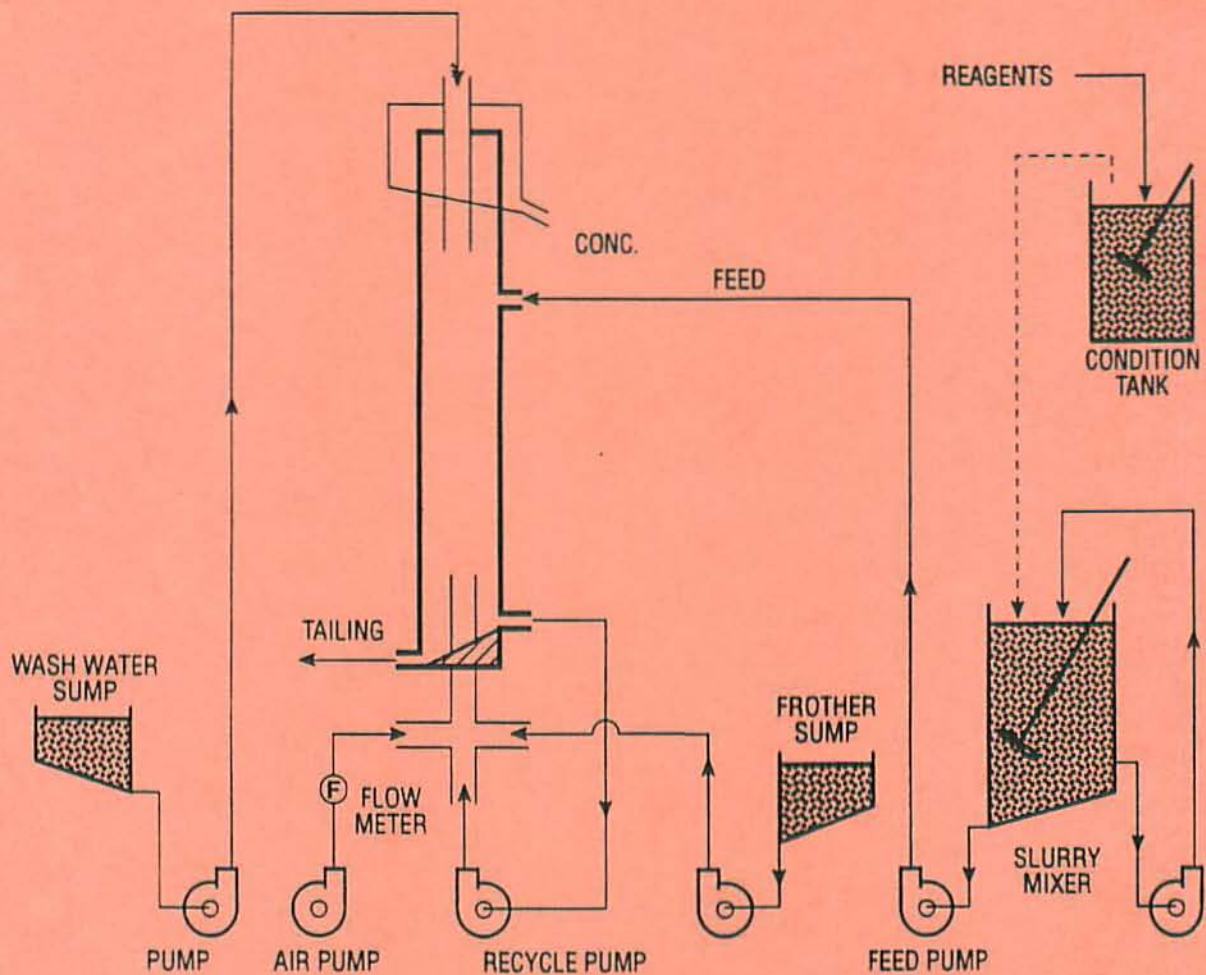
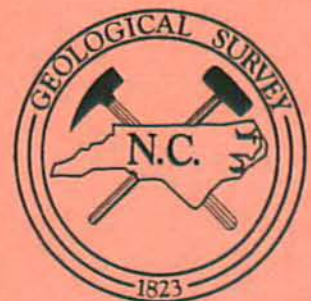


BENEFICIATION STUDY OF CONTINENTAL SHELF PHOSPHORITES, ONSLOW BAY, NORTH CAROLINA



North Carolina Geological Survey
Open-File Report 94-1



BENEFICIATION STUDY OF CONTINENTAL SHELF PHOSPHORITES, ONSLOW BAY, NORTH CAROLINA

by

Ronald A. Crowson, Stanley R. Riggs, Eric R. Powers,
Roe-Hoan Yoon, and Jurgen Schoenherr

North Carolina Geological Survey
Open-File Report 94-1



1994

Charles H. Gardner, Director and State Geologist

STATE OF NORTH CAROLINA
JAMES B. HUNT, JR., GOVERNOR

DEPARTMENT OF ENVIRONMENT,
HEALTH AND NATURAL RESOURCES
JOHNATHAN B. HOWES, SECRETARY

CONTENTS

	<u>Page</u>
Abstract	1
Introduction	1
Purpose and scope.....	2
Field investigations	2
Sample preparation and distribution	4
Freshwater beneficiation studies	4
IMC beneficiation study	5
Freshwater beneficiation results	6
Sample OB-1	6
Sample OB-2	9
Agrico laboratory study	9
Sea water beneficiation studies.....	11
Description of experiment	12
Apparatus and test procedure.....	12
Results and discussion	15
Conclusions and recommendations.....	25
Acknowledgements	26
References cited	27

ILLUSTRATIONS

Figure 1. Location map showing sample collection area	3
2. Schematic geologic cross-section illustrating the relationship of bathymetry, lithology, and stratigraphy at the sample site	4
3. Grain size distribution of samples OB-1 and OB-2.....	13
4. Grain size density of samples OB-1 and OB-2.....	14
5. Phosphate content as a function of grain size of samples OB-1 and OB-2	14
6. Schematic representation of the initial Microcel™ column flotation circuit.....	16
7. Schematic representation of the Microcel™ flotation circuit designed to provide a controlled conditioning time	17
8. Apparatus used in fresh-water rinse of processed phosphate concentrate.....	18
9. Effect of pH on the flotation of samples OB-1 and OB-2 using conventional flotation	18
10. Effect of collector (dodecyl amine) addition on the flotation of samples OB-1 and OB-2 using conventional flotation	19
11. Effect of collector (saponified fatty acid) addition on the flotation of samples OB-1 and OB-2 using conventional flotation	20
12. Effect of wash water rate on the column flotation of sample OB-1 at 500 ml/min of feed rate using saponified fatty acid as collector	20
13. Effect of wash water rate on the column flotation of sample OB-1 and OB-2 using saponified fatty acid as collector	21
14. Effect of feed rate on the column flotation of samples OB-1 and OB-2 using saponified fatty acid as collector after 10 minutes of conditioning time	22

15. Effect of aeration rate on the column flotation of sample OB-1 using saponified fatty acid as collector after 10 minutes of conditioning time.....	22
16. Comparison of column and conventional flotation for the beneficiation of samples OB-1 and OB-2	23
17. Results of the wash tests conducted on the column flotation concentrates using a conductivity probe	24
18. Results of the wash tests conducted on the column flotation concentrates using chloride analysis	25

TABLES

Table 1. Chemical analysis of phosphate concentrate from OB-1 (muddy phosphatic sand) and OB-2 (shelly phosphatic sand)	5
2. Grain size distribution for samples OB-1 and OB-2	6
3. Chemical analysis of three size fractions from samples OB-1 and OB-2	6
4. Apparent grade of phosphate pebble material from OB-1 and OB-2	7
5. Approximate mineral composition of OB-1 and OB-2 feed	7
6. Sample OB-1 laboratory flotation test summary	8
7. Sample OB-2 laboratory flotation test summary	10
8. Typical analysis of phosphate rock from Aurora, NC	11
9. Summary of chemical analysis from vibracores in unit FPS-1	12
10. Chemical analysis of phosphate concentrate from samples OB-1 and OB-2	13

BENEFICIATION STUDY OF CONTINENTAL SHELF PHOSPHORITES, ONslow BAY, NORTH CAROLINA

Ronald A. Crowson, O'Brien and Gere Engineers, Raleigh, North Carolina 27623

Stanley R. Riggs, Dept. of Geology, East Carolina University, Greenville, North Carolina 27858

Eric R. Powers, Geophex, Ltd., Raleigh, North Carolina 27640

Roe-Hoan Yoon, Minerals and Coal Technology, Inc., Virginia Polytechnic Institute and State
University, Blacksburg, Virginia 24060

and

Jurgen Schoenherr, Minerals and Coal Technology, Inc., Virginia Polytechnic Institute and State
University, Blacksburg, Virginia 24060

ABSTRACT

Two samples of phosphate-bearing sand were collected from Unit FPS-1 of the Miocene Pungo River Formation and the reworked Holocene sediments exposed on the sea floor 30 miles southeast of the Cape Fear River in Onslow Bay, North Carolina. Samples of these units were analyzed by three independent laboratories in order to compare metallurgical properties derived by a standard bench-scale freshwater beneficiation with a new single-stage saltwater froth flotation process.

Phosphate concentrate in Onslow Bay, comparable with Texasgulf's phosphate rock product, can be beneficiated from the Miocene Pungo River Formation to a common product utilizing either the standard two-stage freshwater beneficiation technique or a new single stage saltwater flotation column. This saltwater flotation process should eliminate the need for freshwater processing at sea and second stage flotation circuits. In addition, freshwater rinse data indicates that salt contamination from the saltwater process circuit can be eliminated by flushing the concentrate with freshwater. Development of a single stage saltwater flotation circuit should improve the economics of mining and improve the potential of processing of phosphate deposits located on the world's continental shelves.

INTRODUCTION

The North Carolina Coastal Plain and continental shelf was the site of several extensive phosphogenic episodes during the early to middle Miocene. Extensive Miocene phosphatic sands and clays deposited during this period are exposed on the shallow continental shelf, Onslow Bay, North Carolina. These exposed rock sections have been the subject of several investigations sponsored by industry and various state and federal agencies (Riggs and Ames, 1992). A review of these published and unpublished data resulted in an economic feasibility study by Development Planning and Research Associates, Inc. (DPRA) (1987) for the U.S. Department of Interior, Minerals Management Service (MMS). The DPRA study concluded that offshore mining of phosphatic sediments was economically feasible. The DPRA analysis assumed that: (1) certain economic conditions were true, (2) adequate phosphate resources were present, and (3) mining and beneficiation technology were available to develop the phosphate resources.

A review of the DPRA Report by interested parties, including phosphate mining companies, resulted in numerous criticisms or concerns. Of interest to this study were: (1) concerns that the beneficiation studies, which were conducted on unusually small samples collected from cores,

were unreliable, and that large bulk samples should be collected and analyzed to verify the results of the smaller core samples; (2) concerns that fresh process water used in the beneficiation process may not be available in sufficient quantities to permit offshore processing of the ore; and (3) concerns that the ore would be contaminated with chloride from saltwater, and thus may be unsuitable for use as an acid plant feed or direct application on soils.

PURPOSE AND SCOPE

This purpose of this study is to evaluate the above concerns and determine if they are warranted, or if the concerns can be mitigated by advanced technology. The study results are expected to aid MMS in determining future policy aimed at the development of offshore phosphate resources in the United States.

The scope of this study involves field and laboratory investigations including collection of several large bulk samples (collectively weighing approximately 1,000 pounds), a description of the sea floor from which the samples were collected, and the development of SCUBA diving techniques that may be used if future bulk samples are required.

Laboratory investigations include a comparative beneficiation study of both muddy and shelly phosphatic sands utilizing fresh and saline process water. The laboratory investigation also compares a new saltwater beneficiation technology with existing fresh water beneficiation techniques presently utilized by the phosphate mining industry.

FIELD INVESTIGATIONS

In July 1991, MMS contracted Geophex, Limited to collect and analyze a bulk phosphate sample from unit FPS-1 in the Frying Pan sequence of the Miocene Pungo River Formation in southern Onslow Bay, North Carolina (Snyder

and others, 1993). On November 21, 1991, a bulk sample of phosphorite was collected from the sea floor approximately 30 miles due east of the mouth of the Cape Fear River in approximately 80 (24 meters) feet of water (Figure 1). The sea floor in the area is composed of rippled, phosphatic shelly sand overlying a sequence of muddy phosphatic sands and microspherite cobbles. Figure 2 is a composite geologic cross-section illustrating the relationship of observed bathymetry and geology.

A total of 12 dives were made over the study area. Grab samples of the bottom were taken during dives 3 through 12 as described below:

- Dives 1 and 2 were reconnaissance dives and no samples were collected.
- Dives 3, 6, 7, 8, and 9 were made at a bathymetric low. Clean phosphatic shelly sand extends from 1 1/2 to more than 2 feet in depth below bottom. A permanent steel stake, with an attached double red buoy was placed at this site.
- Dives 4 and 5 were located on a bathymetric high. A thin (6-inch thick), rippled phosphatic sand overlies a stiff non-phosphatic clay unit of undetermined thickness.
- Dives 10, 11 and 12 were made along the slope of a small valley, where less than 6 inches of clean phosphatic shelly sand overlies a bed of high grade muddy phosphatic sand (estimated 60 percent phosphate by weight).

The quantity of sample collected varied from a few pounds on dives 4 and 5, to hundreds of pounds on dive 6. Grab samples were collected by scooping undisturbed sediment into 5 gallon buckets. After the sample was collected, a lid was placed over the bucket to prevent mixing and loss of fines. Once on board ship, the samples were labeled and sealed for transport back to the lab.

Sea water to be used in the beneficiation study was also collected and stored in two 35-gallon plastic barrels. All of the samples were then unloaded from the ship at Morehead City

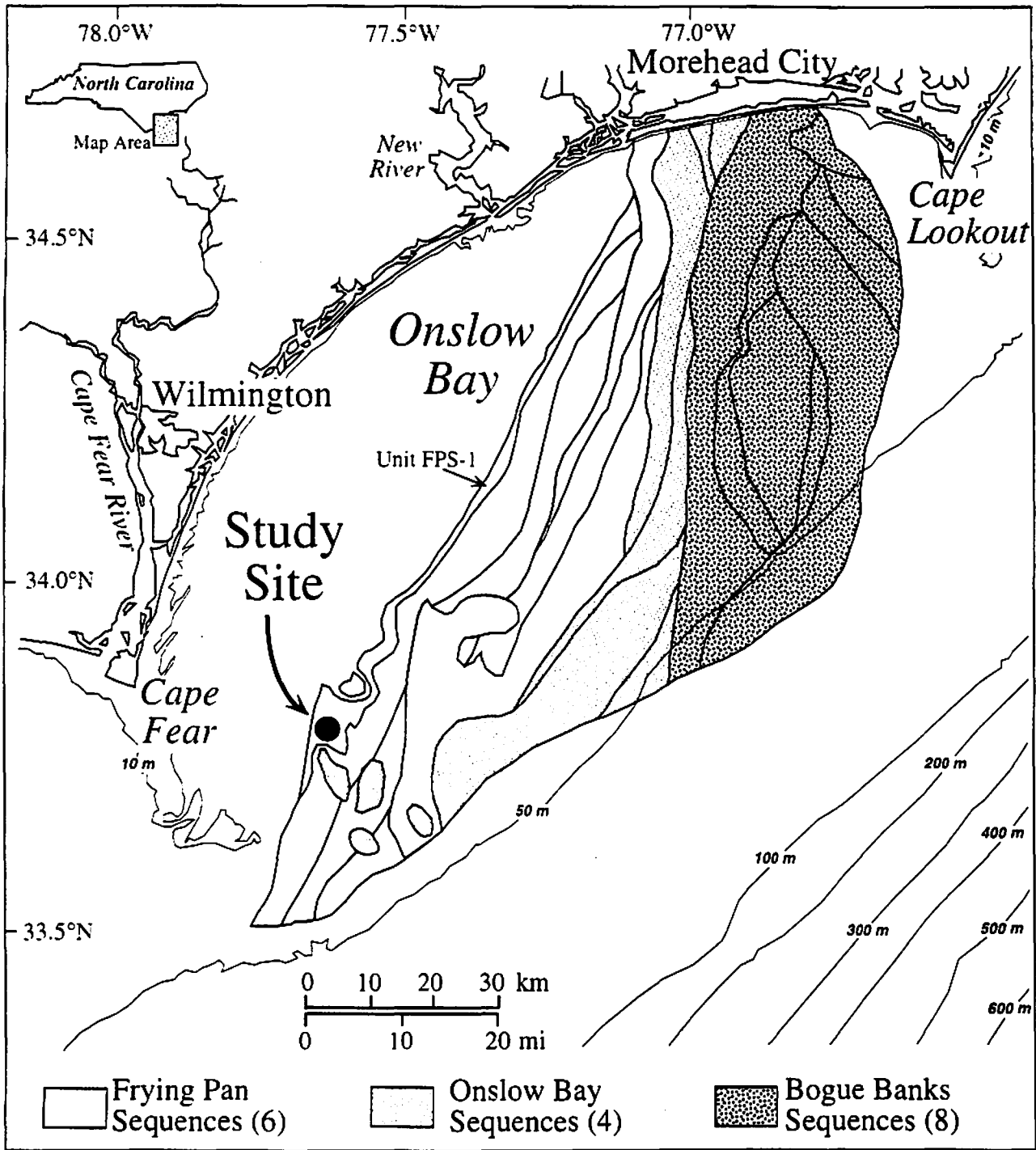


Figure 1. Location map showing sample collection area and area of Onslow Bay underlain by outcropping/subcropping Miocene phosphorite-bearing units (modified after Snyder and others, 1993).

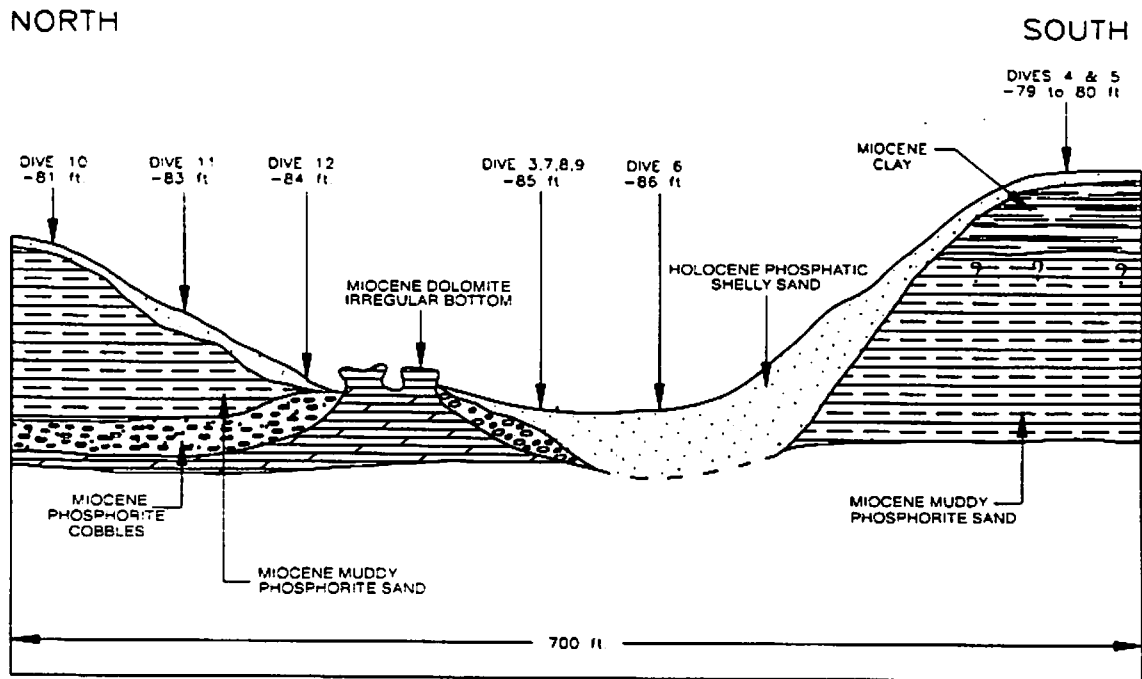


Figure 2. Schematic geologic cross-section illustrating the relationship of bathymetry, lithology, and stratigraphy at the sample site.

and transported to East Carolina University (ECU) in Greenville, North Carolina.

SAMPLE PREPARATION AND DISTRIBUTION

Samples were examined at ECU by Geophex and ECU investigators and two composite samples were prepared.

1) Sample OB-1 represents the Miocene muddy phosphorite sand collected from dives 10, 11, and 12.

2) Sample OB-2 represents the Holocene shelly, phosphatic sands collected from dives 3, 6, 7, 8 and 9.

Each of the bulk samples were homogenized, divided into equal sub-samples, and sealed in plastic bags. Each bag contained approximately 13 pounds of sample. Great care was taken during the sample preparation process to prevent moisture loss. Thus, the samples provided to each laboratory for analysis were not substantially altered from their original composition and moisture content. All unused

samples are archived at the ECU core storage facility located in Greenville, North Carolina.

Two identical sets of samples representing the Miocene muddy phosphorite sand (Sample OB-1), and Holocene shelly phosphatic sand (Sample OB-2) were distributed to the following laboratories for chemical analysis and beneficiation tests on the -20/+150 mesh feed fraction:

- International Minerals and Chemical (IMC), Bartow Lab, and the Florida Institute of Phosphate Research (FIPR), Bartow, Florida;
- Agrico Chemical Company, Mulberry, Florida; and
- Virginia Polytechnic Institute and State University (VPI), Blacksburg, Virginia.

Residual samples from the above laboratories were returned to East Carolina University for storage.

FRESHWATER BENEFICIATION STUDIES

Each cooperating laboratory conducted their studies independently of each other with

methodologies that varied between labs. Each laboratory conducted bench-scale flotation tests on each set of samples using their own standard laboratory methodology and flotation reagents. The following beneficiation analyses were conducted by the respective laboratories.

(1) International Minerals and Chemical and the Florida Institute of Phosphate Research cooperatively studied OB-1 and OB-2 utilizing:

- standard fatty-acid rougher plus cleaners flotation beneficiation process,

- conventional "Crago" double-float beneficiation process (U.S. Patent 2,293,640: 1942), and

- IMC's patented "all-cationic" beneficiation process (U.S. Patent 4,144,959: 3/24/79).

(2) Agrico Chemical Company conducted industry standard double flotation (fatty-acid and amine) process on OB-1 and OB-2 samples.

(3) Virginia Polytechnic Institute conducted single float froth flotation and special Microcel™ flotation tests on samples OB-1 and OB-2 using sea water collected from Onslow Bay.

IMC and Agrico conducted beneficiation studies using fresh process water derived from their laboratory spigots in Florida.

IMC Beneficiation Study

Samples OB-1 and OB-2, were subjected to laboratory tests including IMC's all-cationic patented process, simple fatty acid flotation of phosphate with two froth cleaning stages, and a conventional "Crago" double-float process.

Representative samples of feed from Samples OB-1 and OB-2 were subjected to chemical analyses for percent P_2O_5 , acid insolubles (insol), CaO, MgO, and Iron and Aluminum. Table 1 presents the chemical analyses performed on each total sample and Table 2 presents the wet/dry screen analysis performed on an approximate 300 g of each sample. In comparison, Sample OB-1 (20.5 percent P_2O_5) contained about twice

Table 1. Chemical analysis of bulk sediment from samples OB-1 (muddy phosphatic sand) and OB-2 (shelly phosphatic sand).

<u>Component</u>	<u>OB-1</u>	<u>OB-2</u>
P_2O_5 (Wt. %)	20.50	9.71
CaO (Wt. %)	38.67	35.64
MgO (Wt. %)	1.21	1.19
$Fe_2O_3+Al_2O_3(I+A)$ (Wt. %)	1.90	1.98
Cd (ppm)	11.60	1.90
Ratio I+A/ P_2O_5	0.09	0.20
Ratio CaO/ P_2O_5	1.88	3.67
P_2O_5 at 0 % Insol (Wt. %)	24.90	13.30
Moisture (225° F.) (Wt. %)	25.10	17.10
Insolubles (Wt. %)	21.46	37.08

Recorded weight (plastic bag tare deleted):

OB-1 = 5469 g; OB-2 = 9660 g

Work-up weight (indicated moisture loss):

OB-1 = 5419 g; OB-2 = 9608 g

the phosphate of sample OB-2 (9.71 percent P_2O_5) (Table 1). Sample OB-1 contained 77 weight percent of -20/+150 mesh flotation feed compared to 70.9 weight percent for Sample OB-2 (Table 2). Sample OB-1 contained less +20 mesh pebble and more -150 mesh slime than sample OB-2. The lower grade sample OB-2 contained high concentrations of shell in the pebble, feed, and slime size fractions.

Neither sample contained appreciable concentrations of pebble-sized phosphorite. Hand-picked phosphate pebbles (+20 mesh) from OB-1 assayed 24.7 percent P_2O_5 , 12.3 percent insol, and $CaO/P_2O_5 = 1.72$. The same product from Sample OB-2 assayed on 20.1 percent P_2O_5 , 13.3 percent insol, and $CaO/P_2O_5 = 1.98$.

The IMC process and the "Crago" process were effective with Sample OB-1 flotation feed. Phosphate concentrates were produced from this sample assaying 28.2-28.7 percent P_2O_5 , 2.3-2.8 percent insol, and $CaO/P_2O_5 = 1.66-1.68$ at greater than 95 percent P_2O_5 recovery from the -20/+150 mesh feed.

Table 2. Grainsize distribution of samples OB-1 and OB-2.

Tyler Mesh	OB-1		OB-2	
	Wt. %	Cum. Wt. %	Wt. %	Cum. Wt. %
+10	3.4	3.4	12.8	12.8
-10/+12	0.5	3.9	2.7	15.5
-12/+14	0.5	4.4	3.0	18.5
-14/+16	0.7	5.1	3.4	21.9
-16/+20	1.2	6.3	4.4	26.3
-20/+24	1.4	7.7	3.9	30.2
-24/+28	1.6	9.3	3.7	33.9
-28/+32	3.6	12.9	6.5	40.4
-32/+35	2.6	15.5	4.0	44.4
-35/+42	4.4	19.9	5.6	50.0
-42/+48	11.7	31.6	11.4	61.4
-48/+60	22.6	54.2	15.1	76.5
-60/+65	14.3	68.5	7.9	84.4
-65/+100	11.7	80.2	12.0	96.4
-100/+150	2.0	82.2	3.1	99.5
-150/+200	1.3	83.5	0.3	99.8
<u>-200</u>	<u>16.5</u>	<u>100.0</u>	<u>0.2</u>	<u>100.0</u>
Total	100.0	—	100.0	—

The lower grade sample (OB-2) that contained a high concentration of shell did not respond favorably to any of the flotation feed processes tested. The best beneficiation results were obtained with the IMC all-cationic

process indicating the process' superior carbonate/phosphate separation properties. This process yielded a final phosphate concentrate assaying only 24.8 percent P_2O_5 , 5.5 percent insol, and CaO/P_2O_5 of 1.87 at +80 percent P_2O_5 recovery from the -20/+150 mesh flotation feed. These results represent a reduction in shell from about 24 weight percent in the process feed to about 10 weight percent in the flotation concentrate.

Both samples OB-1 and OB-2 consisted of brown to dark brown phosphate grains, quartz sand, and tan to white shell fragments. Minor amounts of feldspar and trace amounts of iron oxide (limonite) were also present. The clay-size fraction from sample OB-1 was analyzed by X-ray diffraction. The dominant mineral forms detected were apatite, calcite, glauconite, quartz and clinoptilolite (a zeolite).

The remaining bulk samples were slurried in water, wet screened at 20 mesh, and deslimed at 150 mesh to yield pebble, flotation feed, and slime products. Table 3 presents the results of chemical analyses performed on the three size fractions for each sample.

Table 3. Chemical analysis of three size fractions from samples OB-1 and OB-2 (values other than ratios are given as weight percent). Bracketed (composite) values are calculated weighted averages.

Sample OB-1								
Size Fraction	% in size							% P_2O_5 in fraction
	fraction	P_2O_5	Insol	CaO	MgO	I&A	CaO/P_2O_5	
+20	7.1	13.14	19.74	34.94	0.97	2.03	2.66	4.6
-20/+150*	77.5	24.77	11.33	44.04	0.70	1.11	1.78	93.8
-150	15.4	2.18	46.13	21.77	1.74	2.21	9.97	1.6
Composite	100.0	(20.46)	(17.28)	(39.96)	(0.87)	(1.27)	(1.95)	100.0

* Wt. percent P_2O_5 at zero percent Insol = 27.94

Sample OB-2								
Size Fraction	% in size							% P_2O_5 in fraction
	fraction	P_2O_5	Insol	CaO	MgO	I&A	CaO/P_2O_5	
+20	28.5	2.49	12.70	44.29	1.62	1.98	17.79	7.4
-20/+150*	70.9	12.44	33.35	32.60	0.88	1.57	2.62	92.4
-150	0.6	3.06	35.60	30.70	1.51	2.38	10.03	0.2
Composite	100.0	(9.55)	(27.48)	(35.91)	(1.02)	(1.68)	(3.75)	100.0

* Wt. percent P_2O_5 at zero % Insol = 18.67

Table 6. Freshwater laboratory flotation test results for sample **OB-1**. Bracketed values (composite) are calculated weighted averages.

Test #	Product	Wt. % in product	Assay (Wt. percent)					CaO/ P ₂ O ₅	P ₂ O ₅ in product
			P ₂ O ₅	Insol	CaO	MgO	I+A		
IMC CATIONIC PROCESS:									
1	Phos. Concentrate	93.7	26.08	8.53	44.43	0.68	1.18	1.70	98.5
	Shell Tails	0.6	8.19	10.17	38.67	—	—	4.72	0.2
	<u>Silica Tails</u>	<u>5.7</u>	<u>5.49</u>	<u>76.26</u>	<u>9.71</u>	<u>—</u>	<u>—</u>	<u>1.77</u>	<u>1.3</u>
	Composite	100.0	(24.80)	(12.40)	(42.41)	—	—	(1.71)	100.0
2*	Phos. Concentrate	82.4	28.16	2.79	46.82	0.70	1.07	1.66	94.8
	Shell Tails	2.4	9.36	4.47	42.05	—	—	4.48	0.9
	Silica Tails	14.0	7.22	70.93	11.84	—	—	1.64	4.1
	<u>Scrub Slime</u>	<u>1.2</u>	<u>2.85</u>	<u>45.67</u>	<u>47.46</u>	<u>—</u>	<u>—</u>	<u>16.65</u>	<u>0.2</u>
	Composite	100.0	(24.47)	(12.89)	(41.82)	—	—	(1.71)	100.0
3*	Phos. Concentrate	82.6	28.65	2.52	48.31	0.72	1.03	1.68	96.4
	Shell Tails	4.9	12.53	2.95	43.74	—	—	3.49	2.5
	Silica Tails	11.0	1.87	84.69	3.56	—	—	1.90	0.8
	<u>Scrub Slime</u>	<u>1.5</u>	<u>4.20</u>	<u>47.36</u>	<u>39.65</u>	<u>—</u>	<u>—</u>	<u>9.41</u>	<u>0.3</u>
	Composite	100.0	(24.55)	(12.25)	(43.02)	—	—	(1.75)	100.0
“CRAGO” PROCESS:									
4	Phos. Concentrate	89.2	28.16	2.31	47.22	0.70	1.07	1.67	99.4
	Shell Tails(Am.)	1.8	3.31	82.62	5.98	—	—	1.80	0.2
	Acid De-oil Slime	0.4	5.99	(insf.)	46.66	—	—	7.77	0.1
	<u>Silica Tails (F.A.)</u>	<u>8.6</u>	<u>0.82</u>	<u>85.46</u>	<u>4.94</u>	<u>—</u>	<u>—</u>	<u>6.00</u>	<u>0.3</u>
	Composite	100.0	(25.26)	(>10.90)	(42.84)	—	—	(1.69)	100.0
FATTY ACID ROUGHER/CLEANER/RECLENER PROCESS:									
5	Phos. Concentrate	90.4	27.29	4.82	48.81	0.70	1.11	1.79	99.5
	Comb. Cl. Tails	1.6	2.87	72.92	13.17	—	—	4.57	0.2
	<u>Ro. Silica Tails</u>	<u>8.0</u>	<u>0.78</u>	<u>85.29</u>	<u>4.11</u>	<u>—</u>	<u>—</u>	<u>5.25</u>	<u>0.3</u>
	Composite	100.0	(24.78)	(12.35)	(45.48)	—	—	(1.83)	100.0

* Feed scrubbed lightly for 2 minutes at approximately 65% solids and deslimed at 150 mesh.

acid reacted freely with shell fragments and a suitable de-oiling pH of less than 4.5 could not be maintained during scrubbing. Efficient de-oiling could be very difficult to control in commercial operation.

3) Standard fatty acid plus oil flotation process floats phosphate from siliceous impurities in an alkaline circuit followed by cleaner and recleaner flotation of the rougher

concentrate. The fatty acid rougher plus cleaners process (in Test 5) yielded an inferior phosphate concentrate assaying 27.29 percent P₂O₅, 4.82 percent insol, and CaO/P₂O₅=1.79 at 99+ percent P₂O₅ recovery. Concentrate MgO was 0.70 percent and I+A=1.11 percent. The two cleaner flotation stages were only slightly effective in reducing the shell content of the phosphate concentrate.

The comparatively low-grade phosphate

The +20 mesh pebble fraction was hand-picked under a binocular microscope. The resulting brown phosphate pebble concentrates were chemically analyzed (Table 4).

A portion of each -20/+150 mesh flotation feed sample was subjected to a dilute acetic acid leach to dissolve shell particles. The residue was placed in hot 1:1 hydrochloric acid to dissolve phosphate. These dissolutions resulted in the acid insoluble residues consisting of silica/silicates. Approximate mineral compositions of each feed sample were estimated from this data (Table 5).

The approximate theoretical weight percent P_2O_5 of the phosphorite in the -20/+150 mesh fraction, based upon the insoluble residue data in Table 5 and 0 percent insolubles, is 29.9 ± 0.5 for OB-1 and 29.7 ± 0.5 for OB-2.

These calculated values agree with published data (Riggs and others, 1993). Flotation concentrates containing zero percent insol would assay only about 66 percent P_2O_5 , provided that practically all shell particles were also removed during processing. Trace quantities of heavy minerals identified in the flotation feed include garnet, tourmaline, and possibly ilmenite.

Freshwater Beneficiation Results

Sample OB-1

The -20/+150 mesh flotation feed was subjected to 500 g bench scale flotation tests

Table 4. Chemical analysis of the phosphate pebble (+20 mesh) fraction from OB-1 and OB-2.

	Assay(Wt. percent)					CaO/ P_2O_5
	P_2O_5	Insol	CaO	MgO	I+A	
OB-1	24.68	12.32	42.48	0.69	1.84	1.72
Wt. percent P_2O_5 at zero percent Insol = 28.14						
OB-2	20.09	13.33	39.00	1.32	4.50	1.98
Wt. percent P_2O_5 at zero percent Insol = 23.18						

using three processing methods whose descriptions follow. The flotation test results are summarized in Table 6.

1) IMC's all cationic process wherein siliceous impurities are floated from phosphate and then carbonates are flushed using an amine condensate followed by flotation of phosphate from carbonates using a primary amine plus oil in a slightly acid circuit. The IMC cationic process requires mild feed scrubbing and desliming prior to flotation processing in order to remove sufficient slimes to permit efficient silica flotation with minimal amine condensate consumption. Test 1, 2, and 3 show that phosphate concentrates assaying 26.08-28.65 percent P_2O_5 , 2.52-8.53 percent insol, and $CaO/P_2O_5 = 1.66-1.70$ were produced at about 95.0-98.5 percent P_2O_5 recovery. Concentrate MgO was a moderate 0.7 percent, and I+A was favorably low at less than 1.18 percent.

2) Conventional "Crago" process consists of flotation of phosphate from siliceous impurities using a fatty acid plus oil in an alkaline circuit, followed by acid de-oiling of the phosphate rougher concentrate and subsequent amine condensate flotation of the remaining siliceous impurities from phosphate. The Crago process (in Test 4) yielded a phosphate concentrate assaying 28.16 percent P_2O_5 , 2.31 percent insol, and $CaO/P_2O_5 = 1.67$ at 99+ percent P_2O_5 recovery. Concentrate MgO was a moderate 0.70 percent and I+A 1.07 percent. However, the process required "double" acid de-oiling scrubs using an excessive quantity of sulfuric acid in order to yield a suitable amine feed. The

Table 5. Weight percent mineral product in flotation feed.

Product	OB-1	OB-2
Phosphorite	82-84	41-43
Shell	5-6	24-25
Siliceous Insol	11-12	33-34

particles present in sample OB-1 appeared to contain appreciable organic matter that could be removed by calcination to further upgrade the flotation concentrates—probably by several percent P_2O_5 .

The phosphate particle surfaces appeared to be highly reactive with “normal” quantities of either fatty acid or primary tallow amine flotation reagents. Total reagent cost per ton of about 28.5 percent P_2O_5 phosphate concentrate was estimated at less than \$2.00 using the IMC “all cationic” process, and less than \$1.50 using the “Crago” process (1992 dollar estimates).

Sample OB-2

The -20/+150 mesh flotation feed was subjected to six different flotation tests on 500 to 1000 g samples using the same processing methods outlined for in the previous section. Table 7 summarizes the flotation test results.

The IMC cationic process tests (1, 3, and 5) were performed after mild feed scrubbing and desliming as previously described for sample OB-1. The best test results obtained (test 5) showed that a phosphate concentrate assaying only 24.80 percent P_2O_5 , 5.56 percent insol, and $CaO/P_2O_5 = 1.87$ was produced at 80+ percent P_2O_5 recovery. This product contained about 10.5 weight percent of shell impurity compared to about 24 percent shell in the flotation feed. Concentrate MgO was a relatively high 0.9 percent, and I+A was moderately low at about 1.6-1.7 percent.

The “Crago” process (test 4) was discontinued when the de-oiling stage became virtually impossible to perform without using so much acid that the carbonates would partially dissolve, leading to an unreliable material balance. An indication of this serious problem was noted during processing sample OB-1.

The fatty acid/oil rougher plus cleaners

process (tests 2 and 6) yielded poor results. At 99.2 percent P_2O_5 recovery, the concentrate assayed 19.18 percent P_2O_5 , 4.54 percent insol, with a $CaO/P_2O_5 = 2.51$. Very little shell was removed during the cleaner flotation stages. The use of a sodium silicate scrub before cleaner flotation yielded a phosphate concentrate assaying 24.79 percent P_2O_5 , 2.18 percent insol, with a $CaO/P_2O_5 = 1.92$ at a P_2O_5 recovery of only about 26 percent.

As previously mentioned for sample OB-1, the phosphate particle surfaces present in sample OB-2 were highly reactive with normal quantities of either fatty acid or primary tallow amine flotation reagents. IMC metallurgists reported that other flotation processes that utilize fatty acid flotation of carbonates from phosphate in a slightly acid circuit would not work very well with this sample because of the relatively coarse size of the shell fragments present and the high collector reactivity of the phosphate surfaces.

The failure of the IMC cationic process to produce a 29+ percent P_2O_5 concentrate from sample OB-2 was not unexpected in view of the 24-25 weight percent shell present in the flotation feed. After silica pre-flotation, the feed to the phosphate-carbonate separation stage contained about 35 weight percent shell. The IMC cationic process was found to be effective on samples containing up to about 16 weight percent shell during the early stage of process development in early 1977.

Agrico Laboratory Study

Agrico Chemical Company conducted standard Florida double float bench-scale beneficiation tests on sample splits from OB-1 and OB-2. The results from sample OB-1 indicate a concentrate product comparable with the product produced at Texasgulf, in Aurora, North Carolina (Table 8). These results are similar to the average analysis for unit FPS-1 in Onslow Bay presented in Table 9 (Riggs and

Table 7. Freshwater laboratory flotation test results for sample **OB-2**. Bracketed values (composite) are calculated weighted averages.

Test #	Product	Wt. % in product	Assay (Wt. percent)					CaO/ P ₂ O ₅	P ₂ O ₅ in product
			P ₂ O ₅	Insol	CaO	MgO	I+A		
IMC ALL-CATIONIC PROCESS:									
1	Phos. Conc.	45.8	23.47	7.17	45.50	0.98	1.75	1.94	86.1
	Shell Tails	21.1	4.72	4.17	41.56	—	—	8.79	8.0
	Silica Tails	33.0	2.22	87.39	4.56	—	—	2.05	5.9
	<u>Scrub Slime</u>	<u>0.1</u>	<u>2.22</u>	<u>30.86</u>	<u>31.10</u>	<u>—</u>	<u>—</u>	<u>14.01</u>	<u>Tr</u>
	Composite	100.0	(12.48)	(33.03)	(31.11)	—	—	(2.49)	100.0
3	Phos. Conc.	36.1	24.88	6.74	47.80	0.97	1.62	1.92	72.2
	Shell Tails	29.1	8.65	4.19	47.80	—	—	5.51	20.2
	Silica Tails	34.6	2.68	85.45	6.38	—	—	2.38	7.5
	<u>Scrub Slime</u>	<u>0.2</u>	<u>2.22</u>	<u>30.86</u>	<u>31.10</u>	<u>—</u>	<u>—</u>	<u>14.01</u>	<u>0.1-</u>
	Composite	100.0	(12.43)	(33.27)	(33.44)	—	—	(2.68)	100.0
5	Phos. Conc.	40.2	24.80	5.56	46.56	—	—	1.87	80.8
	Shell Tails	24.2	6.17	3.39	48.51	—	—	7.85	12.1
	Silica Tails	35.3	2.47	81.62	4.89	—	—	1.98	7.1
	<u>Scrub Slime</u>	<u>0.3-</u>	<u>2.22</u>	<u>30.86</u>	<u>31.10</u>	<u>—</u>	<u>—</u>	<u>14.01</u>	<u>Tr</u>
	Composite	100.0	(12.34)	(31.96)	(32.28)	—	—	(2.61)	100.0
“CRAGO” PROCESS:									
4	Phos. Conc.								
	Silica Tails (Am.)	70.9							
	Acid De-oil Slime								
	<u>Silica Tails (F.A.)</u>	<u>29.1</u>							
	Composite	100.0							
FATTY ACID ROUGHER/CLEANER/RECLENER PROCESS:									
2	Phos. Conc.	65.3	19.18	4.54	48.30	1.24	1.81	2.51	99.2
	Comb. Cl. Tails	3.9	0.51	74.01	1.50	—	—	24.39	0.1
	<u>Ro. Silica Tails</u>	<u>30.8</u>	<u>0.28</u>	<u>91.20</u>	<u>2.52</u>	<u>—</u>	<u>—</u>	<u>9.03</u>	<u>0.7</u>
	Composite	100.0	(12.63)	(33.94)	(32.81)	—	—	(2.59)	100.0
6*	Phos. Conc.	13.2	24.79	2.18	47.66	—	—	1.92	25.7
	Comb. Cl. Tails	46.2	19.39	3.68	48.71	—	—	2.51	70.3
	<u>Ro. Silica Tails</u>	<u>40.6</u>	<u>1.02</u>	<u>79.73</u>	<u>10.12</u>	<u>—</u>	<u>—</u>	<u>9.92</u>	<u>4.0</u>
	Composite	100.0	(12.65)	(34.36)	(32.90)	—	—	(2.60)	100.0

* Rougher phosphate concentrate conditioned 2 minutes at 65% solids with sodium silicate before cleaner flotation.

others, 1985; DPRA 1987; Powers and others 1990). and the reported uncalcined double float concentrate of North Carolina Phosphate Co. (Agrico,1982).

SEA WATER BENEFICIATION STUDIES

Homogeneous sample splits from OB-1 and OB-2 were analyzed by the Virginia Center for Coal and Minerals Processing at Virginia Polytechnic Institute (VPI). The scope of the VPI investigation was different from IMC's basic bench-scale beneficiation study. The VPI study was aimed at establishing a database for processing offshore phosphate resources from the Onslow Bay deposit with four primary

objectives: (1) to determine the possibility of beneficiating the ore using sea water. (2) to test the possibility of using a column flotation technology for beneficiation. (3) to compare the results of column flotation with those of conventional flotation, and (4) to evaluate the amount of fresh water needed to wash chlorine from the phosphate concentrates.

There is little experience in the United States in processing phosphate ores with sea water. It is possible that the reagents used in conventional flotation cannot be used in sea water. Also, it may be difficult to use conventional flotation machines for sea water flotation because of corrosion problems. Recent developments in

Table 8. Typical analysis of phosphate rock from Aurora, North Carolina (Data from Agrico, 1982).

	Uncalcined		Calcined	
	Range	Typical	Range	Typical
Moisture	2-3 wt. %	2.5 wt. %	0-0.4 wt. %	0.30 wt. %
Phosphate (% P ₂ O ₅)	29.8-30.8	30.52	0-33.0	32.26
Calcium (CaO)	47.9-49.6	48.83	50.9-53.1	51.60
Sand and Insoluable	3.0-4.0	3.5	3.0-4.0	3.50
Total Silica (SiO ₂)	3.3-4.3	3.6	3.4-4.4	3.80
Acid Soluable Silica (SiO ₂)	0.8-1.0	0.90	0.9-1.3	1.05
Iron (Fe ₂ O ₃)	0.6-0.8	0.65	0.6-0.8	0.69
Aluminum (Al ₂ O ₃)	0.3-0.5	0.40	0.3-0.5	0.42
Magnesium (MgO)	0.5-0.7	0.58	0.5-0.7	0.61
Sodium (Na ₂ O)	0.9-1.1	0.99	0.9-1.2	1.05
Potassium (K ₂ O)	0.08-0.12	0.09	0.08-0.13	0.10
Carbon Dioxide (CO ₂)	5.7-6.1	5.82	3.5-4.6	3.90
LOI (900°C)	9.5-10.4	10.00	3.9-5.0	4.40
Fluorine (F)	3.3-3.8	3.41	3.6-4.0	3.65
Total Sulfur (S)	0.95-1.2	1.13	1.0-1.3	1.20
Sulfide Sulfur (S)	0.01-0.07	0.05	0.10-0.20	0.14
Organic Carbon	0.9-1.3	1.10	0.1-0.2	0.14
Arsenic (As ₂ O ₃)	13-21 ppm	17 ppm	14-22ppm	18 ppm
Cadmium (Cd)	33-41 ppm	39 ppm	35-43ppm	40 ppm
Chromium (Cr)	14-44 ppm	29 ppm	15-45ppm	30 ppm
Manganese	95-285 ppm	140 ppm	100-300ppm	150 ppm
Uranium (U ₃ O ₈)	38-95 ppm	76 ppm	40-100ppm	80 ppm
Chlorine (Cl)	10-90 ppm	60 ppm	100-300ppm	200 ppm

¹ Chemical Analysis adjusted to an industry standard of 3.50 percent sand and insoluable.

Table 9. Summary of chemical analyses (in weight percent) from vibracores in unit FPS-1 (concentrate data reported by DPRA (1987) from Riggs and others, 1985).

Core													
Number	P ₂ O ₅	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	CO ₂	SO ₂	F ₂	C	MgO	Na ₂ O	K ₂ O	Insol
OB-14	30.18	4.84	0.20	0.59	46.37	5.30	4.16	3.59	1.48	0.82	0.98	0.09	3.90
OB-29	28.59	4.40	0.18	0.58	47.40	7.45	4.84	3.57	1.17	0.85	0.99	0.08	3.80
OB-22	29.31	17.84	0.39	0.52	39.40	5.37	4.24	3.15	1.10	0.72	0.95	0.13	18.80
OB-24	30.31	6.80	0.19	0.43	45.69	4.62	4.00	3.16	0.96	0.88	0.99	0.08	6.30
OB-26	30.41	5.20	0.19	0.47	48.09	4.59	4.20	3.61	1.10	0.96	1.00	0.08	4.30
OB-64	30.39	5.36	0.18	0.49	47.06	5.30	4.12	3.70	0.88	0.93	0.98	0.08	4.90

column flotation technology may offer an alternative to the conventional flotation.

In general, column flotation is more selective than conventional flotation mainly because of the provisions for using wash water to remove the entrained gangue material. With this advantage, it may be possible to use the column flotation technology for processing ores in a single stage. Currently, flotation is carried out in two stages because of difficulties in achieving a high degree of selectivity. Because of problems at the downstream end, it is also important to remove chlorine from the phosphate concentrates using minimum amounts of fresh water.

Two different samples from the Onslow Bay deposit were tested. The Microcel™ flotation column technology developed at VPI was used for beneficiation of the phosphate. The results are compared with those obtained using a laboratory Denver flotation machine.

Description of Experiment

Two phosphate samples, named OB-1 and OB-2, were delivered to VPI by Geophex. OB-1 refers to the Onslow Bay phosphate sample containing a large amount of clay. OB-2 refers to the phosphate sands from the Holocene surface sediments which contain a significant amount of shell (calcite).

Table 10 shows the particle size analysis results of the OB-1 and OB-2 samples and the

chemical analysis of each size fraction. Figure 3 shows the cumulative particle size distributions for the OB-1 and OB-2 samples, while Figure 4 shows the corresponding density distributions.

The OB-1 sample is significantly finer grained than OB-2. Most of the phosphate is found in the -35/+200 mesh (-425/+75 μm) fraction as shown in Figure 5. Almost no phosphate is present in the -200 mesh (75 μm) fraction; however, a significant amount of phosphate is present in the +35 mesh (425 μm) fraction.

All tests were conducted in sea water. Initial tests were conducted using natural sea water (110 gallons) sent to VPI by Geophex. When the natural sea water ran out, artificial sea water was used. The artificial sea water was prepared using a product provided by Aquarium Systems, Mentor, Ohio in distilled water.

Apparatus and Test Procedure

Flotation tests were conducted using a 2-inch diameter Microcel™ flotation column, which was developed by Virginia Polytechnic Institute and State University. The technology is currently being marketed by Control International and ICF Kaiser Engineers. Figure 6 shows the experimental set up used initially. Approximately 3,000 grams of a phosphate sample was conditioned at 50 percent solids for 10 minutes in a separate conditioning device. The conditioned pulp was then transferred to the

Table 10. Chemical analysis of phosphate concentrates from OB-1 (muddy phosphatic sand) and sample OB-2 (shelly phosphatic sand). Analyses were performed by Agrico Mining.

OB-1

Mesh	P ₂ O ₅	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	F	CO ₂	SO ₃	MgO	As ₂ O ₃	K ₂ O	Na ₂ O	C	H ₂ O	BPL	Insol	LOI
+6	15.55	40.5	40.90	0.36	21.83	2.82	14.51	1.23	0.74	.0024	0.13	0.80	0.54	1.55	33.98	20.44	16.60
-6+14	12.42	37.76	1.41	0.36	26.03	1.66	15.92	1.11	1.25	.0026	0.10	0.81	0.46	1.80	27.14	24.89	18.18
-14+20	16.75	39.58	1.15	0.32	19.74	2.20	—	—	1.30	—	0.10	0.90	—	—	36.60	18.70	—
-20+35	25.30	47.76	0.84	0.28	5.24	3.24	10.42	1.87	.85	.0025	0.09	1.01	0.69	1.70	55.28	4.45	12.81
-35+200	28.10	46.65	0.53	0.33	7.97	3.41	5.72	2.05	0.75	.0016	0.11	1.19	0.86	2.25	61.40	6.78	8.83

OB-2

Mesh	P ₂ O ₅	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	F	CO ₂	SO ₃	MgO	As ₂ O ₃	K ₂ O	Na ₂ O	C	H ₂ O	BPL	Insol	LOI
+6	3.21	47.91	1.35	0.20	7.29	0.49	35.64	0.84	1.78	.0029	0.05	0.43	0.14	1.96	7.01	6.73	37.74
-6+14	2.05	45.46	2.07	.27	14.75	0.30	33.13	0.87	2.17	.0038	0.04	0.30	0.14	1.98	4.48	14.36	35.25
-14+20	2.94	40.74	2.19	0.28	19.34	0.40	—	—	2.34	—	0.40	0.29	—	—	6.42	18.95	—
-20+35	10.86	47.84	2.17	0.29	4.59	1.48	26.60	1.16	2.15	.0039	0.06	0.70	0.31	2.50	23.72	3.48	29.41
-35+200	23.86	47.80	1.23	0.39	4.00	3.13	12.24	1.66	1.40	.0056	0.09	1.01	.82	2.41	52.13	2.88	15.47

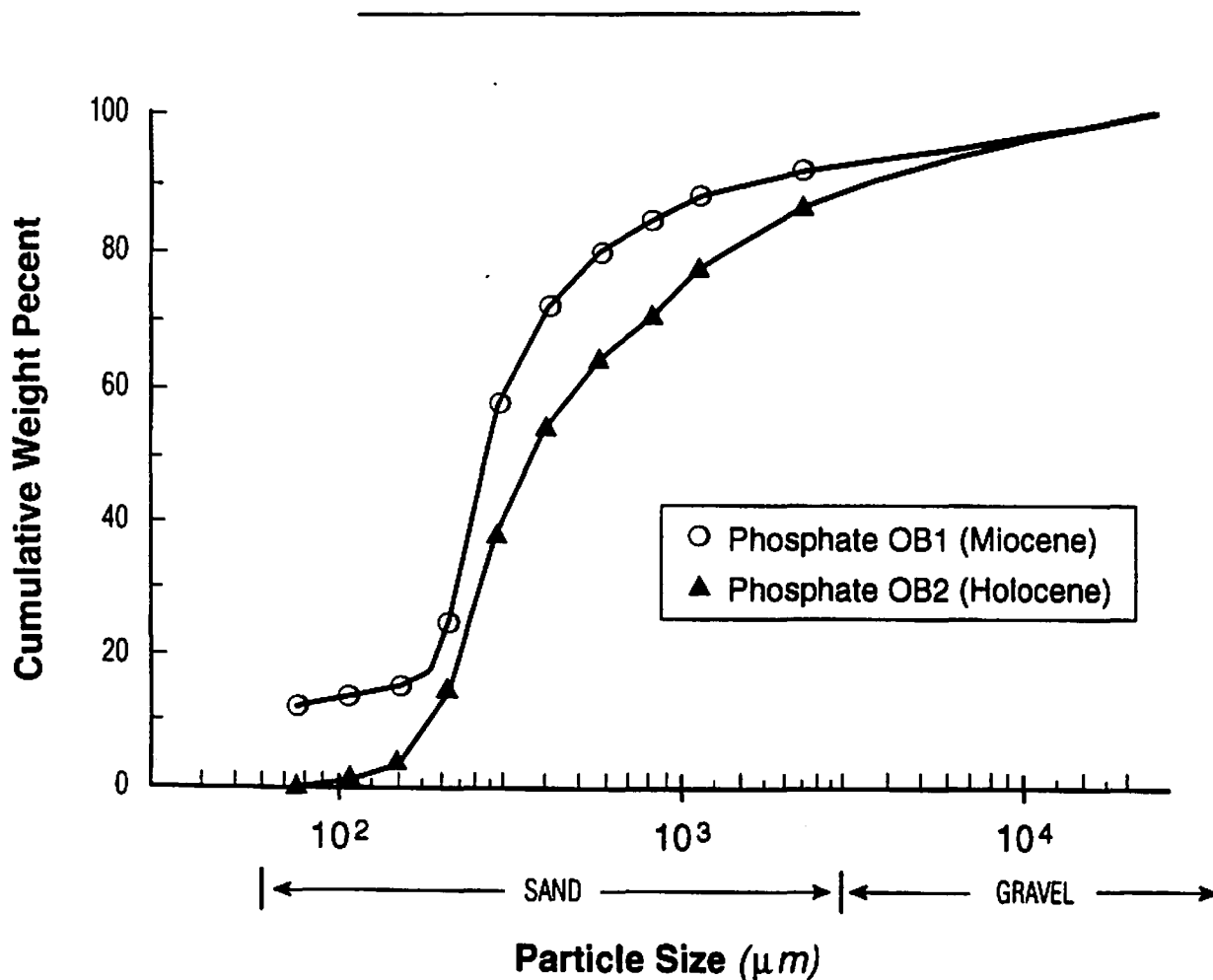


Figure 3. Grain size distribution of samples OB-1 and OB-2.

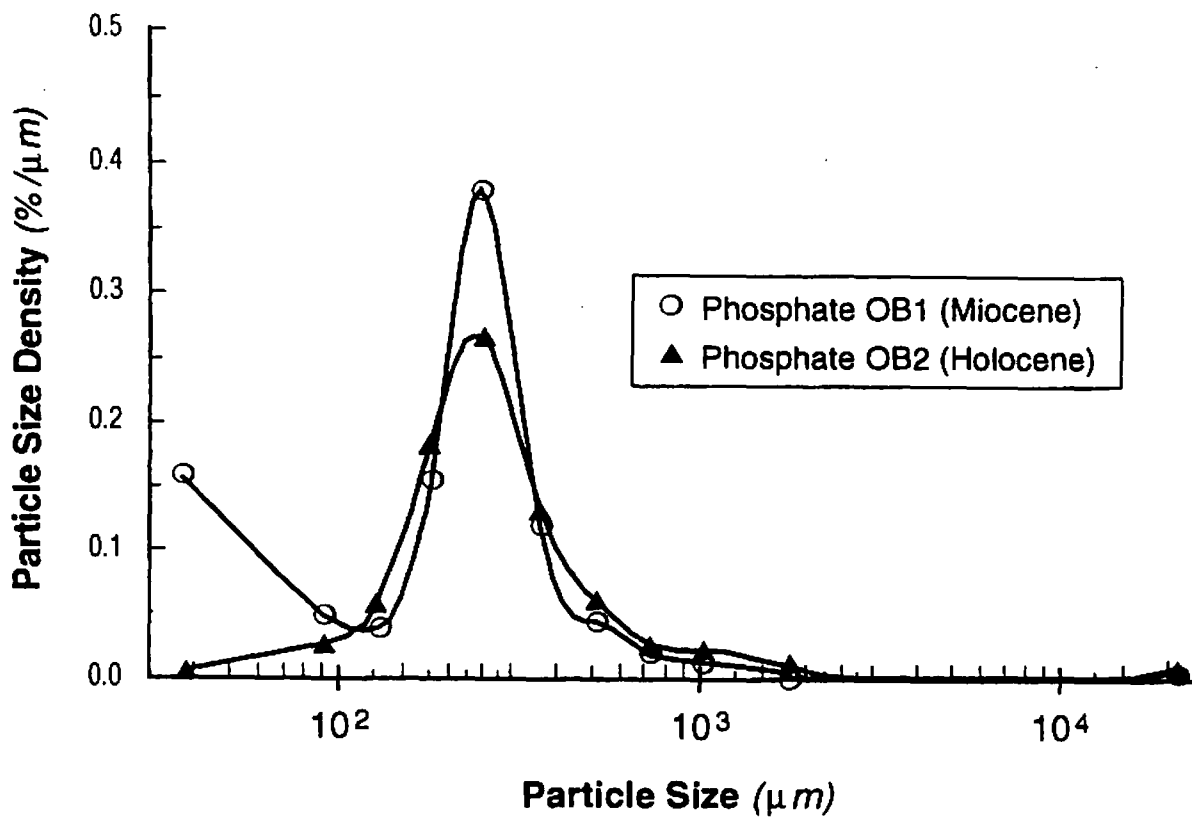


Figure 4. Grain size density of samples OB-1 and OB-2.

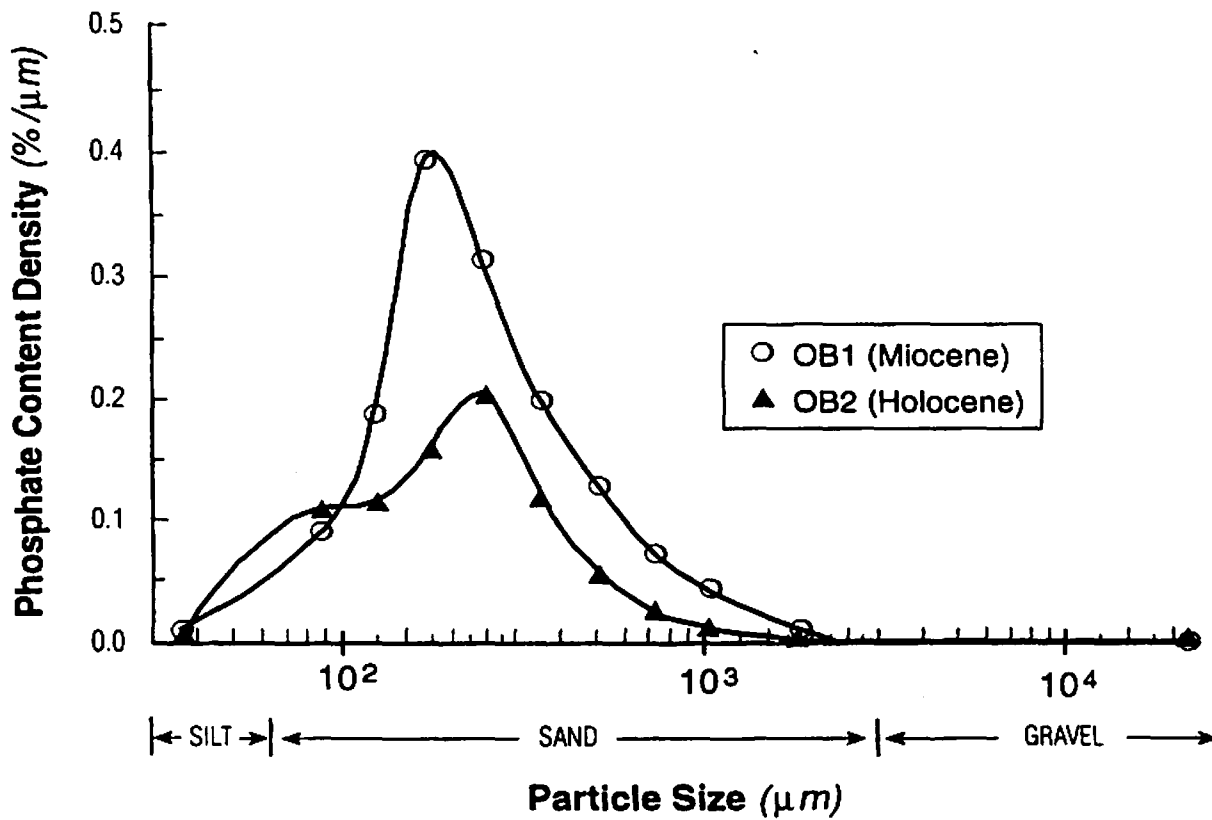


Figure 5. Phosphate content as a function of grain size of samples OB-1 and OB-2.

slurry mixer and diluted to 10 percent solids by weight. The diluted slurry was fed to the column by means of a peristaltic pump at a desired feed rate.

The column tests were run under various feed rates, aeration rates, wash water rates and frother addition rates. The test procedure usually took more than one hour to complete. It was found that during this time the flotation deteriorated gradually. This was probably due to the long agitation time in the slurry mixer before flotation.

In order to confirm that long agitation time is detrimental to flotation, a series of flotation tests were conducted on OB-2 using different conditioning (agitation) times. The results showed that no flotation was possible after 55 minutes of conditioning time.

In order to conduct flotation tests after a relatively short conditioning time, a new flotation circuit was designed and constructed as shown in Figure 7. In this set-up, a slurry was prepared in the slurry mixer in sea water and then pumped to a conditioning tank in which a collector solution and fuel oil were added continuously using appropriate reagent pumps. The conditioning time was controlled by controlling the slurry volume in the conditioning tank. The reagent feed rates were also controlled to provide required reagent addition rates.

Conventional flotation tests were conducted using a Denver laboratory flotation machine with a 5-liter cell. Typically, a desired amount of collector was added to the slurry (10 percent solids) and conditioned for 5 minutes before an extender (No. 2 fuel oil) was added. The agitation continued for another 5 minutes, so that a total of 10 minute conditioning time was achieved before the air was introduced to start the flotation. The flotation experiment was continued until most of the phosphate was recovered.

In order to determine how readily chlorine

can be removed from the flotation products, the flotation concentrates were subjected to fresh water washing using the apparatus shown in Figure 8. It consisted of a vibrating screen (270 mesh), on which a known amount of a phosphate concentrate was placed and washed with a known amount of tap water. The whole procedure usually took 10 minutes. The spent water was collected and analyzed for chlorine and sodium. The conductivity was also monitored.

Results and Discussion

Figure 9 shows the results obtained using saponified fatty acid (SFA) and dodecyl amine (DDA) as collectors and the effect of pH on recovery and grade. SFA was used for floating phosphate, while DDA was used for floating silica. The latter process is referred to as "reverse flotation." When using SFA, the best results were obtained at neutral and alkaline pH's.

With OB-1 and OB-2, the reverse flotation produced very high recoveries but with poor grades. With OB-1, SFA produced better results at the natural pH; using 7.1 lbs/ton of SFA, the recovery was about 85 percent and the grade was 27.8 percent P_2O_5 .

Figure 10 shows the flotation results obtained using varying amounts of DDA as collector. Very high recoveries were obtained but the grades were poor. The grade was improved slightly from 22.9 percent P_2O_5 in the feed to 23.3 percent P_2O_5 in the product. At 7.4 lbs/ton of DDA, the P_2O_5 content of the flotation product was 4 percent and the weight recovery was only 1.8 percent. Obviously, the reverse flotation using the DDA as collector did not work with this sample.

A possible reason for the difficulty may be that the collector precipitates out in sea water as dodecyl amine hydrochloride. It is therefore, recommended to test other cationic collectors, such as quaternary amine, that are more soluble in water. In Figure 11, the flotation results

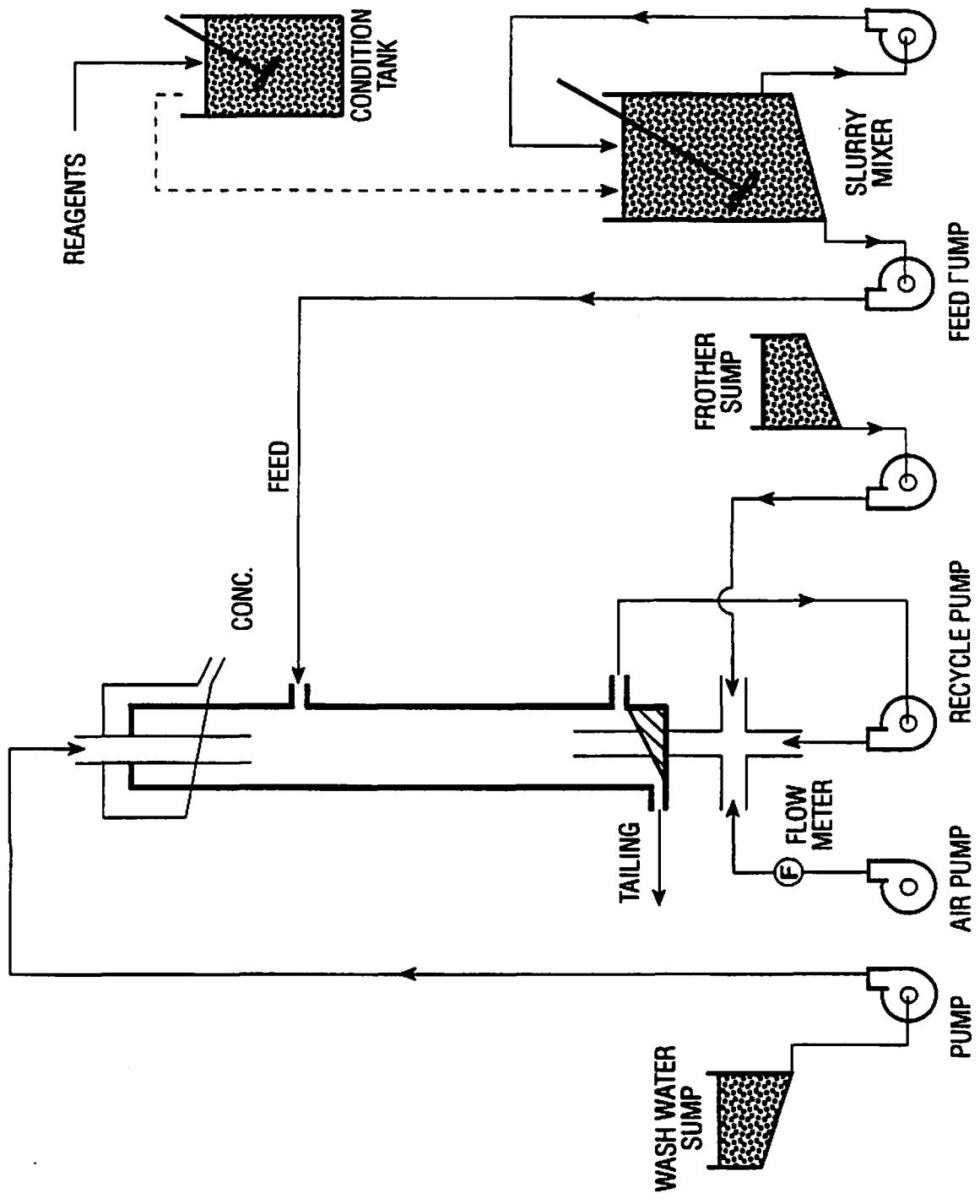


Figure 6. Schematic representation of the initial Microcel™ column flotation circuit.

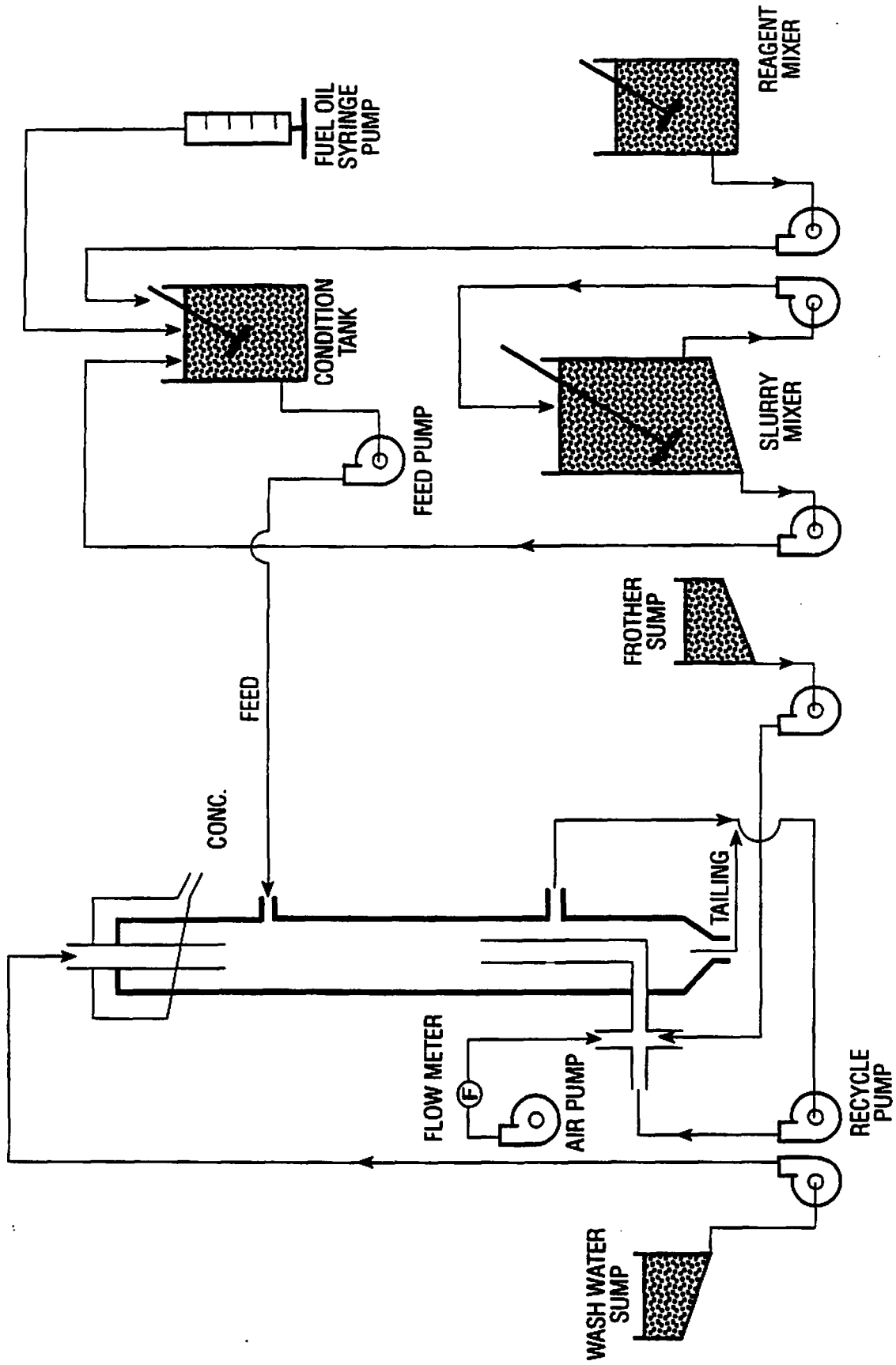


Figure 7. Schematic representation of the Microcel™ flotation circuit designed to provide a controlled conditioning time.

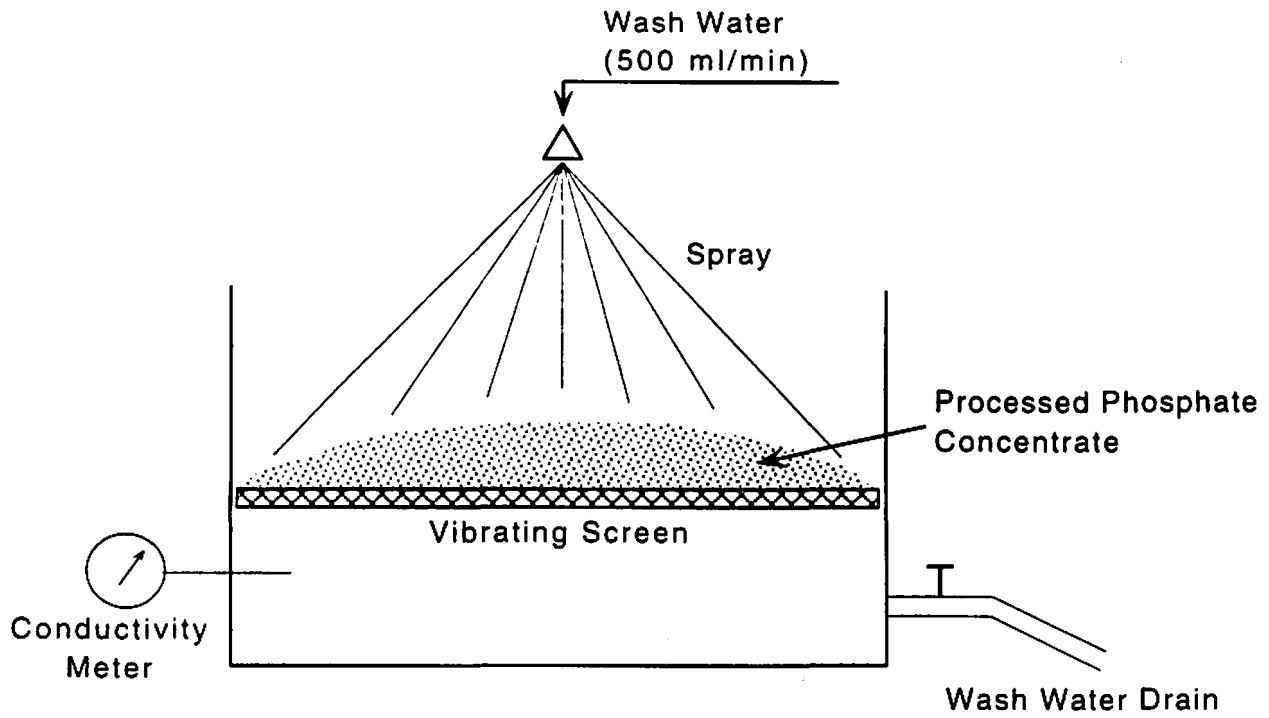


Figure 8. Apparatus used in fresh-water rinse of processed phosphate concentrate.

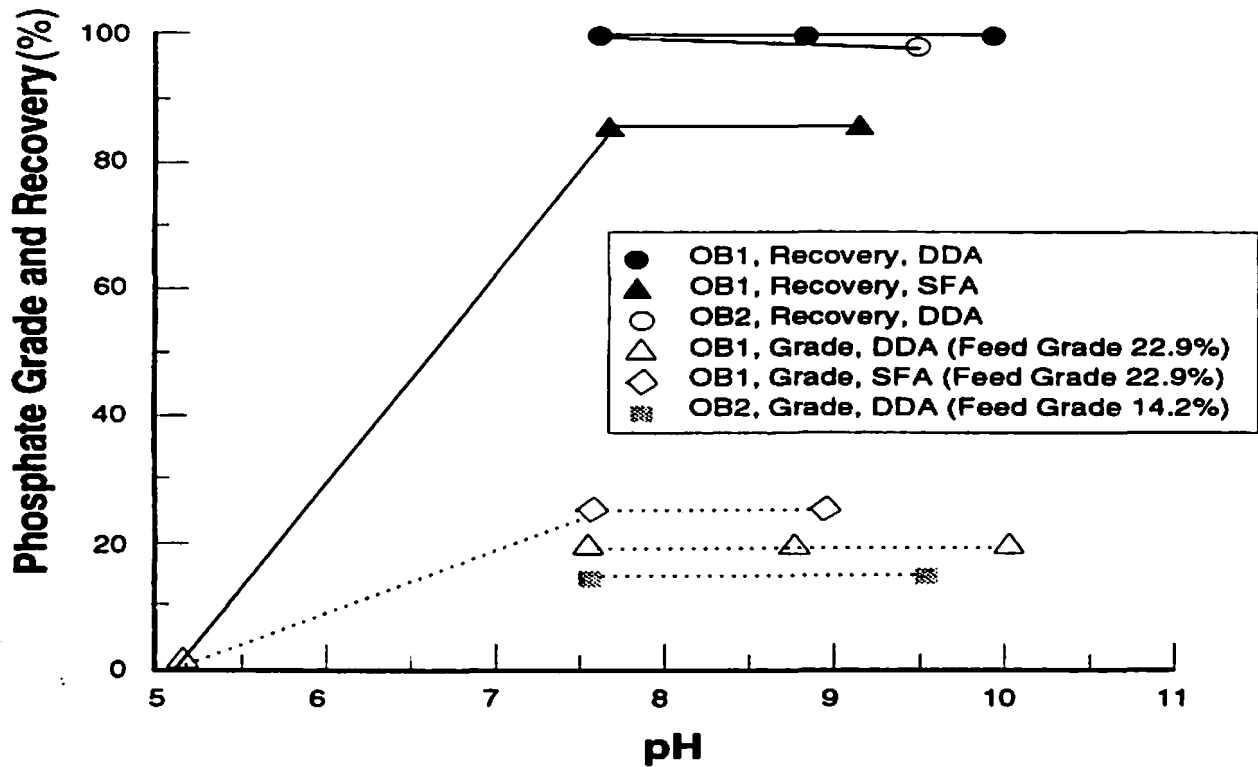


Figure 9. Effect of pH on the flotation of samples OB-1 and OB-2 using conventional flotation (collector dosages: OB-1-DDA=7.4 lbs/ton; OB-2-DDA=6.0 lbs/ton; OB-1-SFA=7.1 lbs/ton).

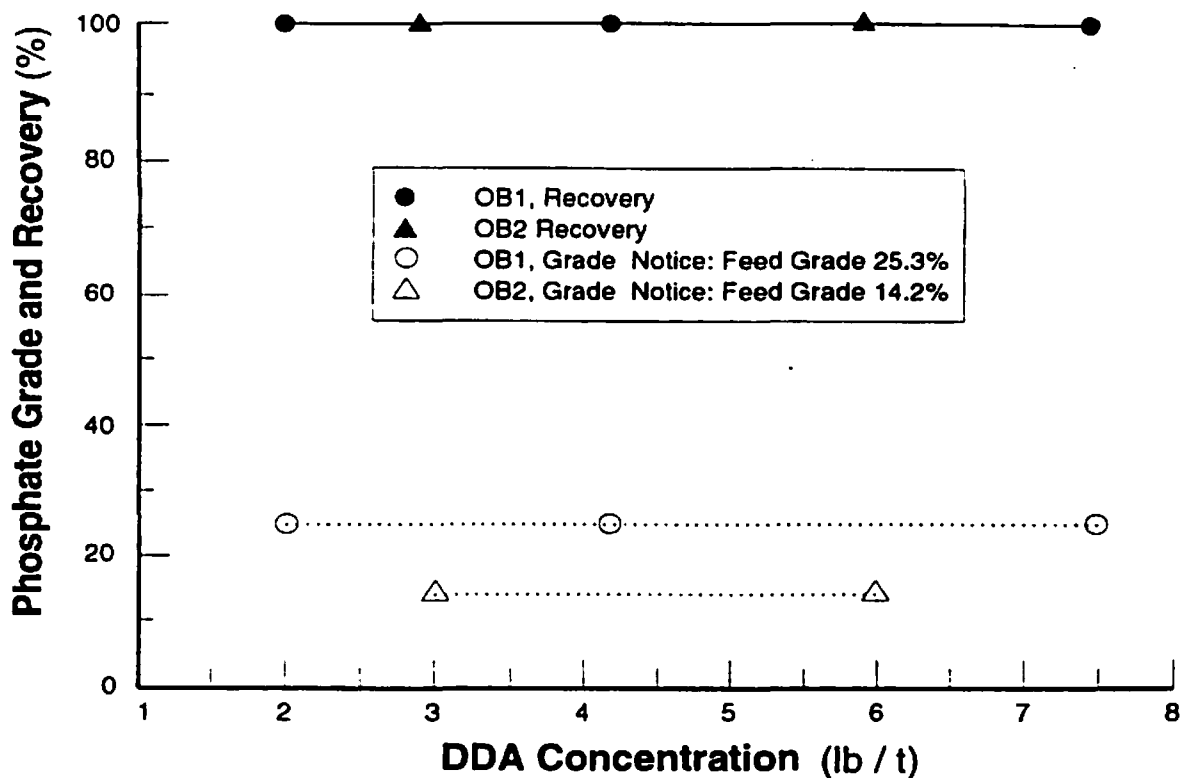


Figure 10. Effect of collector (dodecyl amine) addition on the flotation of samples OB-1 and OB-2 using conventional flotation (1.8 lbs/ton of No. 2 fuel oil at natural pH).

obtained using varying amounts of SFA as collector are shown. All the tests were carried out at the natural ph (pH=7.6).

The flotation recoveries obtained with OB-2 were 100 percent for all collector dosages employed. At 3 lbs/ton of SFA, the grade was improved from 14 percent P_2O_5 in the feed to 22.1 percent P_2O_5 in the product. All the tests were conducted using 1.3 lbs/ton of fuel oil as extender.

With OB-1, the flotation recovery was sensitive to changes in SFA dosages. The best results were obtained at 7 lbs/ton. The recovery was 85.1 percent and the grade was 27.9 percent P_2O_5 . Note here that the improvement in grade was only 3 percent P_2O_5 , because the feed grade was high (25 percent P_2O_5). Further improvement in both grade and recovery may be possible when the process is optimized.

To further improve the product grade, it may

be necessary to develop a calcite depressant, or to develop a more selective collector. A third possibility may be to implement a reverse flotation to remove quartz and possibly calcite from the fatty acid concentrates.

Figure 12 shows the effect of wash water flow rates on the flotation of the OB-1 sample at 500 ml/min of feed rate. In general, an increase in wash water rate increases the product grades, but the improvement was less than 1 percent P_2O_5 . The fact that the product grade did not improve significantly by the wash water suggests that there is no serious entrainment problem for floating coarse phosphate particles. The wash water showed no significant effect in terms of grade or recovery even at 1,100 ml/min of feed rate (Figure 13).

To facilitate the flotation of coarse particles, the pulp level was set close to the overflow lip, creating a shallow froth depth. This may have

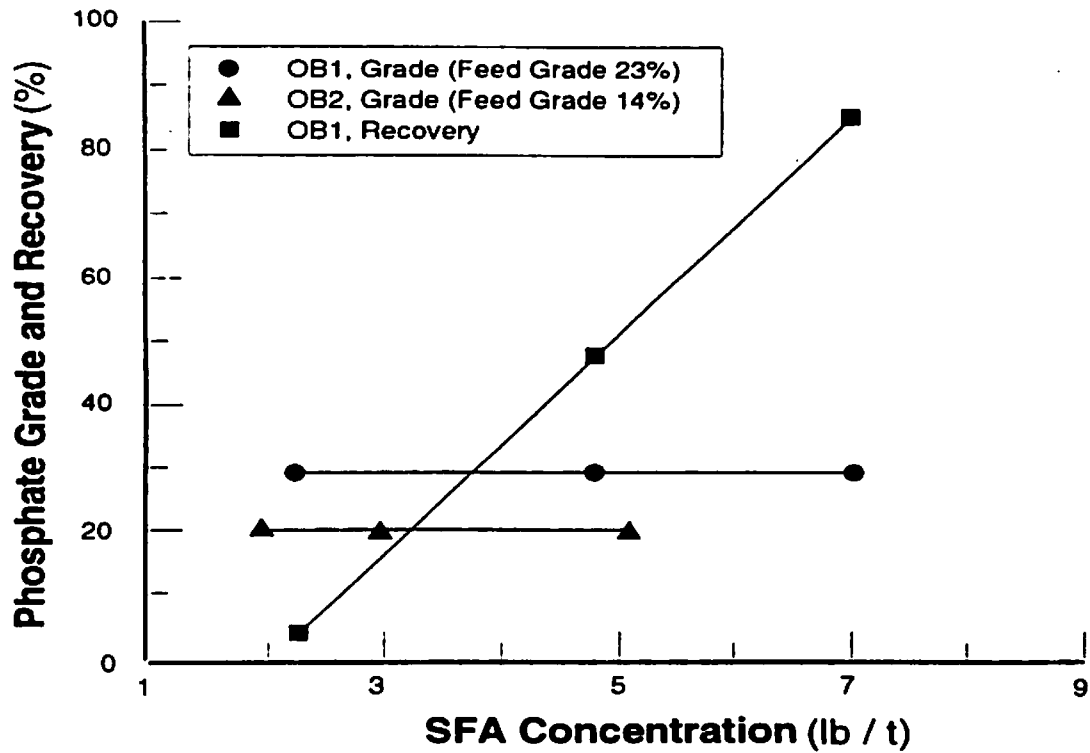


Figure 11. Effect of collector (saponified fatty acid) addition on the flotation of samples OB-1 and OB-2 using conventional flotation (1.3 lbs/ton of No. 2 fuel oil at natural pH).

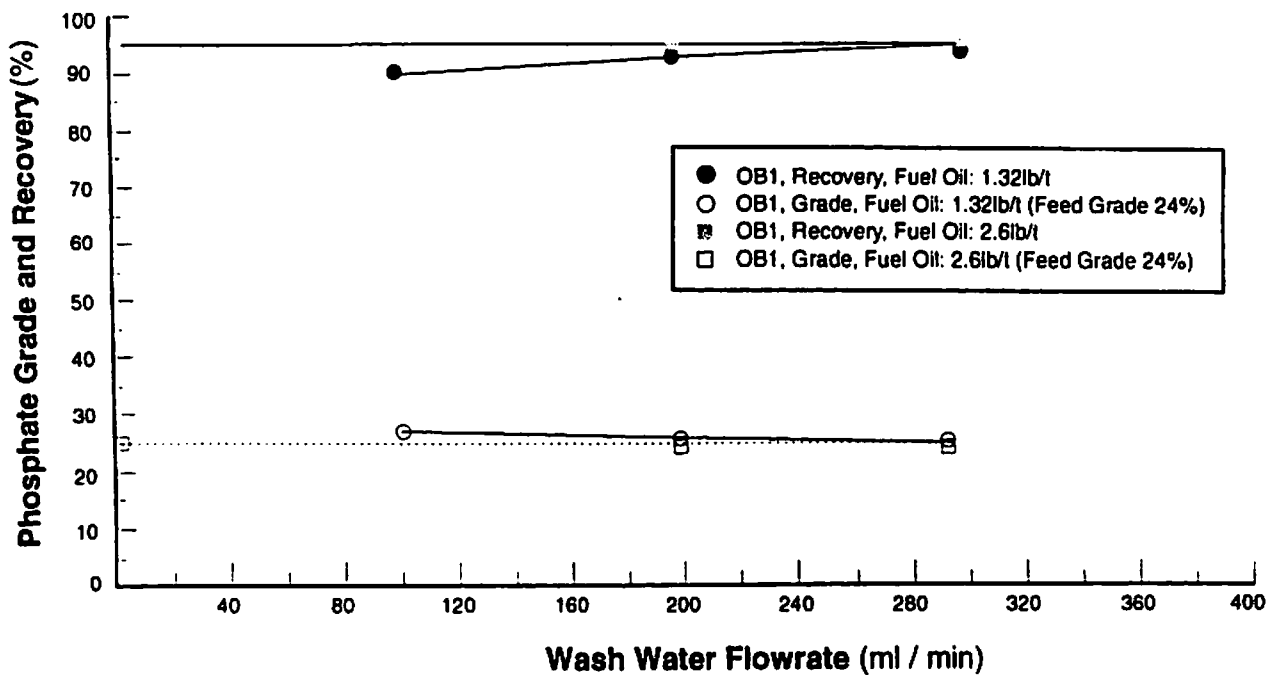


Figure 12. Effect of wash water rate on the column flotation of sample OB-1 at 500 m³/min of feed rate using saponified fatty acid as collector (conditioning time=10 minutes: collector addition rate=7 lbs/ton: aeration rate=1,700 ml/min).

contributed to the ineffectiveness of wash water. By operating the column at a deeper froth depth, the wash water could have been more effective and higher grade products might have been obtained.

Figure 12 also shows that, with OB-1, the recovery increased a little by doubling the amount of fuel oil; however, the grade was reduced by approximately 1 percent P_2O_5 .

Figure 14 shows the results obtained by changing the feed rate to the column. In general, as the feed rate is increased, the retention time is reduced. The result of not increasing the feed rate is an improvement in grade and a decrease in recovery of total P_2O_5 . With the OB-1 sample, there was an improvement in grade of approximately 1 percent P_2O_5 as the feed rate was increased from 500 to 1,100 ml/min. This was achieved without apparent loss of recovery. This

finding suggests that the column was not operated at its full capacity. Further tests should have been conducted at 2,000 to 3,000 ml/min feed rate. At such high feed rates, the recovery may have been reduced to some extent, but the grade might have improved significantly.

Figure 15 shows the results obtained by changing the aeration rate. As shown, the grade improved and the recovery decreased as the aeration rate was increased. This can be explained as follows. As the aeration rate is increased, the bubble size becomes larger, causing a decrease in flotation rate. This will reduce the recovery but improve the grade. Therefore, it is possible to improve the column performance at higher aeration rates.

Figure 16 compares the grade versus recovery relationships obtained by using the column and conventional flotation technologies

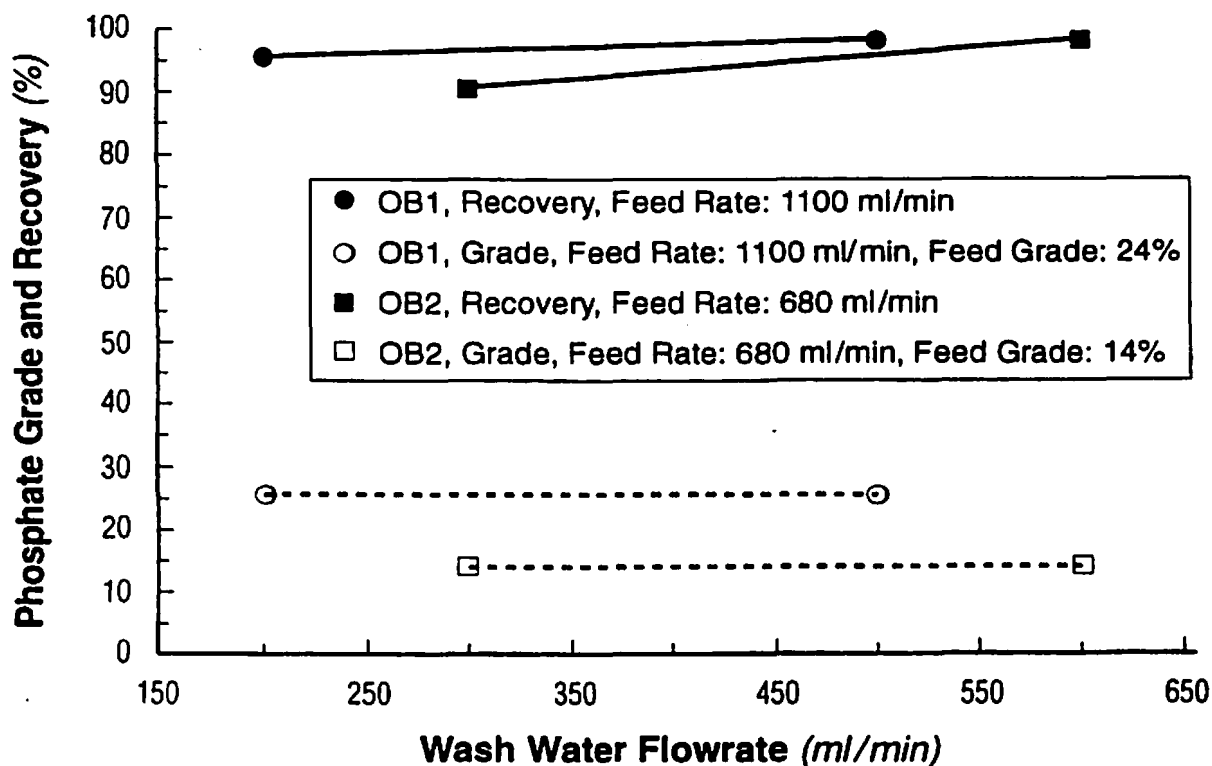


Figure 13. Effect of wash water rate on the column flotation of samples OB-1 and OB-2 using saponified fatty acid as collector (conditioning time=10 minutes; collector addition rate=7 lbs/ton for OB-1; 3 lbs/ton for OB-2; fuel oil addition rate=2.6 lbs/ton for OB-1, 1.3 lbs/ton for OB-2; aeration rate=800 ml/min for OB-1, 1,200 ml/min for OB-2).

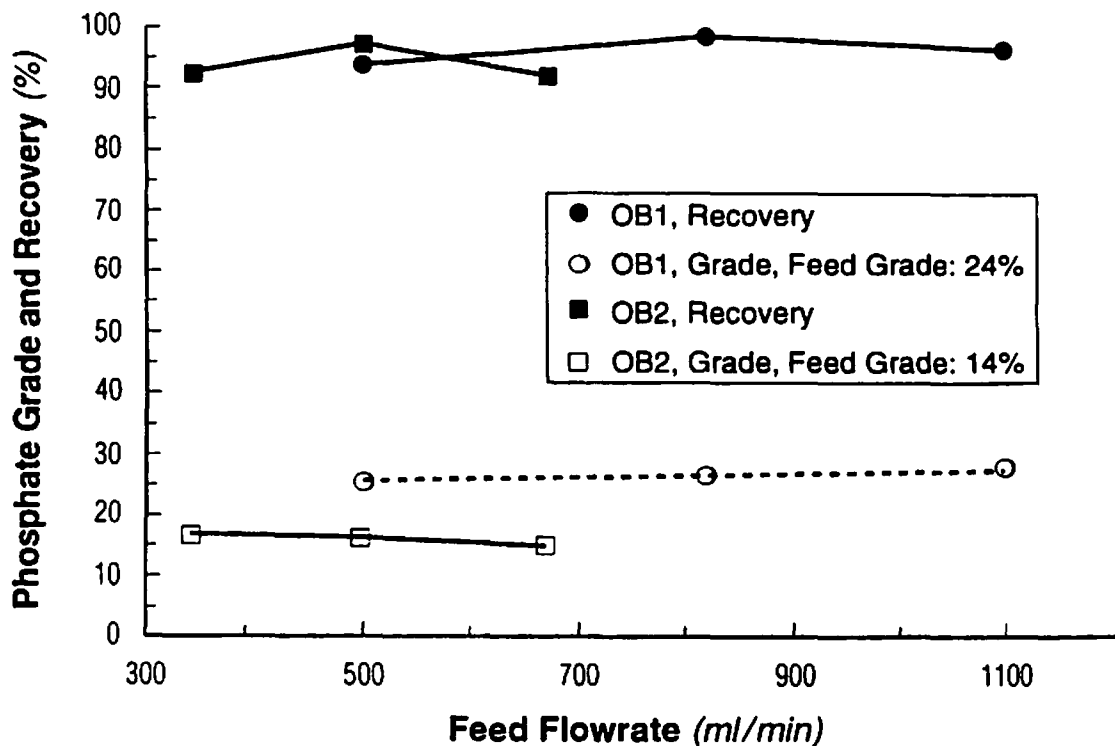


Figure 14. Effect of feed rate on the column flotation of samples OB-1 and OB-2 using saponified fatty acid as collector after 10 minutes of conditioning time. (aeration rate=800 ml/min for OB-1, 1,200 ml/min for OB-2; wash water rate=200 ml/min for OB-1, 300 ml/min for OB-2; collector addition rate=7 lbs/ton for OB-1, 3 lbs/ton for OB-2; extender=2.6 lbs/ton for OB-1, 1.3 lbs/ton for OB-2).

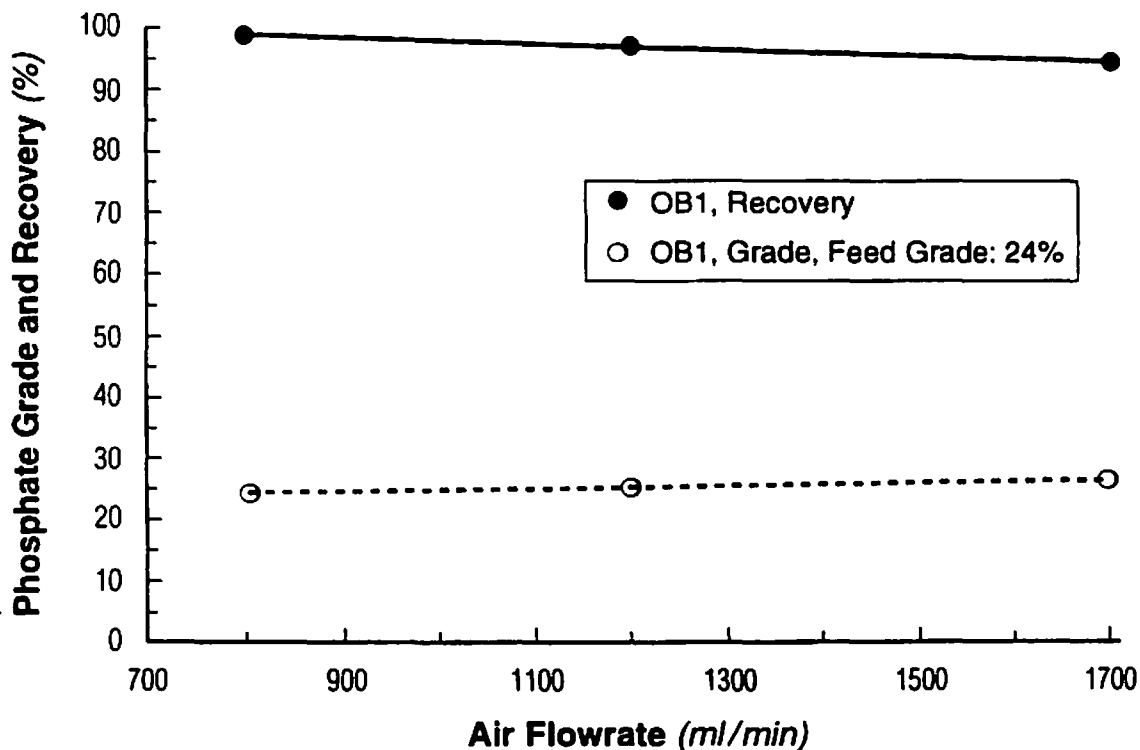


Figure 15. Effect of aeration rate on the column flotation of sample OB-1 using the saponified fatty acid as collector (7 lbs/ton) after 10 minutes of conditioning time (wash water rate=300 ml/min; feed rate=500 ml/min; extender=1.3 lbs/ton).

for the OB-1 and OB-2 samples. All of the test results represent single stage anionic flotation tests using SFA as the collector. The solid lines represent the results obtained using the Denver cell and the open symbols represent those obtained using Microcel™. As shown, sample OB-2 is more difficult to upgrade than OB-1. Using the Denver cell, OB-2, which contains a large amount of shell, has been upgraded to 21 percent P_2O_5 from 14 percent P_2O_5 in the feed with a 99.9 percent recovery. The OB-1 product, which contains a large amount of clay, has been upgraded to about 27 percent P_2O_5 from 24 percent P_2O_5 in the feed with a recovery of 85 percent.

The single stage column flotation test conducted on OB-1 upgraded it from 24 percent to 27 percent P_2O_5 at a 95 percent recovery. These results are superior to the conventional flotation results. Further improvement might have been possible if the column flotation had been optimized.

To optimize the column flotation, the

following parameters must be studied:

- retention time (or feed rate)
- conditioning time
- aeration rate
- wash water rate
- froth height
- reagent type
- reagent dosage.

The column flotation had difficulty with the OB-2 sample. Although the recovery was high (92.8 percent), the upgrading was not as significant as with the conventional flotation. The main problem was probably that the particle size was too large to be floated in a column. To cope with this problem, the column was operated with a shallow froth, which contributed to lowering the product grade.

It may be possible, however, for the column performance to be improved by optimizing the operating conditions. For example, the column should have been operated at much higher feed rates than those employed in the present work.

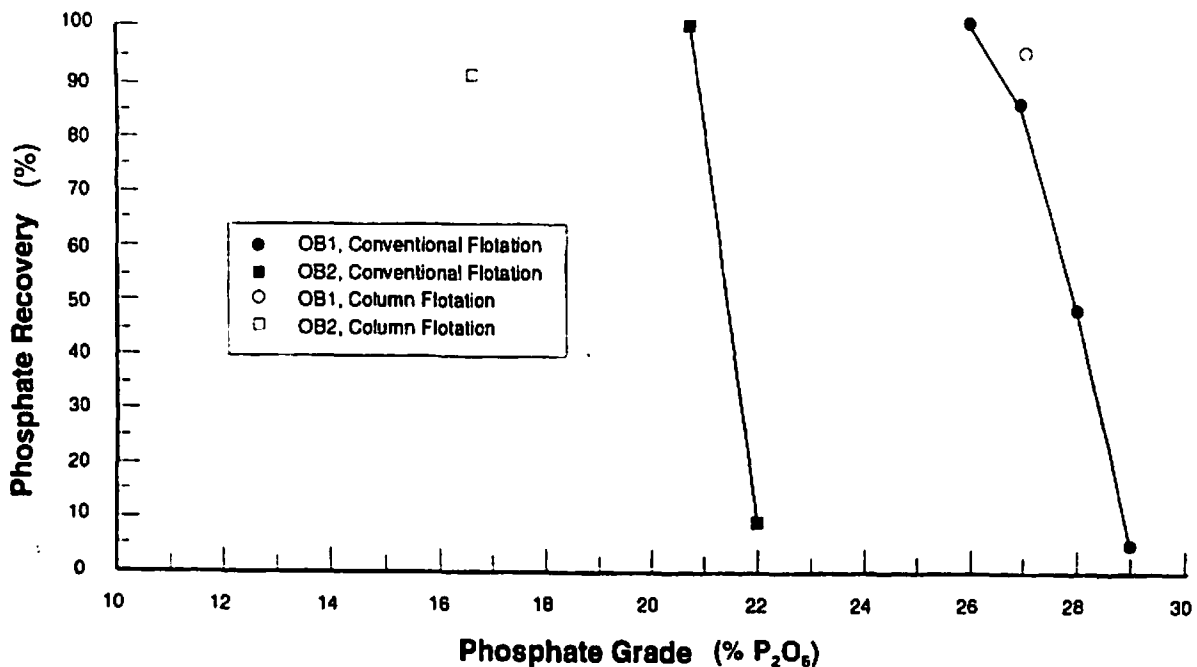


Figure 16. Comparison of column and conventional flotation for the beneficiation of samples OB-1 and OB-2.

Also, the column height could have been reduced to accommodate the high flotation rates of larger particles. These changes in operating conditions could not be implemented because of the shortage of test samples.

Results of the wash tests are given in Figure 17. The conductivity of the spent wash water was comparable to that of the tap water after washing the concentrate using about 2.5 to 3.5 liters of water per kg of the concentrate.

Chloride content was drastically reduced after washing the concentrate with 2.5 to 3.0 l/kg of fresh water, but was significantly higher

than in the tap water (Figure 18). With the OB-1 sample, the spent wash water contained 0.0036 moles/l of chloride and 0.0065 moles/l of sodium after spending 2.5 l/kg of fresh water. Tap water, on the other hand, contained 0.0003 moles/l chloride and 0.0004 moles/l sodium.

With the OB-2 sample, the spent wash water assayed 0.0022 moles/l chloride and 0.0034 moles/l sodium after spending 2.5 l/kg of fresh water. It appears, therefore, that OB-1 was a little more difficult to wash than OB-2, which can be attributed to the difference in particle size distribution.

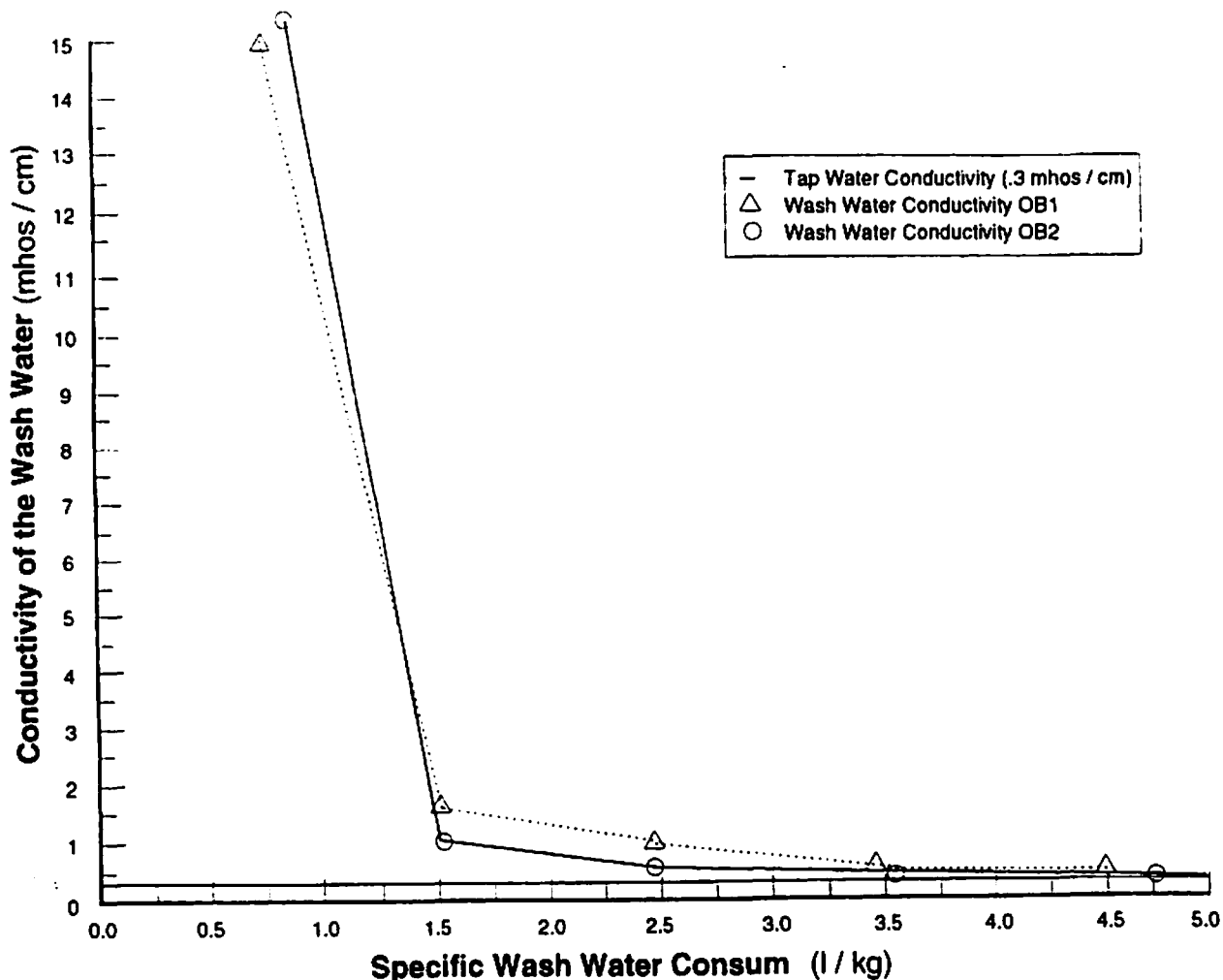


Figure 17. Results of the wash tests conducted on the column flotation concentrates using a conductivity probe.

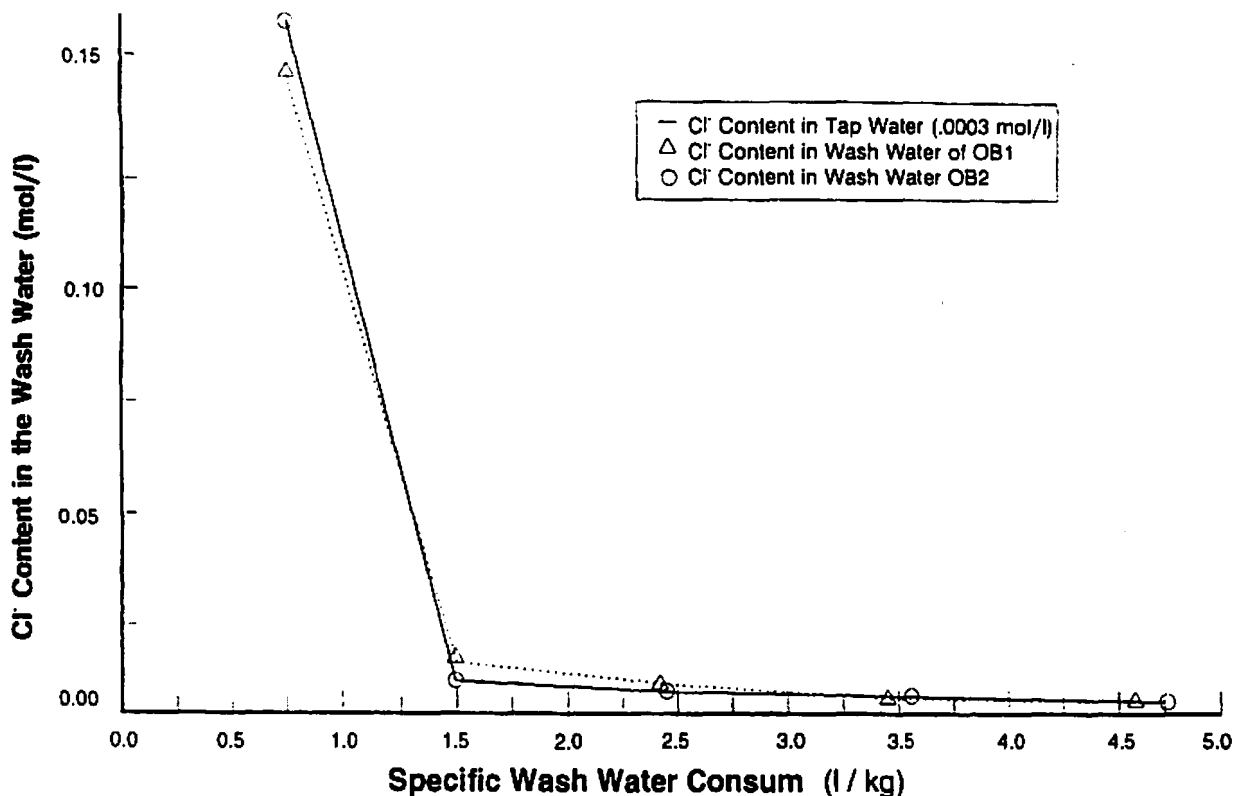


Figure 18. Results of the wash tests conducted on the column flotation concentrates using chloride analysis.

CONCLUSIONS AND RECOMMENDATIONS

(1) A simple SCUBA-diver-aided technique for collecting large bulk samples of surface or shallow subsurface samples of unconsolidated sediment was successfully used to collect two large bulk phosphate samples in Onslow Bay, North Carolina.

(2) Bulk rock analysis of the sample OB-1 (Miocene muddy phosphorite sand) is nearly identical to the average grade of phosphate sands from the Miocene unit FPS-1 in published manuscripts (Riggs and others, 1985; DPRA, 1987; Powers and others, 1990). The close agreement of analysis indicates that small samples collected by coring are representative of unit FPS-1. Additionally, beneficiation test results of large bulk samples from this study also agree with published beneficiation data, suggesting that small samples collected from core

holes can be used to describe general metallurgical qualities of phosphate sediment.

(3) Beneficiation studies conducted by three independent laboratories indicate that the high-grade Miocene muddy phosphorite sand can be beneficiated using either fresh (IMC and Agrico studies) or saltwater (VPI) to produce a phosphate product comparable in quality to phosphate currently being sold at Texasgulf's Lee Creek Mine in Aurora, North Carolina.

(4) A new technology developed by VPI scientists utilizes seawater for beneficiation of phosphate ore. Although the new seawater beneficiation process is not as efficient in upgrading phosphate sands as existing freshwater technology, further refinement will likely result in improved recovery rates.

(5) The new salt water beneficiation technique is especially suitable for an ocean

installation because capital cost for construction is likely to be significantly lower than conventional processes, since it requires less process area on board a factory ship and can be constructed from economical and corrosion resistant plastic.

(6) Miocene muddy phosphorite sands can be upgraded to a concentrate product comparable to the products currently produced at the Lee Creek Mine. Both double and single float, single-column, bench-scale tests produced concentrates of marketable value.

(7) Clean, shelly phosphate sands of Holocene age were beneficiated to produce low-grade concentrates with elevated MgO concentrations. This beneficiated concentrate is not currently suitable for producing phosphoric acid. Additional studies are needed to determine if grade and MgO concentrations can be improved for these very shell-rich surface sediments.

(8) The use of sea water for beneficiation of continental shelf phosphate is feasible. In tests using an anionic collector (saponified fatty acid), both the OB-1 and OB-2 samples responded favorably to the sea water flotation. OB-2 was upgraded to 21 percent P_2O_5 from the feed grade of 14 percent P_2O_5 with a 99 percent recovery in a single-stage conventional flotation. With OB-1, the grade was improved from 24 percent P_2O_5 in the feed to 27.9 percent P_2O_5 in the concentrate with 85 percent recovery.

(9) Results with the OB-1 sample were further improved using the Microcel™ flotation column. The grade was improved from 24 percent P_2O_5 to 27 percent P_2O_5 at a recovery of 95 percent. However, the column flotation produced inferior results with the OB-2 sample as compared to conventional flotation. This may be attributed to the fact that OB-2 sample is significantly coarser than OB-1 sample. The operating conditions of the Microcel™ column

was not adjusted properly for coarse particle flotation.

(10) The Microcel™ column flotation tests suggest that the wash water addition may not be necessary for flotation of coarse phosphates and that 2.5 minutes of retention time is sufficient for the Microcel™ flotation. The results obtained by changing feed rates suggest that a shorter retention time could have produced better results in terms of product grade.

(11) Initial tests conducted with a cationic collector (dodecyl amine), which is commonly used in the phosphate industry, produced poor results. OB-1 grade was improved from the feed grade of 22.9 percent P_2O_5 to 23.3 percent P_2O_5 with high recoveries (99 percent). The results obtained with sample OB-2 were also poor. The difficulty in using dodecyl amine is possibly due to the collector precipitating as dodecyl amine hydrochloride. Use of less soluble collector such as quaternary amine may be more useful.

(12) OB-1 and OB-2 concentrates produced by flotation and subjected to fresh water wash tests required 2.5-3.5 l/kg of fresh water to remove most (99.7 percent) of the chloride. Desalting of chloride-contaminated phosphate concentrate should be conducted before the concentrate is allowed to dry.

ACKNOWLEDGEMENTS

We are indebted to Ms. Bonnie Dodson for technical assistance and beneficiation analysis of samples at Agrico Mining, Mulberry, Florida, and Mr. John Bernardi of International Minerals and Chemical of Bartow, Florida.

Charles W. Hoffman, Kathleen M. Farrell, Robert H. Carpenter, and Jeffrey C. Reid of the N. C. Geological Survey and Charles H. Gardner, State Geologist of North Carolina, contributed comments that significantly improved the manuscript. Their efforts are greatly appreciated.

REFERENCES CITED

- Agrico Chemical Company, 1982, Technical data. North Carolina phosphate rock: Advertisement for the Agrico Chemical Company distributed to potential customers.
- Development Planning and Research Associates, Inc., (DPRA), 1987, The economic feasibility of mining phosphorite deposits of the continental shelf adjacent to North Carolina: a report to the office of Planning and Assessment, North Carolina Department of Natural Resources and Community Development, Raleigh, North Carolina Manhattan, Kansas. 257p.
- Powers, E.R., Crowson, R.A., Riggs, S.R., Snyder, S.W., Snyder, S.W., and Hine, A.C., 1990, Chemical characteristics and reevaluation of the phosphate resource potential in Onslow Bay, North Carolina Continental Shelf: *Marine Mining*, v. 9, p. 1-41.
- Riggs, S.R., Snyder, Stephen W., Hine, A.C., Snyder Scott W., Ellington, M.D., and Mallette, P.M., 1985, Geologic framework of phosphate resources in Onslow Bay, North Carolina continental shelf: *Economic Geology*, v. 80, p. 716-738.
- Riggs, S.R., and Ames, D., 1992, Upper Cenozoic geology of the Onslow Bay and Aurora embayments, North Carolina: compilation of published abstracts from the literature: North Carolina Geological Survey Information Circular 28, 209 p.
- Riggs, S.R., Ames, D., Wyrick, R.A., Lueck, K.L., Powers, E.R., and Crowson, R.A., 1993, Compilation of analytical data for phosphate-rich sediments in Onslow Bay, North Carolina: North Carolina Geological Survey Open-File Report 93-36, 235 p.
- Snyder, Stephen W., Riggs, S.R., and Snyder, Scott W., 1993, Miocene geology of the continental shelf: Onslow Bay, North Carolina: North Carolina Geological Survey Map 3, 1 sheet, scale 1:430,000.