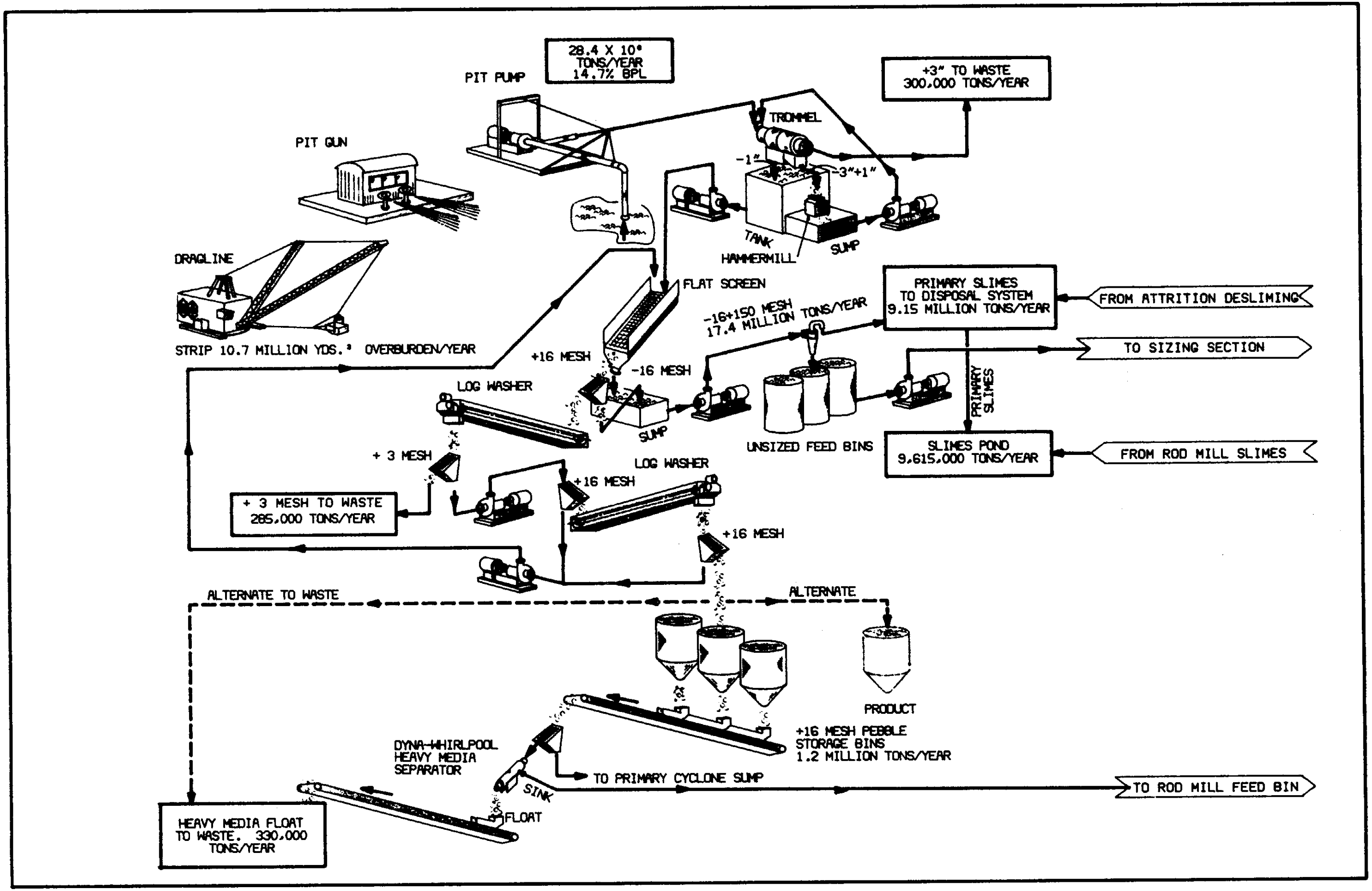
CONCEPTUAL FLOW SHEET

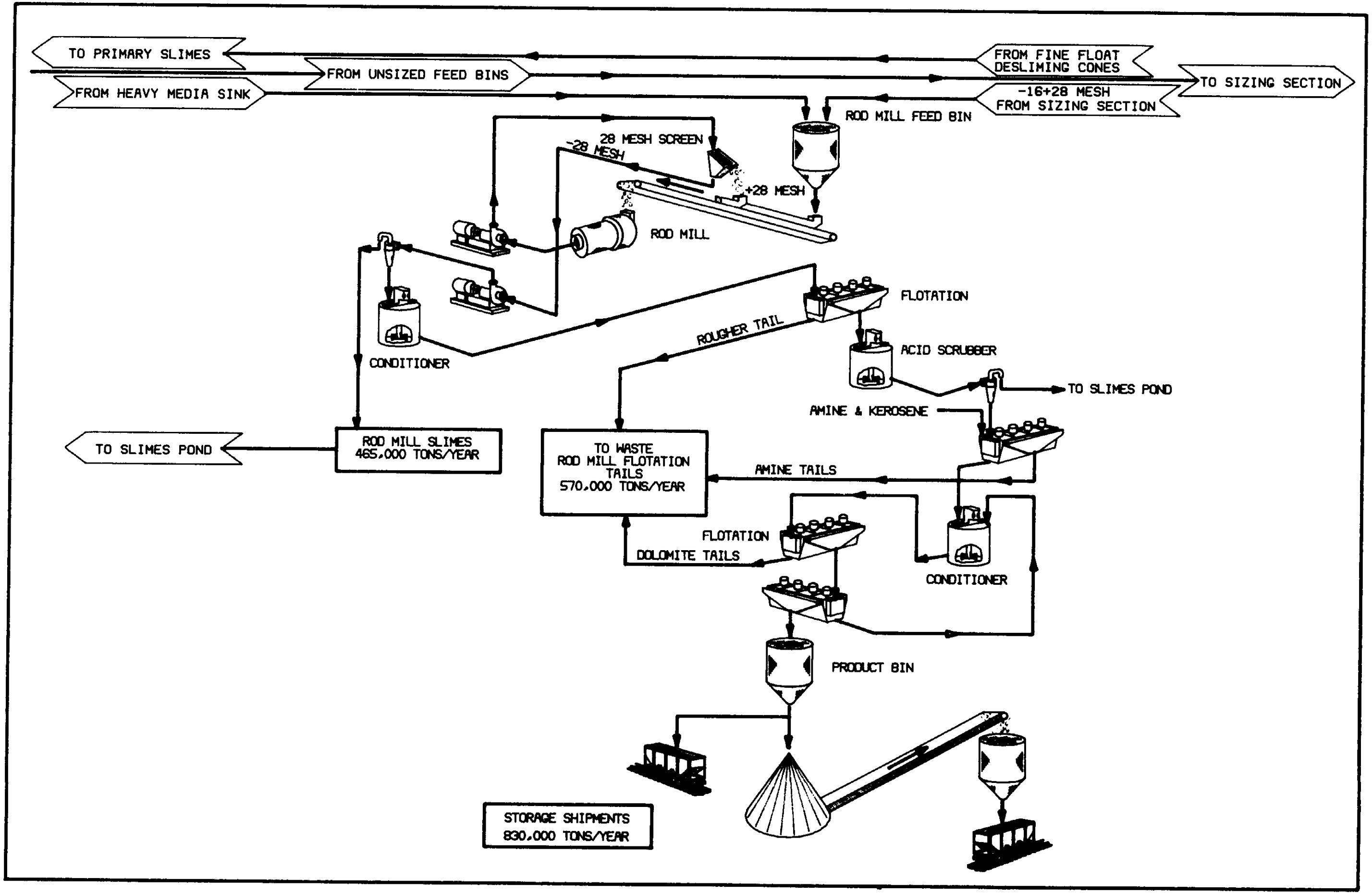
SOUTH FLORIDA DEPOSIT

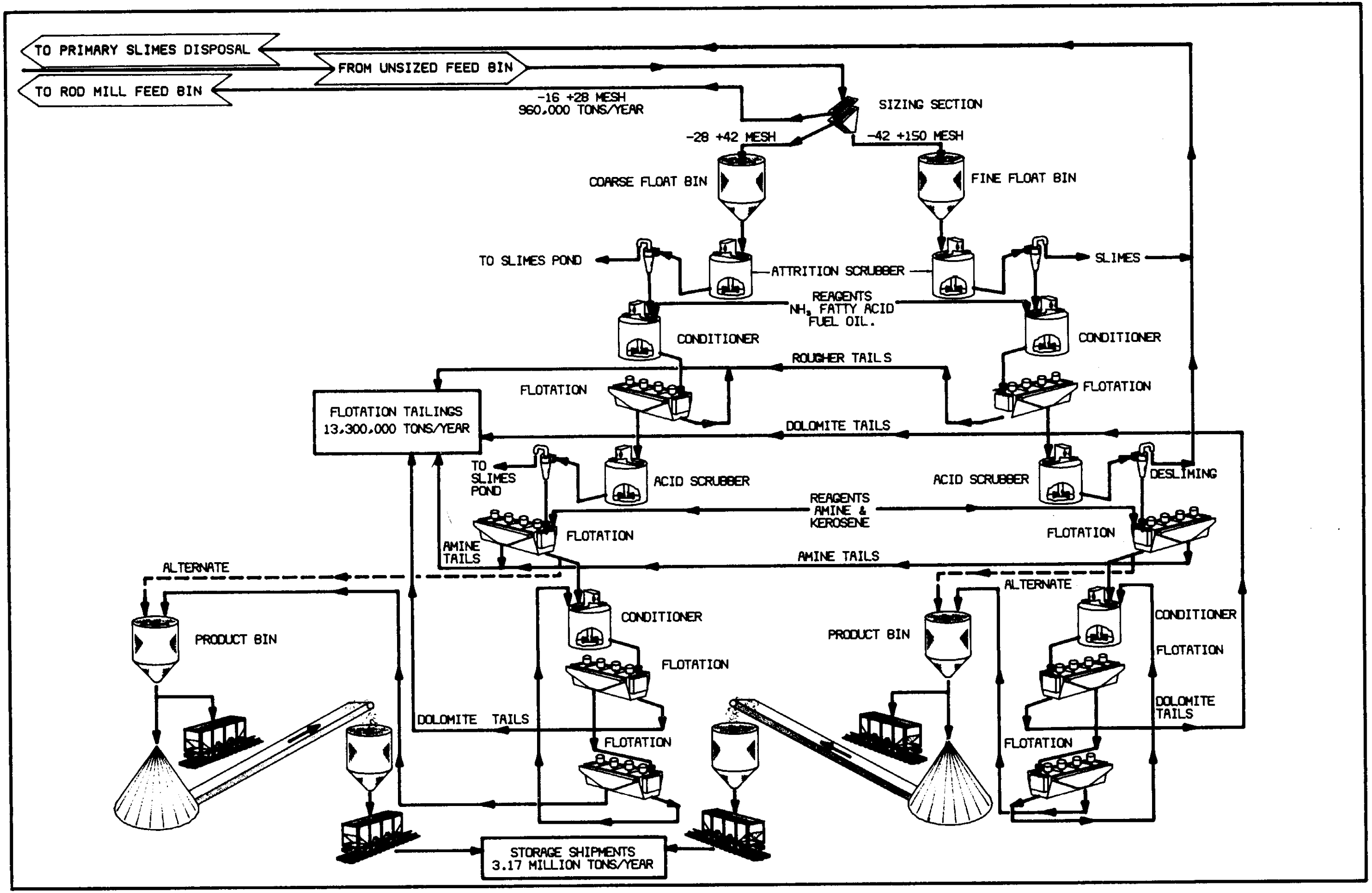
4 MILLION TONS OF PRODUCT PER YEAR

TYPICAL ANALYSIS

BPL	>	65%	CaO/P_2O_5	$\leq$	1.55
INS	<	5%	$I\&A/P_2O_5$	<	0.085
MgO	$\leq$	1%	F/P_2O_5	<	0.11


28.4 X 10^6
TONS/YEAR
14.7% BPL
PIT PUMP
+3" TO WASTE
300,000 TONS/YEAR
TROMMEL
PIT GUN
-1"
-3"+1"
TANK
HAMMERMILL
SUMP
DRAGLINE
FLAT SCREEN
PRIMARY SLIMES
TO DISPOSAL SYSTEM
9.15 MILLION TONS/YEAR
FROM ATTRITION DESLIMING
-16+150 MESH
17.4 MILLION TONS/YEAR
STRIP 10.7 MILLION YDS.^{3} OVERBURDEN/YEAR
TO SIZING SECTION
+16 MESH
-16 MESH
LOG WASHER
SUMP
PRIMARY SLIMES
UNSIZED FEED BINS
SLIMES POND
9,615,000 TONS/YEAR
FROM ROD MILL SLIMES
+ 3 MESH
LOG WASHER
+16 MESH
+ 3 MESH TO WASTE
285,000 TONS/YEAR
+16 MESH
ALTERNATE TO WASTE
ALTERNATE
PRODUCT
+16 MESH PEBBLE
STORAGE BINS
1.2 MILLION TONS/YEAR
DYNA-WHIRLPOOL
HEAVY MEDIA
SEPARATOR
TO PRIMARY CYCLONE SUMP
SINK
TO ROD MILL FEED BIN
FLOAT
HEAVY MEDIA FLOAT
TO WASTE. 330,000
TONS/YEAR


TO PRIMARY SLIMES
FROM UNSIZED FEED BINS
FROM HEAVY MEDIA SINK
FROM FINE FLOAT DESLIMING CONES
TO SIZING SECTION
-16+28 MESH FROM SIZING SECTION
ROD MILL FEED BIN
28 MESH SCREEN
-28 MESH
+28 MESH
ROD MILL
FLOTATION
ROUGHER TAIL
ACID SCRUBBER
CONDITIONER
TO SLIMES POND
AMINE & KEROSENE
TO SLIMES POND
ROD MILL SLIMES 465,000 TONS/YEAR
TO WASTE ROD MILL FLOTATION TAILS 570,000 TONS/YEAR
AMINE TAILS
FLOTATION
DOLOMITE TAILS
CONDITIONER
PRODUCT BIN
STORAGE SHIPMENTS 830,000 TONS/YEAR


TO PRIMARY SLIMES DISPOSAL
FROM UNSIZED FEED BIN
TO ROD MILL FEED BIN
-16 +28 MESH
960,000 TONS/YEAR
SIZING SECTION
-28 +42 MESH
-42 +150 MESH
COARSE FLOAT BIN
FINE FLOAT BIN
TO SLIMES POND
ATTRITION SCRUBBER
SLIMES
REAGENTS
NH3 FATTY ACID
FUEL OIL.
CONDITIONER
CONDITIONER
ROUGHER TAILS
FLOTATION
FLOTATION
FLOTATION TAILINGS
13,300,000 TONS/YEAR
DOLOMITE TAILS
TO
SLIMES
POND
ACID SCRUBBER
ACID SCRUBBER
DESLIMING
REAGENTS
AMINE &
KEROSENE
FLOTATION
FLOTATION
AMINE
TAILS
AMINE TAILS
ALTERNATE
ALTERNATE
PRODUCT BIN
CONDITIONER
FLOTATION
PRODUCT BIN
CONDITIONER
FLOTATION
DOLOMITE TAILS
DOLOMITE
TAILS
FLOTATION
FLOTATION
STORAGE SHIPMENTS
3.17 MILLION TONS/YEAR

Note the following:

1. In the Central Florida flow sheet more than half of the total product and about 40% of the P_2O_5 values in the matrix is recovered as pebble simply by sizing. In the South Florida flow sheet all the +16 mesh (Pebble) is subjected to the beneficiation, and that the product produced from all of the +28 mesh material is about 20% of the total product.

2. In both the Central Florida and the South Florida flow sheets about 18% of the P_2O_5 values in the matrix is lost as slimes.* (in some Central Florida deposits the slime loss is much higher).

3. The overall P_2O_5 recovery from the matrix in Central Florida ranges from about 60% to 75% compared to an expected value of about 60 to 65% in South Florida.

4. The grade of the product in South Florida will be lower than in current products from Central Florida viz; 64-68% BPL in South Florida vs. a product distribution such as is shown in Figure 2 for Central Florida.

5. The MgO content of South Florida rock will be about 1%, a value appreciably higher than the rock currently being used for wet-process acid. It is expected that the higher MgO content and other impurities may cause problems in current technology chemical plants due to increased viscosity of acid, increased defoamer usage, and possibly some difficulty in producing a standard 18-46-0 DAP product because of the dilution effect of increased MgO.

Little can be done to lower the MgO in the flotation concentrate by beneficiation because the Francolite mineral contains about 0.7% MgO. It is certainly possible, and it may be necessary, to modify existing chemical plant flow sheets in order to use the somewhat higher MgO rock in wet-process acid and DAP plants.

At present IMC is conducting large scale tests to evaluate potential problems in using 1% MgO rock both for the manufacture of wet-process acid and in the production of diammonium phosphate from the acid.

* In Central Florida most of the usable P_2O_5 values are contained in the +325 mesh fraction of the slimes. Most of the P_2O_5 values in the -325 mesh plus 2 micrometers is in the form of Wavellite and would not produce a salable product even if it were concentrated.

REFERENCES

1. Stowasser, W. F., U.S. Bureau of Mines; Florida Phosphate Council, Lakeland, Florida.

2. Stowasser, W. F., U.S. Bureau of Mines, Personal Communications.

3. Stowasser, W. F., U.S. Bureau of Mines, Personal Communications.

4. Fountain, R. C., *Florida Phosphate Rock Reserves - Quality - Mining Time Table*, Presentation for Central Florida and Peninsular Florida Sections of the American Institute of Chemical Engineers, May 1977.