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SEPARATION OF DOLOMITE FROM THE SOUTH FLORIDA PHOSPHATE ROCK
VOLUME III

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SEPARATION OF DOLOMITE FROM THE SOUTH FLORIDA PHOSPHATE ROCK

VOLUME III

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DISCLAIMER

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Any opinions, findings, and conclusions or recommendations expressed in this report are those of the authors and do not necessarily reflect the views of the Florida Institute of Phosphate Research.

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CONCLUSIONS

The objectives of the proposed research are to establish the mode of existence of dolomite, specifically magnesium, in Florida phosphate and to develop suitable techniques for separation of dolomite from apatite. Highlights of major accomplishments are briefly discussed below.

Conclusions of the Salt Flotation studies discussed in this volume and other investigations conducted to meet the above objectives are presented below.

Mineralogical Studies

Quantitative X-ray diffraction analysis, combined with chemical analysis of a number of phosphate samples revealed that more MgO than accounted for by dolomite alone was associated with these samples. The amount of excess MgO, as Mg substituting in the apatite lattice, averaged about 0.57%, which is in agreement with values reported in the literature (0.41-0.493).

X-ray diffraction analysis and microscopic observations of the color fractions constituting five phosphate samples demonstrated that a considerable amount of dolomite existed as discrete grains. However, samples containing more than two percent dolomite were found to contain a significant number of interlocked grains. It was also determined that more dolomite in such grains existed on the surface of the particles than in grains with fewer dolomite inclusions. It is envisioned that interlocked particles will have to be ground to extremely small size in order to achieve liberation of apatite from dolomite. Grinding, however, was determined to cause changes in the properties of dolomite samples which could influence separation behavior. It is to be noted that the amount of dolomite inclusions is best determined with a polarizing microscope while SEM techniques are more appropriate for studying the amount of dolomite on the apatite surface.

Study of size fractions of phosphorite samples revealed that most of the dolomite was preferentially segregated in the coarse and fine fractions.

Microscopic studies and X-ray analysis of a number of dolomite samples from Florida indicated that different dolomite samples had varying physical and compositional characteristics. This may be of significance in developing procedures to separate dolomite from apatite.

Apatite-Dolomite Separation Studies

Aging Studies: Aging behavior of selected samples was studied with the objective of establishing a procedure to achieve consistent pH during the flotation tests. The pH of the mineral suspension containing dolomite drifted toward an equilibrium pH of about 8.2 while the pH of the apatite suspension reached an equilibrium value in the range of 5.5 to 6.5.

Particle size and pulp density had a noticeable effect on the kinetics of the pH drift but only a minor effect on the final pH value. It was difficult to maintain suspensions containing dolomite at acidic pH values due to a rapid drift towards equilibrium pH at about 8.2.

Kinetics of Apatite-Dolomite Flotation: It has been reported in the past that separation of apatite and dolomite might be achieved because of differences in their rates of flotation. A systematic study of the flotation kinetics of apatite and dolomite indicated that the rate of flotation of the two minerals are similar, and under present experimental conditions, desired separation may not be achieved.

Conventional Conditioning: Flotation behavior of single and mixed mineral systems was investigated as a function of the collector concentration over a pH range varying from 3 to 11. Selectivity, predicted by single mineral flotation tests at pH 7 to 10, was not observed in mixed minerals. This is attributed to the depletion of oleate by precipitation with cations dissolved from dolomite. At pH 11, the loss of selectivity in mixed mineral systems is due to possible modification of the apatite surface when in contact with dolomite.

Two Stage Conditioning Process: This process involves conditioning the feed at pH 10 followed by reconditioning at a lower pH before flotation. Selective flotation of dolomite from apatite was observed both for single and mixed minerals by reconditioning at pH 4. To understand the mechanisms of observed selective flotation, further studies involving electrokinetic behavior, oleate adsorption, infrared spectroscopy, and solubility of the minerals were conducted. Selective flotation of dolomite by reconditioning at pH 4 is attributed to the combined effect of higher oleate adsorption on dolomite and hydrolysis of the adsorbed oleate molecules to oleic acid at lower pH values.

The method has been tested at bench scale level with several dolomite-apatite mixtures and natural magnesium phosphate samples from the Florida phosphate field. Reductions of the MgO content of the samples from 1.8-4.0% MgO to below 1% MgO at recoveries of about 90% P_2O_5 in the sink fraction have been obtained in bench scale flotation tests. Reconditioning pH was determined to be one of the most important process parameters in this process.

Selective Flocculation Studies: Although exhaustive data about the nature and extent of interlocking of apatite and dolomite grains in the South Florida deposit is not available, limited mineralogical results suggest that certain phosphorites would need to be ground to fine sizes for complete liberation. Selective flocculation is a promising technique for processing of mineral fines. Preliminary tests using PEO as a flocculant resulted in reducing the MgO levels below 1%, although recoveries were low. It is further indicated that adsorption-of PEO on apatite needs to be reduced or eliminated to achieve higher recoveries.

Salt Flotation Process: The effect of sodium chloride and other salt addition on dolomite and apatite flotation has been studied. It was demonstrated that sodium chloride acts as apatite depressant during flotation at acidic pH values with oleic acid, while dolomite flotation is not affected. It was, however, observed that dolomite particles larger than 48 mesh are difficult to float and they tend to remain in the sink fraction. The trends observed during Hallimond cell tests of single and mixed minerals were confirmed with mixtures of minerals and a natural ore at bench scale level. Under more favorable conditions in the bench scale tests, MgO content of the mineral mixtures was reduced from 5% to 1% or less with at least 90% recovery of P_2O_5 in the sink fraction.

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Chapter IX

SEPARATION OF DOLOMITE FROM PHOSPHATES BY FLOTATION IN THE PRESENCE OF SALT

In this chapter the flotation process based on the depression of apatite with sodium chloride and flotation of dolomite with fatty acids is described. In the first section, studies forming the basis for using salt to bring about the separation of dolomite from apatite are presented. These basic studies allowed the determination of flotation conditions where separation would be possible and also lead to the establishment of a probable mechanism to explain the observed flotation behavior of dolomite and apatite in the presence of salt.

In the second section, the developmental work carried out at bench scale to apply this new process to different apatite-dolomite mixtures and also natural oresis presented.

BASIC STUDIES

Flotation behavior of apatite and dolomite was studied in a Hallimond cell under a wide pH range (3-11) using dodecylamine-hydrochloride (DDA-HCl) or sodium oleate as the collector. Results obtained from flotation of single minerals were corroborated using mixtures of various ratios. Separation of apatite from dolomite using either collector in pure water appeared to be limited, however, flotation experiments in the presence of NaCl yielded favorable results. It was decided to study the anionic collector (sodium oleate) system in more detail, which would permit flotation of the minor mineral (dolomite) as opposed to apatite, the major constituent of the float feed.

Therefore, flotation response of apatite and dolomite was examined was a function of NaCl concentration, pH and sodium oleate concentrations. Results indicate that separation of dolomite from apatite in the presence of NaCl at pH 4.0 ± 0.2 is feasible. Flotation tests were followed by electrokinetic measurements, calcium dissolution and chlorine abstraction tests to elucidate the mechanism of observed selectivity in the presence of sodium chloride.

It is planned to investigate adsorption behavior of the collector in the final phase of this study. This would permit bench scale optimization of the process to beneficiate natural ores.

EXPERIMENTAL

Materials

Minerals

Apatite: A sample of Agrico Chemical Company's (ACC) high-grade product was used in this study. This sample (16 x 150 mesh size) was first screened to obtain a 65 x 100 mesh fraction, which was deslimed, dried and passed through an electrostatic separator to remove the silica grains. The sample was next scrubbed at 70% solids in the pH range of 3.5 to 4.0 using nitric acid. The cleaned sample was rinsed with triple distilled water 15 times, dried at 50°C in an oven for about 12 hours, and stored in a glass bottle. One batch of this sample was ground to -325 mesh in an alumina mortar and pestle for electrophoresis experiments.

Dolomite: Initial flotation tests with cationic collectors were conducted using a sample prepared from Agrico Chemical Company's dolomitic matrix. This sample, however, was low-grade dolomite and contained apatite (12.0% P_2O_5).

Therefore, it was replaced with a hand-picked sample supplied by the International Minerals and Chemical Corporation (IMC), Bartow, Florida. This sample was crushed using a laboratory size chipmunk crusher and then hand-ground to maximize the 65 x 100 mesh fraction. The silica from this sample was removed by the electrostatic separator. The sample was rinsed with triple distilled water 15 times and dried before storing in a glass jar. A hand-ground sample of -325 mesh sample was used for electrokinetic measurements.

Mineral Characterization

Chemical Analysis: Chemical analysis of the apatite and dolomite samples were conducted using an inductively coupled plasma (ICP) spectraphotometer. It is clear from the data presented in Table 1, that the apatite sample is essentially free of dolomite and vice versa.

Surface Area and Porosity: The surface area and pore size distribution of the apatite (ACC) and dolomite (IMC) samples were determined with a Quantachrome Autosorb- unit. The surface area of 65 x 100 mesh fraction calculated by the BET technique using nitrogen gas as the adsorbate was determined to be 11.49 m^2/g and 6.04 m^2/g for apatite and dolomite, respectively. Average pore radius for these minerals was 82 A. Relatively high specific surface area of apatite and dolomite samples indicate that these minerals are porous, which was confirmed by the SEM micrographs (see Figures 1 and 2).

X-ray Analysis: X-ray diffraction analysis for apatite presented in Figure 3 indicated the presence of a small amount of quartz but no dolomite was detected from these scans. The dolomite sample exhibited the presence of minor quartz and feldspar peaks along with the characteristic peak of dolomite as seen in Figure 4.

Table 1

Chemical Analysis (%)

Mineral	P_2O_5	MgO	Acid Insolubles	CaO
Apatite (AAC)	35.28	0.28	2.14	42.08
Dolomite (AAC)	12.06	9.94	3.39	30.88
Dolomite (IMC)	0.90	18.86	3.12	27.01

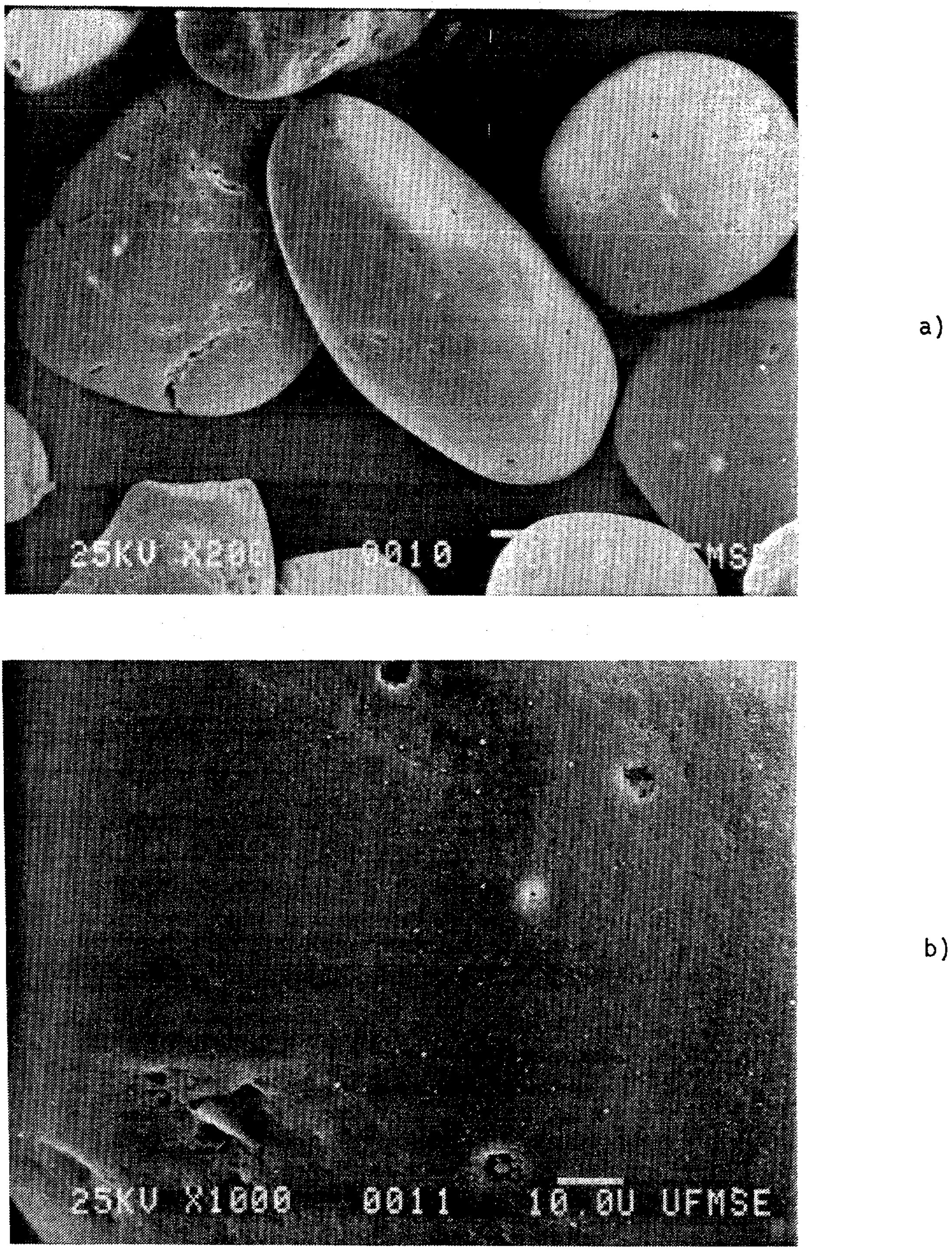

Figure 1. SEM micrograph of apatite (65 x 100 mesh size fraction), a) 200X; b) 1000X.

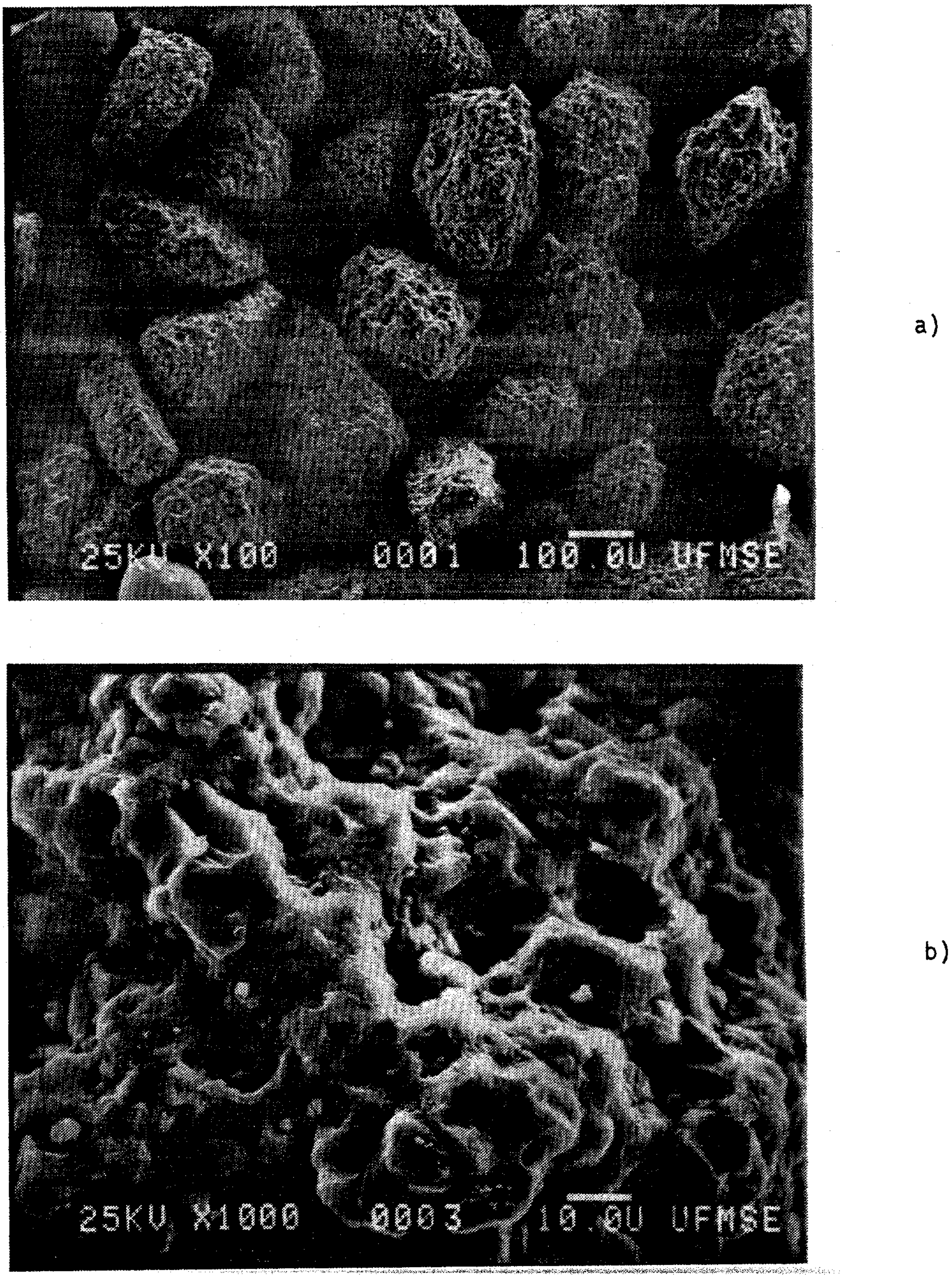

Figure 2. SEM micrograph of dolomite (65 x 100 mesh size fraction), a) 100X; b) 1000X.

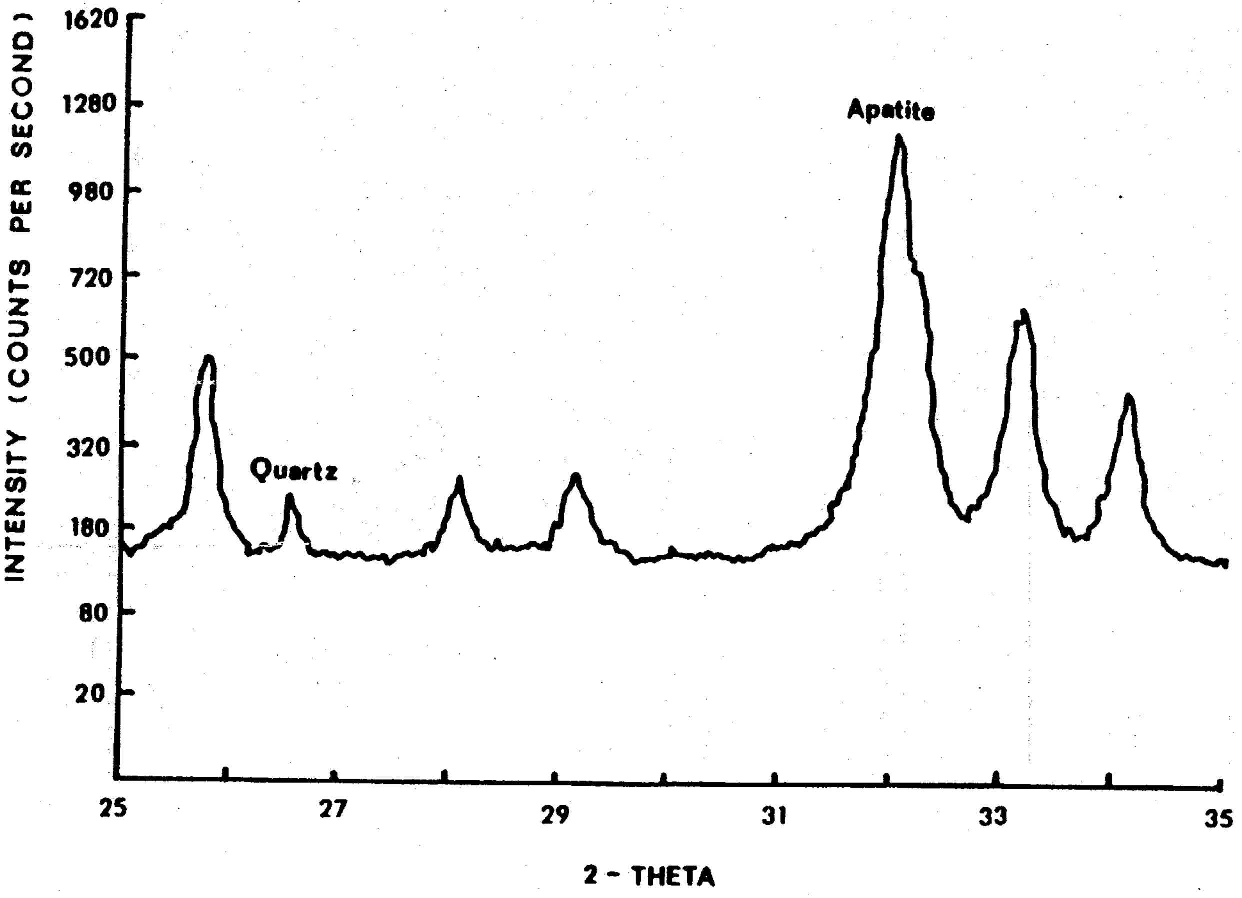

Figure 3. Diffractogram of Agrico apatite.

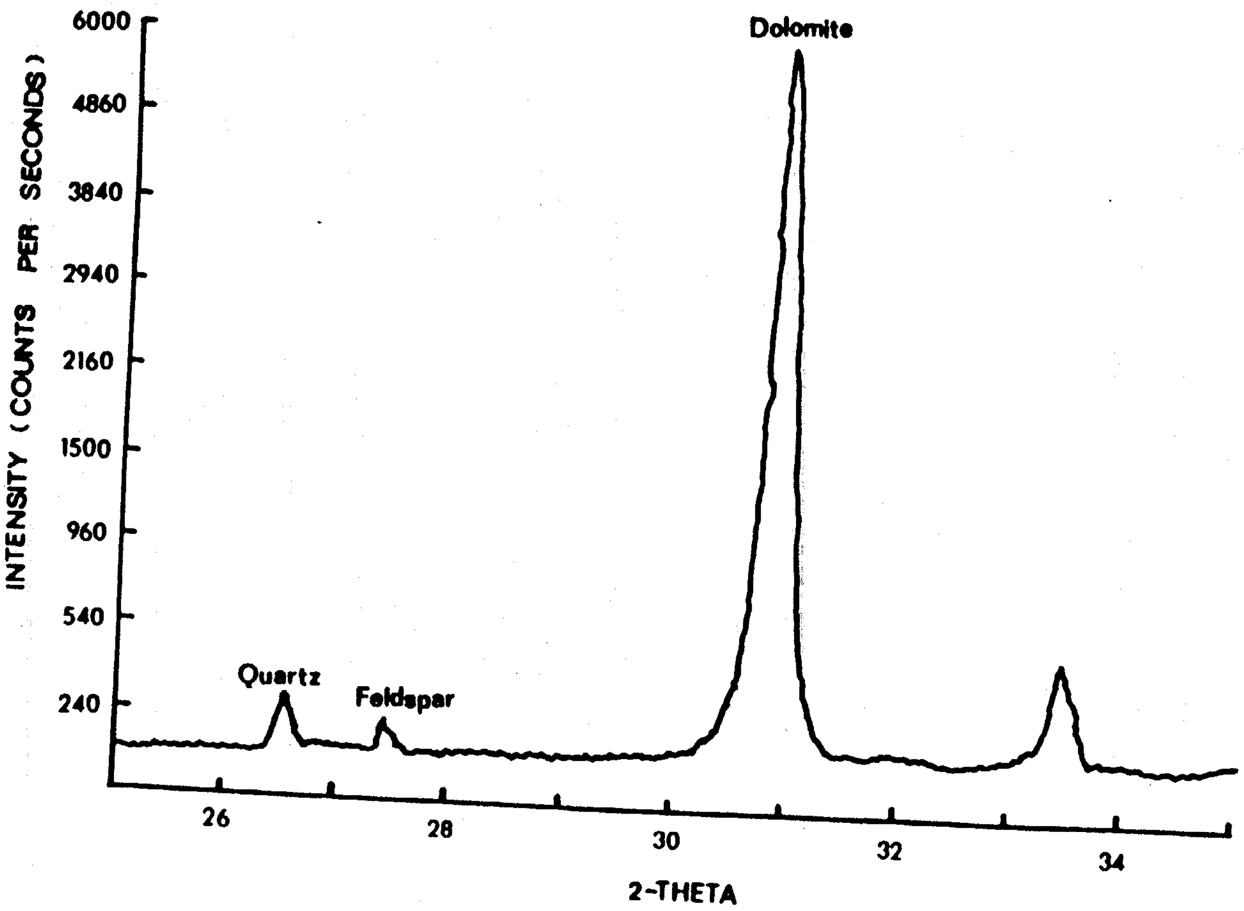

Figure 4. Diffractogram of IMC dolomite.

Chemicals

Purified sodium oleate from Fisher Scientific Company and dodecylamine hydrochloride (DDA-HCl) from Eastman Kodak Company were used as the anionic and cationic collectors, respectively. ACS certified grade potassium hydroxide and nitric acid were used to modify pH. Also, reagent grade sodium and potassium chloride and nitrate and sodium fluoride were used. Triple distilled water of less than 1.1 micromhos specific conductivity was used unless otherwise specified.

Methods

Flotation Tests

Flotation tests were conducted using a modified Hallimond cell. All flotation experiments were carried out with 1 gram of 65 x 100 mesh material as follows.

The apatite, dolomite, or a mixture of these minerals was suspended in 107 ml (the approximate total volume of a 100 ml flask) of distilled water. The pH of this water was preadjusted to obtain the desired pH for flotation. The samples were aged for 20 minutes, without agitation, and at room temperature. This was followed by collector addition and 5 minutes conditioning by tumbling at 8 rpm. Whenever needed, the sodium or potassium salts were added to the solution before addition of the mineral samples. After conditioning, the pH of the slurry was measured and reported as flotation pH. The suspension was next transferred to the Hallimond cell and floated for 1 minute using nitrogen gas at a flow rate of 50 cc per minute. Floated and unfloated fractions were collected and dried at 50°C, and flotation recovery was calculated based on the dried weight of the samples. In the case of mixtures, both float and sink fractions were pulverized and analyzed for P_2O_5 and MgO contents.

Solution Preparation

Stock solutions of 5.0 x 10^{-3} kmol/m^3 sodium oleate and dodecylamine hydrochloride were prepared and used for 5 days after which time the remainder was discarded and new solutions were made. Salt solutions of desired concentrations were prepared fresh.

Electrokinetic Measurements

Zeta potential of apatite and dolomite was measured using a Laser Zee Meter (Model 501). Suspensions of 0.1 wt % solids were prepared using -325 mesh mineral samples and were stirred with teflon-coated magnetic bars for approximately 21 hours at natural pH. Fifty ml samples of the aged suspension were equilibrated at desired pH for 3 hours before they were transferred to the cell for zeta potential measurements.

Dissolution and Ion Depletion Tests

In these experiments,one gram of apatite was added to 107 ml of solution, with or without salt, and aged for 36 hours by tumbling at 8 rpm. The pH of the suspensions was adjusted during aging to maintain a constant value. After aging, the solids were removed from the supernatant after aging by centrifuging, then dried. The dried solids were ground to -325 mesh with elemental silicon to study the changes in crystal structure of apatite by the X-ray diffraction method. The supernatants were analyzed using an inductively coupled plasma (ICP) chemical analysis system to determine the amount of calcium and sodium in the solution. In another series of tests, the amount of chloride ions depleted from solution was determined using ^{36}Cl labeled sodium chloride. These tests were conducted by suspending 1 gram of apatite in 11 ml of NaCl solution, then conditioned for 45 minutes on a wrist action shaker. Chloride concentrations in the supernatant from these tests were determined by Liquid Scintillation Counter (Model LS 1800, made by Beckman Instruments, Inc.) A calibration curve obtained using solutions containing known amounts of ^{36}Cl is presented in Figure 5 which indicates that the measurements are valid in the range of 7.0×10^{-3} to 6.5×10^{-2} kmol/m^3 chloride concentrations.

RESULTS AND DISCUSSION

Flotation Studies with Cationic Collectors

Flotation behavior of apatite and dolomite was examined with dodecylamine hydrochloride (DDA-HCl) as the collector, using the Hallimond tube flotation technique. Single mineral flotation tests were conducted at different levels of pH and collector concentrations, followed by mixed mineral flotation tests under selected experimental conditions.

Apatite-Dodecylamine System

The flotation recovery versus pH curves for apatite at two concentrations of DDA-HCl are presented in Figure 6. It is observed from the data that 100% of apatite floats between pH 4 and pH g at a collector concentration of 1.0×10^{-3} kmol/m^3. Apatite recovery at this concentration, however, decreased precipitously beyond pH 9.5. It is also observed that at a collector

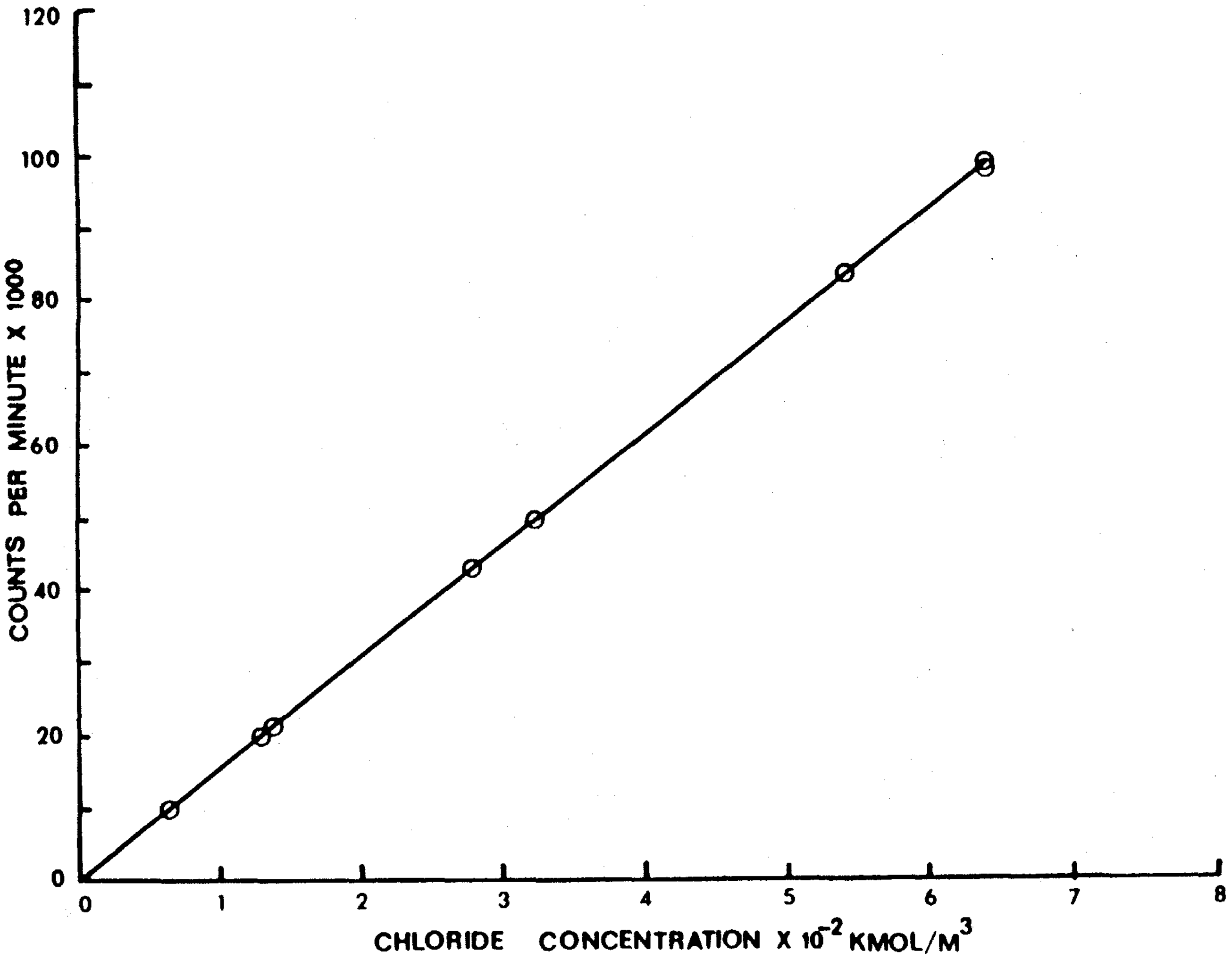

Figure 5. Calibration curve of ^{36}Cl radionuclide.

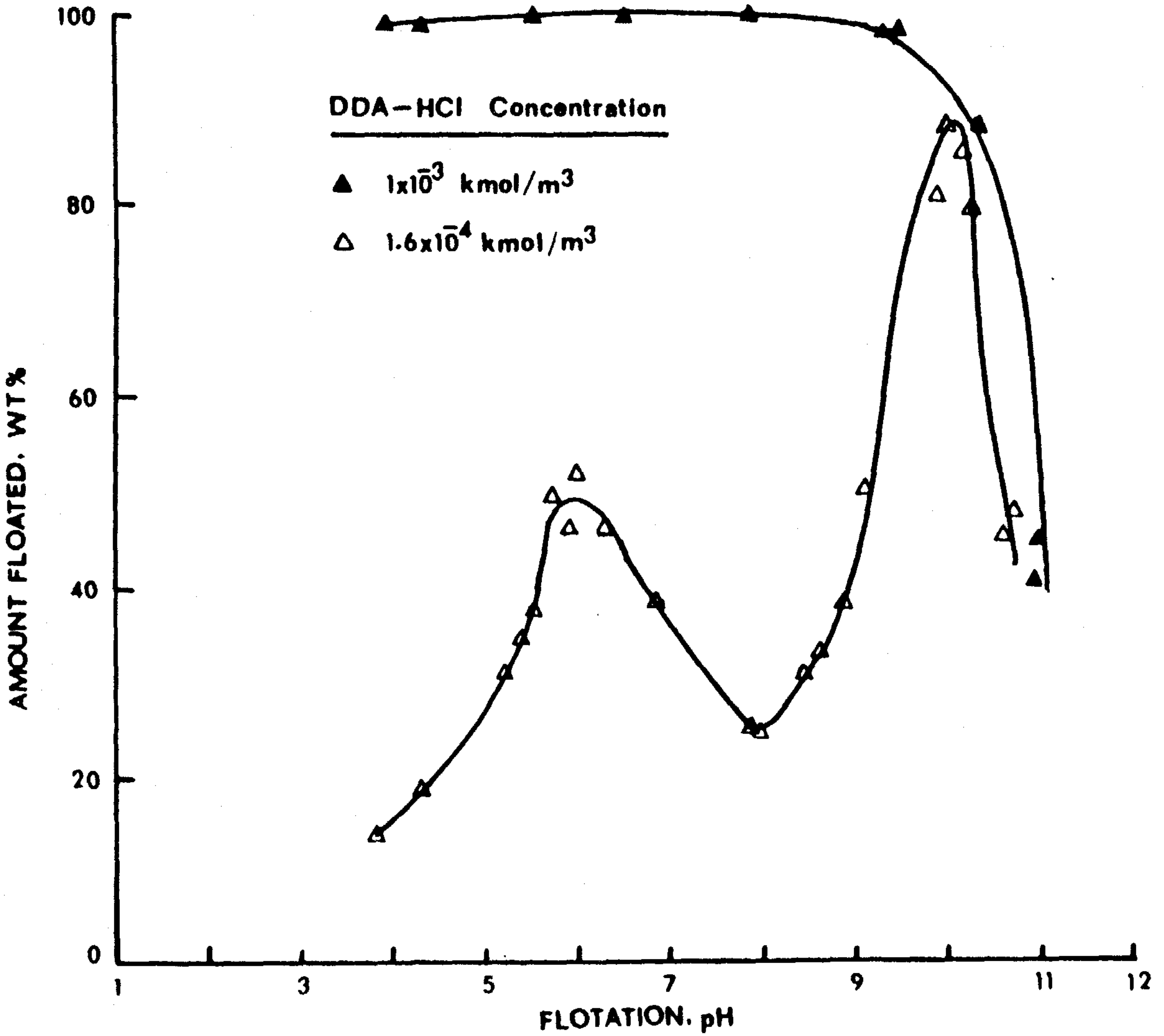

Figure 6. Flotation of apatite as a function of pH at two DDA-HCl concentrations.

concentration of 1.6 x 10^{-4} kmol/m^3, two peaks appear, one at pH 6 where 50% of apatite floated, and another at pH 10 where apatite recovery was 92%.

At higher collector concentrations,flotation behavior of apatite in the entire pH range examined indicates that there is a specific interaction of the collector (DDA-HCl) with the surface, as has been pointed out by Soto and Iwasaki (1). If there was no specific adsorption on apatite, flotation below the IEP (pH 5.4), due to the electrostatic repulsion between the collector molecule and the surface,. would not have been significant. On the other hand, it is believed that the collector adsorption above the IEP is a combination of electrostatic attraction and specific interaction.

At a lower collector concentration (1.6 x 10^{-4} kmol/m^3), flotation recovery as a function of pH exhibits two peaks for apatite. The large peak at pH 10.0 can be attributed to the highly surface active character of ionomolecular (amine-aminium) complexes formed by the hydrolysis reaction of dodecylamine. The maximum amine-aminium complex at this level of DDA-HCl addition has been estimated to be at pH 9.9 (2). The concentration of these complexes decreases as the pH is lowered; therefore, a drop in flotation recovery is observed. The reasons for the minor peak near the IEP of apatite are not clear at this time, and need further investigation.

Dolomite-Dodecylamine System

Flotation behavior of dolomite at 1.0 x 10^{-3} and 1.6 x 10^{-4} kmol/m^3 DDA-HCl as a function of pH is plotted in Figure 7. Dolomite recovery at a dodecylamine concentration of 1.0 x10^{-3} kmol/m^3 rises sharply above its first IEP (pH 5.3) and reaches 100% at pH 5.8. Flotation recovery starts decreasing above pH 9.0, descending to 25% at pH 11.0. At the lower collector

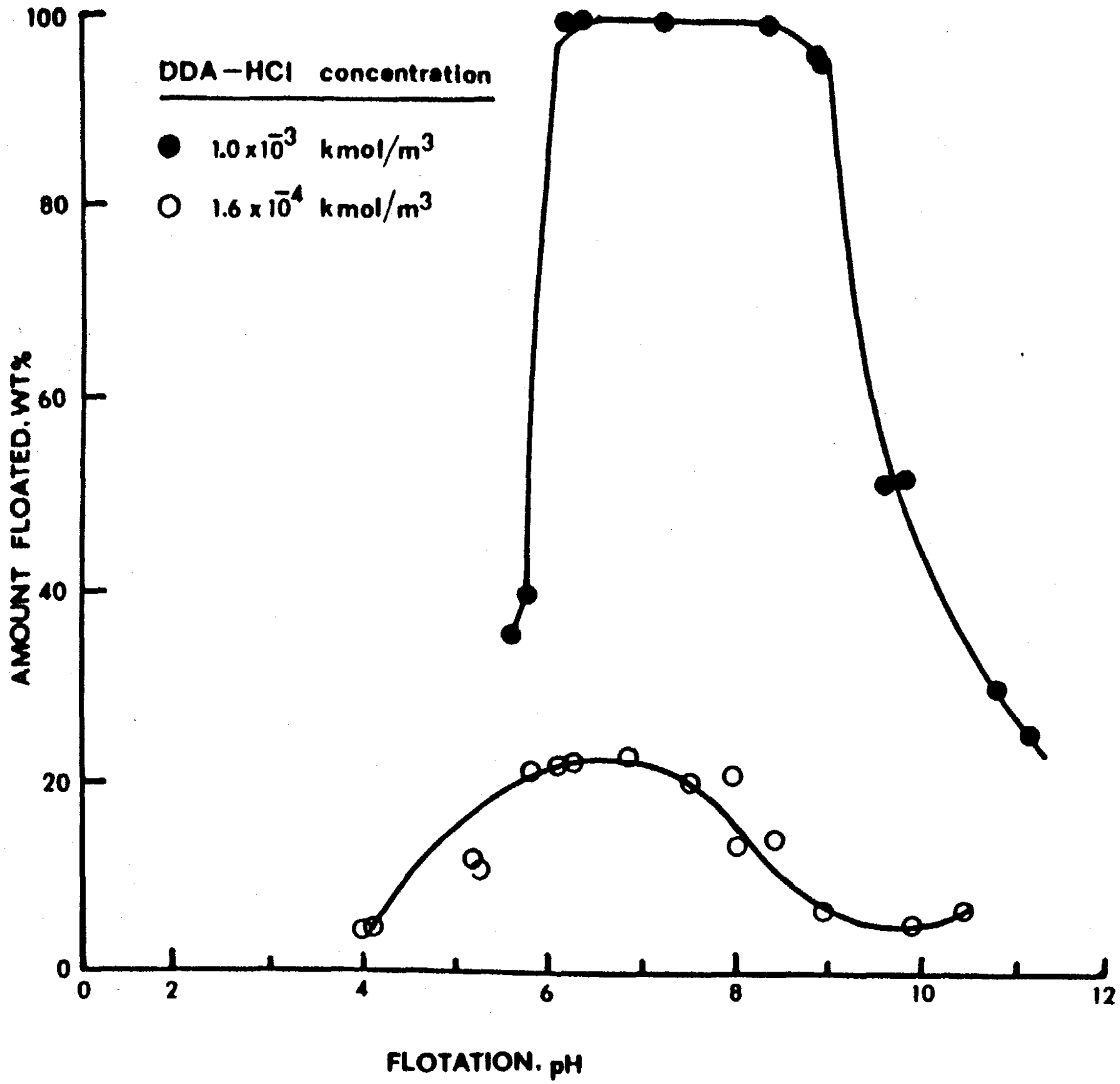

Figure 7. Flotation of dolomite as a function of pH at two DDA-HCl concentrations.

concentration (1.6×10^{-4} kmol/m^3), recovery as a function of pH is seen to decrease appreciably, exhibiting a peak (~25% recovery) at pH 7.0.

Flotation behavior of dolomite correlates well with its electrokinetic behavior (see Figure 20). Thus, there does not seem to be any specific adsorption of DDA-HCl on the dolomite surface as evidenced by flotation recovery, which decreases sharply below the first IEP at pH 5.3, and above the second IEP above pH 11.2.

Selective Flotation Ranges

Comparison of the recovery versus pH curves as shown in Figure 8 for both apatite and dolomite at a DDA-HCl concentration of 1.0×10^{-3} kmol/m^3 indicates that it may be possible to float apatite at pH < 5.0 while keeping dolomite depressed. Another region of apatite-dolomite separation is observed at pH 10.0 at the collector concentration of 1.6×10^{-4} kmol/m^3 (see Figure 9).

Mixed Mineral Flotation Behavior

A 1:1 apatite to dolomite mixture was conditioned and floated at pH < 5.0 using a DDA-HCl concentration of 1.0×10^{-3} kmol/m^3. Results of these tests presented in Table 2 indicate that at lower pH (3.9), apatite floats in preference to dolomite. The selectivity predicted on the basis of single mineral flotation tests, however, is not fully observed (see Figure 8), but it should be noted that as predicted by single mineral tests, flotation of apatite is greater than that of dolomite.

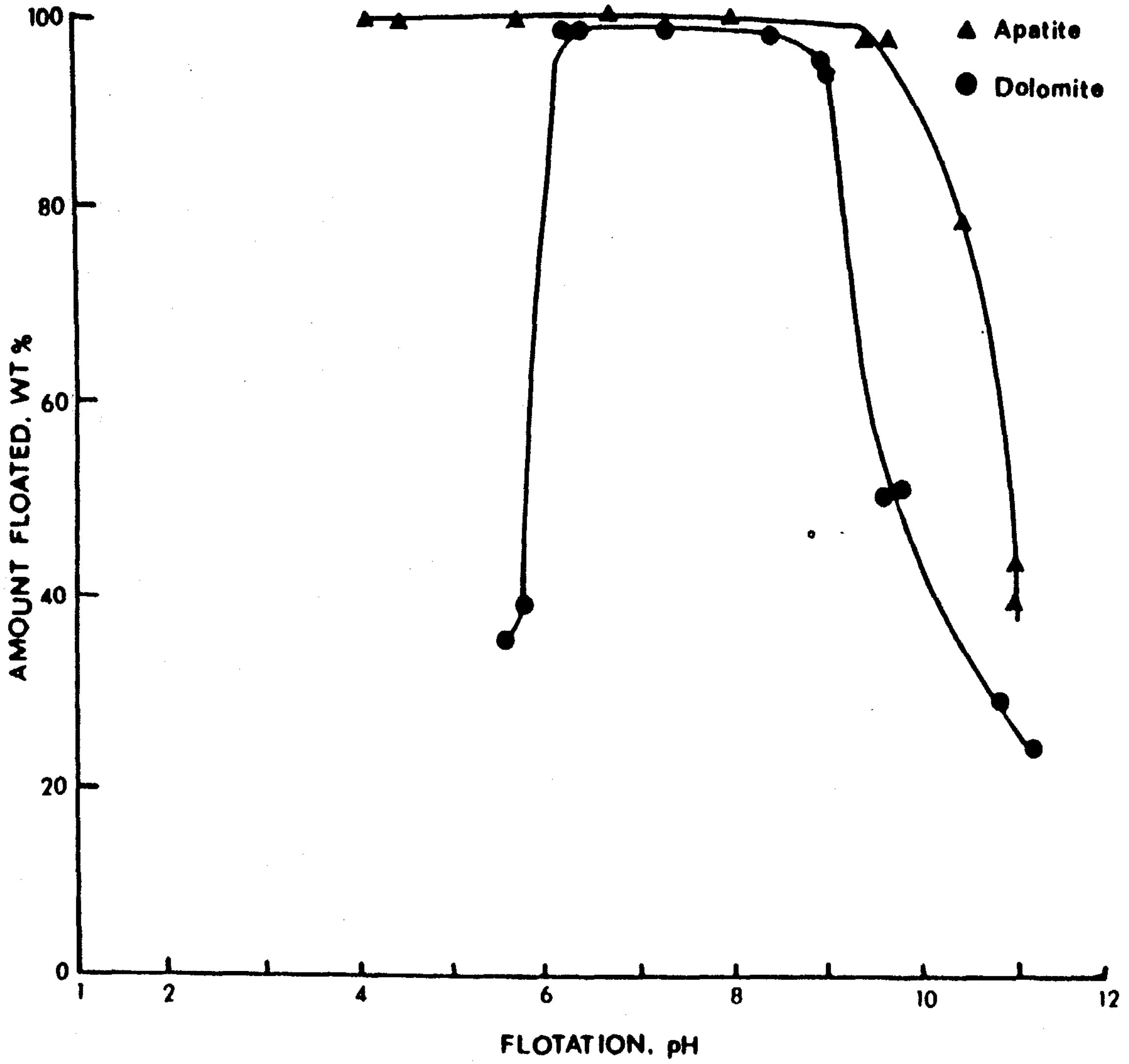

Figure 8. Flotation of apatite and dolomite (single minerals) as a function of pH at DDA-HCl concentration of 1.0 x 10^{-3} kmol/m^3.

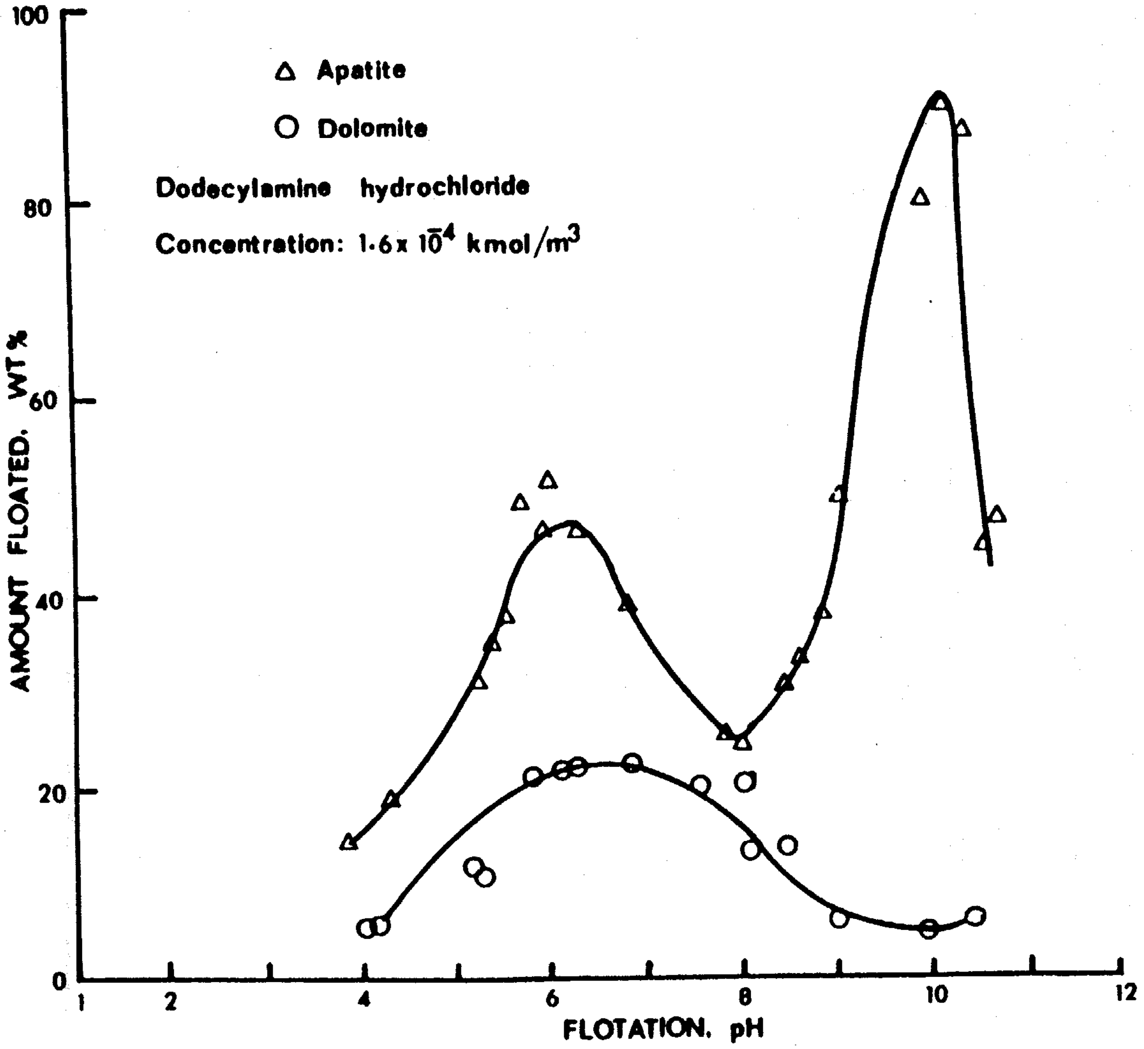

Figure 9. Flotation of apatite and dolomite (single minerals) as a function of pH at DDA-HCl concentration of 1.6 x 10^{-4} kmol/m^3.

Table 2

Flotation of a 1:1 Apatite-Dolomite Mixture Using DDA-HCl as the Collector

Collector Amount : 1.0 x 10^{-3} kmol/m^3

Flotation pH	Products	Wt %	Analysis, %		Distribution of the Minerals, %	
			P_2O_5	MgO	Apatite	Dolomite
4.5	Float	64.5	26.53	4.15	72.3	53.4
	Sink	35.5	18.48	6.57	27.7	46.6
	Feed	100.0	23.67	5.01	100.0	100.0
4.0	Float	66.5	26.61	4.20	74.7	55.7
	Sink	33.5	17.83	6.62	25.3	44.3
	Feed	100.0	23.67	5.01	100.0	100.0
3.9	Float	54.0	28.23	2.97	64.7	32.0
	Sink	46.0	18.30	7.41	35.3	68.0
	Feed	100.0	23.67	5.01	100.0	100.0

Mixed mineral flotation at pH 9.8 and at a collector concentration of 1.6 x 10^{-4} kmol/m^3 (see Table 3), also resulted in more apatite recovery in the float fraction, but selectivity was poor due to increased dolomite flotation.

In general,results of mixed mineral tests with DDA-HCl as the collector indicated apatite depression along with activation of dolomite. Hence, the selectivity predicted by the single mineral tests was only partially observed in the flotation of mixtures. The possible reasons for loss of selectivity can be attributed to a) smearing of dolomite on the apatite surface, and b) the effect of dissolved species from dolomite and apatite. The first possibility was studied by Chanchani (3) using sodium oleate as the collector and it was shown that smearing did not influence the flotation behavior. However, the dissolved species from both minerals could influence the selectivity in two ways: 1) alteration of the electrokinetic behavior, and 2) depletion of collector available for adsorption due to complexation with dissolved anions. The loss in selectivity at pH 9.8 can be partially attributed to the surface modification of the minerals by dissolved species, since in the case of single minerals, dolomite flotation, at the same collector concentration, was lower. The fact that PO_4^{-3} ions rendered the dolomite surface more negatively charged (see Figure 1 in the Appendix), in the alkaline pH range (3), supports this hypothesis. On the other hand, it is also possible that apatite depression occurs because there is less collector available for adsorption due to complexation between dissolved ions and the collector. This would be the case if there are more dissolved species in the mixed mineral system as compared to that of a single mineral (apatite) system. Dolomite solubility is higher that apatite, thus resulting in an overall increase in the concentration of dissolved ions as compared to apatite alone, especially

Table 3

Flotation of a 1:1 Apatite-Dolomite Mixture Using DDA-HCl as the Collector

Collector Amount: 1.6×10^{-4} kmol/m^3

Flotation pH	Products	Wt %	Analysis, %		the Minerals, %	
			P_2O_5	MgO	Apatite	Dolomite
9.9	Float	49.0	25.40	3.82	53.3	37.6
	Sink	51.0	21.25	5.85	46.8	62.4
	Feed	100.0	23.67	5.01	100.0	100.0
9.7	Float	47.4	25.87	4.00	51.8	38.2
	Sink	52.6	21.64	5.75	48.2	61.8
	Feed	100.0	23.67	5.01	100.0	100.0

at pH < 5.0. In brief, complexation and surface charge alteration could be the main reasons for loss of selectivity in the apatite-dolomite-dodecylamine hydrochloride system.

The above results suggest that with DDA-HCl as the collector, selective flotation of apatite from dolomitic gangue is not feasible without high losses in phosphate recovery. Thus, it is necessary to devise new conditions for modification of surface chemical properties of these minerals to achieve the desired separation at acceptable phosphate recovery levels.

Results obtained in this study and the work conducted by Soto and Iwasaki (1), and Snow (4), suggest that adsorption of DDA-HCl on dolomite surfaces is electrostatic in nature. On apatite, however,it appears to be due to a combination of coulombic and specific interactions. This means that, theoretically, it should be possible to minimize electrostatic interaction by compressing the electrical double layer (EDL) on the particle surface. This can be achieved by the addition of indifferent electrolytes to the system. It was hypothesized that if the EDL is compressed in the apatite-dolomite system (with DDA-HCl as the collector), apatite can be selectively floated out due to the specific interaction of the collector with the surface of this mineral. Therefore, it was decided to conduct further flotation experiments in NaCl solutions. It should be noted that sodium could possibly substitute for calcium in the apatite lattice (5). This substitution, however, will have an added advantage due to the expected change towards more negative surface charge with displacement of a bivalent cation from the lattice with a monovalent one. Experimental results obtained with addition of NaCl as well as with some other salts are presented in the following sections.

Effect of Salt Addition on Flotation

Single Mineral Flotation

Flotation experiments conducted in the pH range of 5.5-7.0, indicated 85-90% apatite recovery at a DDA-HCl concentration of 1.6 x 10^{-4} kmol/ms and a NaCl concentration of 0.5 kmol/m^3. Apatite recovery at this level of collector addition in distilled water (see Figure 9) was in the 50% range. The increased flotation recovery in the presence of NaCl is attributed to the salting out effect,and possible surface modifications by added ionic species. Dolomite recovery under similar experimental conditions was unchanged from that in distilled water (15-20%), indicating that added NaCl had no major effect on the dolomite flotation.

Mixed Mineral Flotation

To examine the selectivity observed on the basis of single mineral tests in the presence of NaCl, an 88:12 apatite:dolomite mixture was floated using 1.6 x 10^{-4} kmol/m^3 dodecylamine hydrochloride as the collector. Results presented in Table 4 indicate that apatite can be selectively floated from the mixture leaving dolomite in the sink fraction. MgO content was lowered from 2.5% in the feed to 1.0% in the concentrate at an apatite recovery of 80%; however, since apatite constitutes the major mineral in the feed, flotation would require more collector than if dolomite, a minor constituent, was floated out. It was therefore decided to examine the possibility of floating out dolomite using an anionic collector such as sodium oleate.

Table 4

Flotation of an 88:12 Apatite-Dolomite Mixture Using DDA-HCl as the Collector

Collector Amount: 1.6×10^{-4} kmol/m^3

Flotation pH	Products	Wt %	Analysis, %		Distribution of the Minerals, %	
			P_2O_5	MgO	Apatite	Dolomite
6.3	Float	76.4	33.65	0.97	79.0	28.2
	Sink	23.6	23.71	7.96	21.0	71.8
	Feed	100.0	31.54	2.50	100.0	100.0
6.3	Float	77.3	33.49	1.02	79.8	30.2
	Sink	22.7	23.86	8.05	20.2	69.8
	Feed	100.0	31.54	2.50	100.0	100.0
6.3	Float	78.3	33.59	1.03	81.2	30.9
	Sink	21.7	23.14	8.31	18.8	69.1
	Feed	100.0	31.54	2.50	100.0	100.0

FLOTATION STUDIES WITH SODIUM OLEATE

Single Mineral Flotation Tests

Results of flotation experiments conducted using 4.0 x 10^{-5} kmol/m^3 sodium oleate as the collector without salt addition, as shown in Figure 10, exhibit similar behavior as previously observed in our laboratories (3). Mixed mineral flotation tests were also carried out in the acidic pH range using a 50:50 apatite and dolomite mixture. Results of these tests are summarized in Table 5.

It is observed that at pH 4.0 and above, although dolomite floated out almost completely, a significant amount of apatite also floated, thus decreasing phosphate recovery in the concentrate (sink fraction). Effect of salt addition was examined next.

Effect of Sodium Chloride Addition on Flotation

Flotation of apatite and dolomite using sodium oleate (4.0 x10^{-5} kmol/m^3) as the collector at pH 4.2 was studied as a function of salt concentration. Results illustrated in Figure 11 indicate that no change in dolomite flotation occurred in the presence of NaCl. However, a major effect on apatite flotation was observed. Apatite recovery, which was 55% in the absence of salt, decreased to 3% as the salt addition increased to 2.0 x 10^{-2} kmol/m^3. Another series of tests were conducted at pH 5.2 since single mineral results without salt had indicated excellent recovery of dolomite with negligible apatite flotation at this pH (see Figure 10). Dolomite recovery as a function of added salt, seen in Figure 12, remained at 100% over the entire range of NaCl concentrations examined. On the other hand, apatite flotation

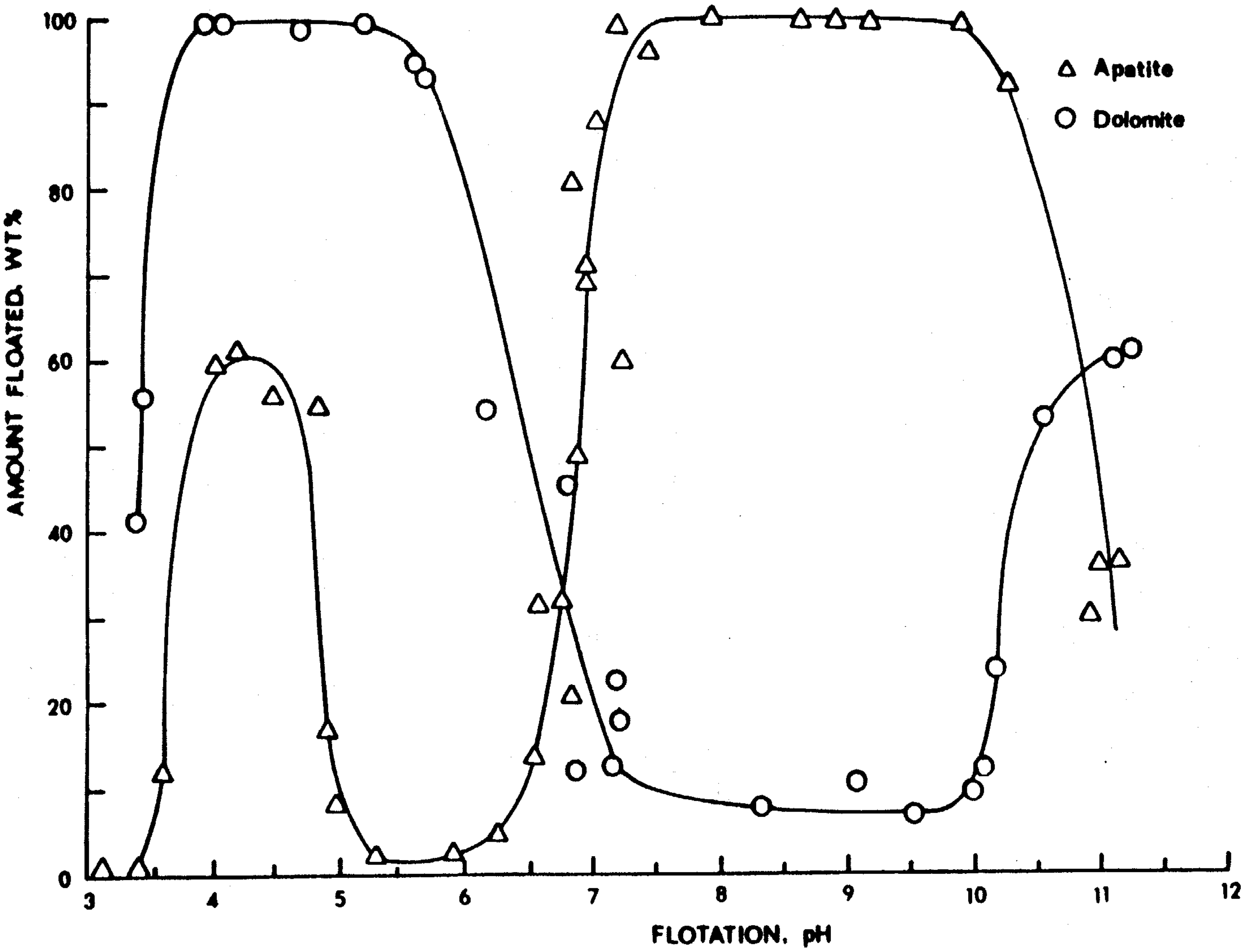

Figure 10. Flotation of apatite and dolomite (single minerals) as a function of pH at sodium oleate concentration of 4.0×10^{-5} kmol/m^3.

Table 5

Flotation of a 50:50 Apatite-Dolomite Mixture Using Sodium Oleate as the Collector

Collector Amount: 4.0×10^{-5} kmol/m^3

Flotation pH	Products	Wt %	Analysis, %		Distribution of the Minerals, %	
			P_2O_5	MgO	Apatite	Dolomite
4.0	Float	52.2	5.94	16.86	17.2	91.7
	Sink	47.8	31.23	1.68	82.8	8.3
	Feed	100.0	17.61	9.38	100.0	100.0
4.6	Float	74.6	15.21	12.90	58.3	96.1
	Sink	25.4	31.98	1.52	41.7	3.9
	Feed	100.0	18.43	9.48	100.0	100.0
5.1	Float	60.2	10.17	15.12	32.2	96.0
	Sink	39.8	32.82	1.22	67.8	4.0
	Feed	100.0	17.52	9.52	100.0	100.0
5.5	Float	63.7	9.86	14.98	33.3	95.3
	Sink	36.3	33.36	1.28	66.1	4.7
	Feed	100.0	17.32	9.36	100.0	100.0

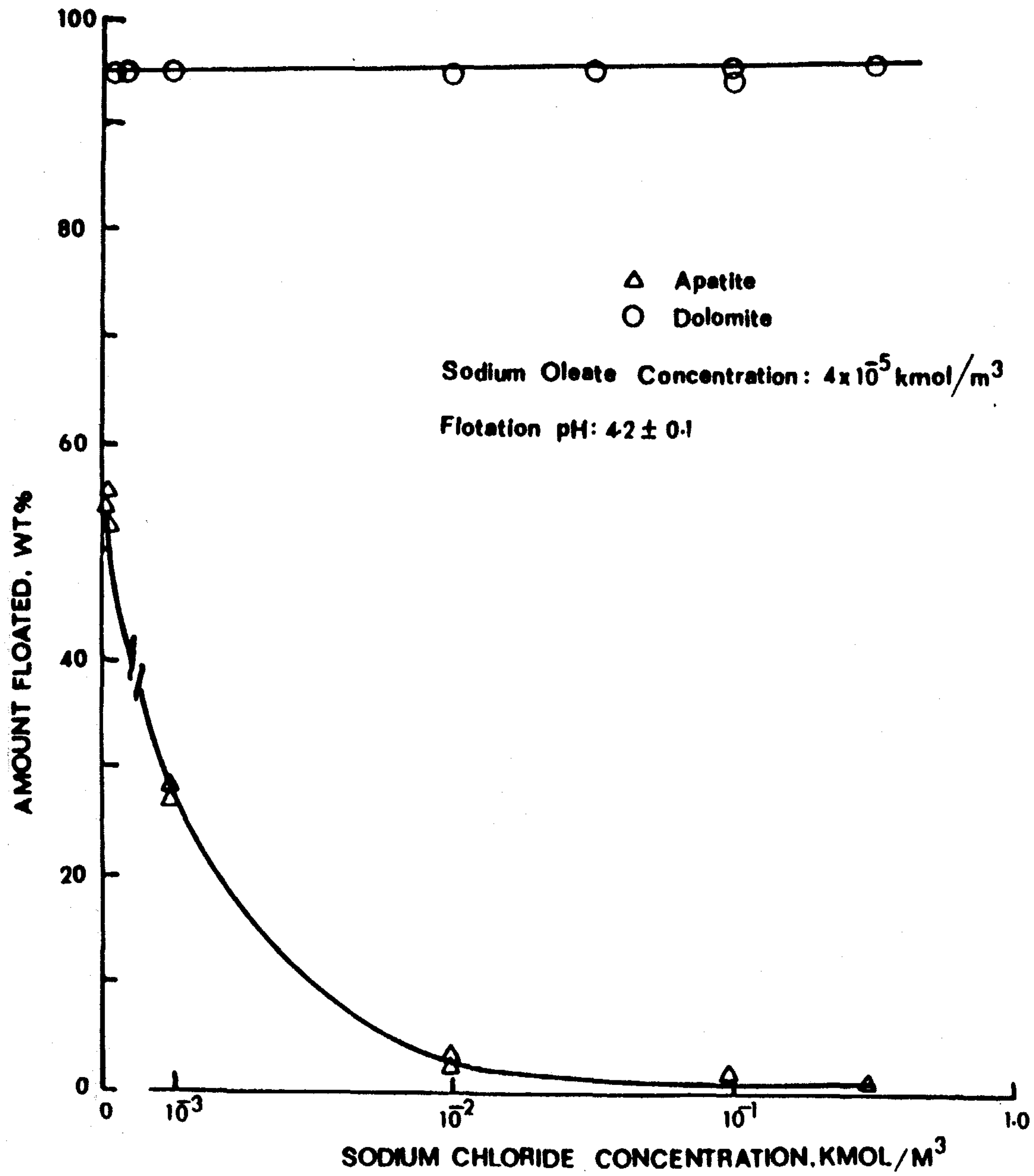

Figure 11. Flotation of apatite and dolomite as a function of NaCl addition at pH 4.2 and sodium oleate concentration of 4.0 x 10^{-5} kmol/m^3.

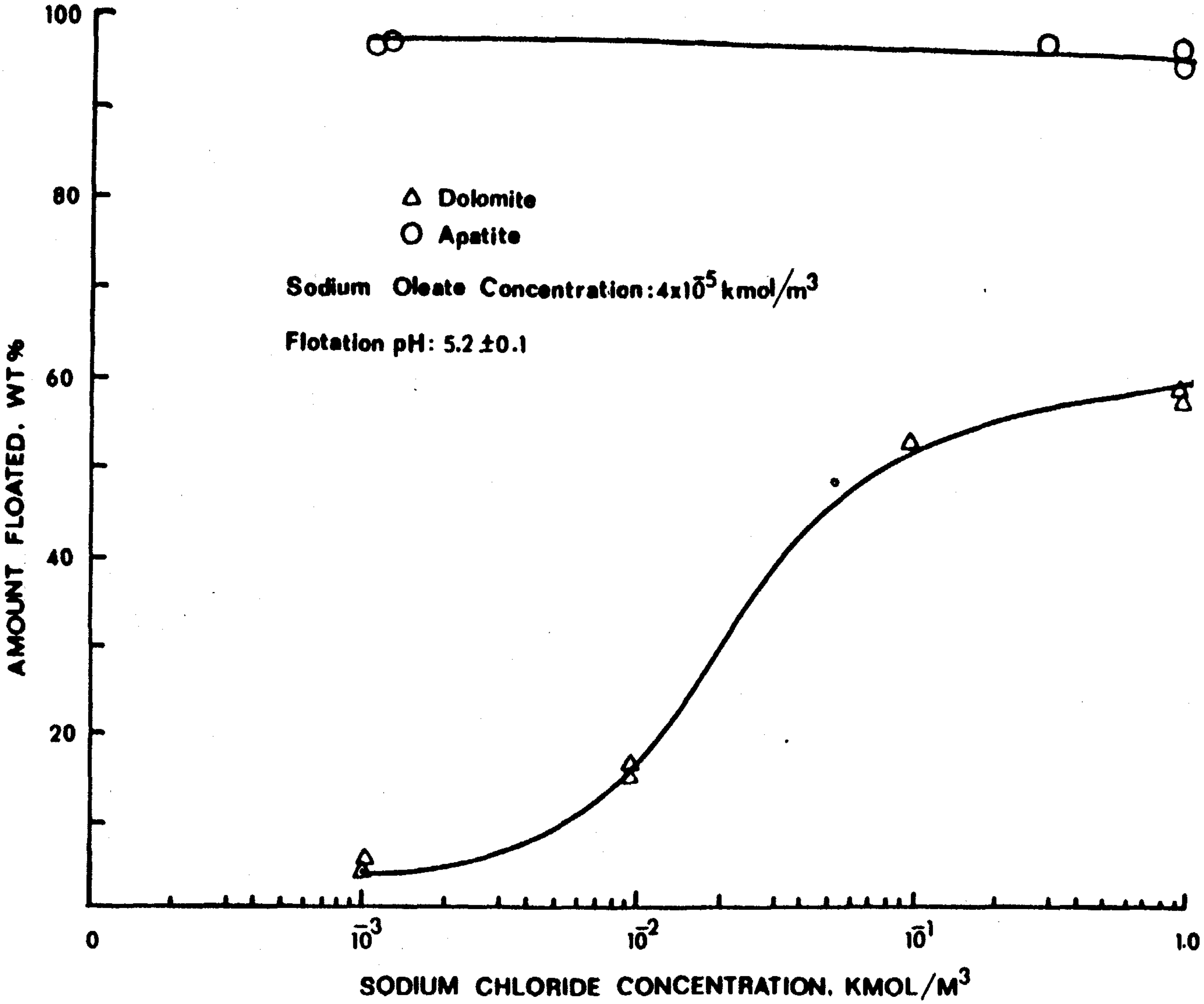

Figure 12. Flotation of apatite and dolomite as a function of NaCl addition at pH 5.2 and sodium oleate concentration of 4.0×10^{-5} kmol/m^3.

showed an increase from 3% to 50% at a NaCl concentration of 2.0 x $10m^{-2}$ $kmol/m^3$. The increased flotation recovery of apatite at this pH is under study.

From the above results, it is established that the optimum salt concentration is 2.0 x 10^{-2} $kmol/m^3$ for effective depression of apatite at pH 4.2. This concentration was used in the subsequent tests unless otherwise stated.

Effect of Collector Concentration

Flotation recovery of the single minerals at pH 10.0 and 4.0, with and without salt additions, as a function of collector concentration is presented in Figures 13 and 14 respectively. It was observed that at pH 10.0 apatite, in the absence of salt, required less collector to float as compared to dolomite. In the presence of NaCl at pH 10.0, apatite flotation remained the same while that of dolomite showed a slight depression. It should be noted that flotation of apatite and dolomite is extremely sensitive to sodium oleate concentration. For example, the difference between the concentration of sodium oleate required for 100% flotation of these minerals is only a factor of 2.5 at pH 10.0.

Flotation behavior of apatite and dolomite at pH 4.0 resulted in an opposite trend as compared to that at pH 10.0. At lower pH, dolomite requires less collector (see Figure 14) as compared to apatite. The difference in collector concentrations for complete flotation is a factor of 5 as opposed to 2.5 at pH 10.0. With added NaCl this difference in collector concentration increases to 13 times, which should be more effective in achieving the desired separation. It is observed from Figure 14 that based on the single mineral tests at NaCl concentrations of 2.0 x lO^{-2} $kmol/m^3$, the optimum amount of sodium oleate is 4.0 x 10^{-5} $kmol/m^3$.

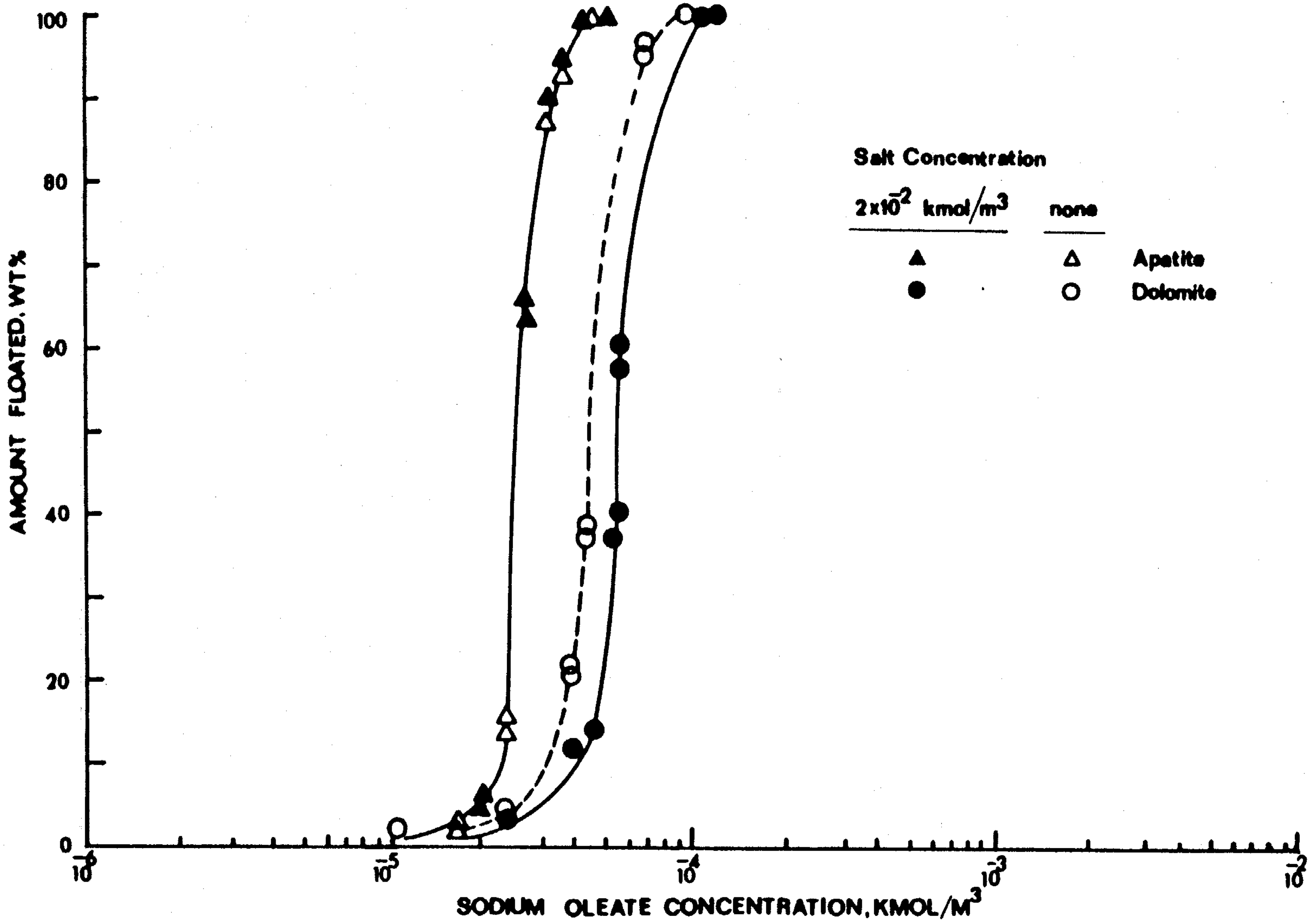

Figure 13. Flotation of apatite and dolomite as a function of sodium oleate concentration at pH 10.0 (single minerals).

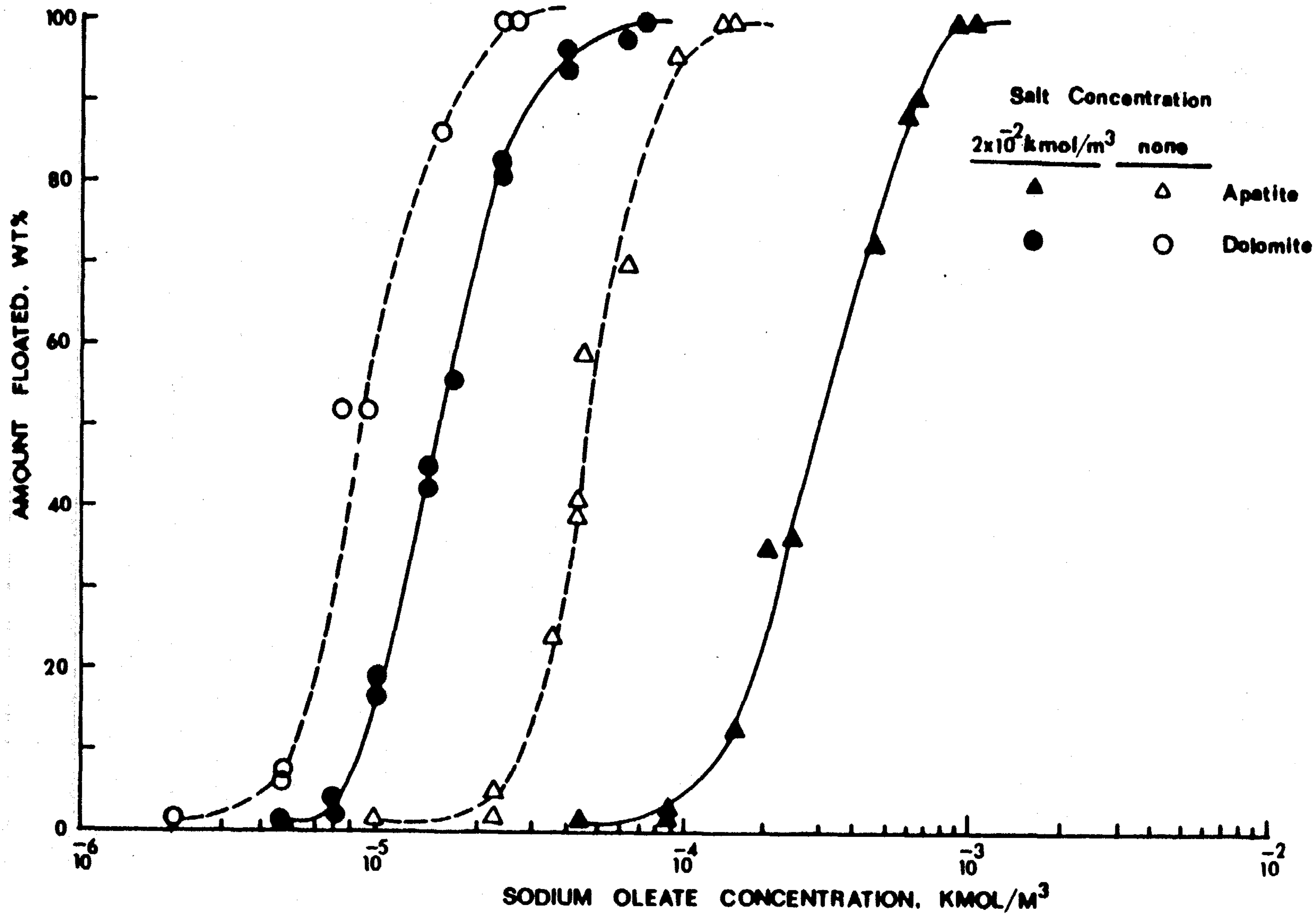

Figure 14. Flotation of apatite and dolomite as a function of sodium oleate concentration at pH 4.0 (single minerals).

Effect of Flotation pH

Having determined the optimum salt and sodium oleate concentration, tests were conducted to investigate the effect of pH on apatite and dolomite flotation. Results presented in Figure 15 indicate that apatite floats only above pH 4.2, whereas without added salt its flotation was nearly 60% at this same pH (see Figure 16). At pH 9.5 apatite flotation is completely depressed. A similar effect of NaCl on apatite flotation is also reported by Maslow (6) and Strelitsyn et al. (7). The primary objective of their study, however, was to lower the freezing point during the winter months by adding NaCl to the run of mine ore.

Flotation behavior of dolomite does not show a change, except for slight activation at pH 7 and above as compared to the results obtained in the absence of salt.

Flotation of Mixed Minerals in the Presence of Salt

To evaluate the selectivity predicted from single minerals tests, flotation of a 50:50 apatite-dolomite mixture as a function of pH was conducted at a sodium oleate concentration of 4.0×10^{-5} kmol/m^3 in the presence of 2.0×10^{-2} kmol/m^3 NaCl. In general, as illustrated in Figure 17, the selectivity predicted by the single mineral experiments, is achieved in the mixed mineral tests. In fact, the selectivity in mixed mineral tests in the pH range of 4.0-5.0 is higher than predicted on the basis of single mineral flotation behavior. The best selectivity was observed at pH 4.0, where 95% of dolomite was floated at an apatite recovery of 99%. In these tests, the MgO content of the concentrate (sink fraction) was reduced to 0.5-0.6% from a feed containing 9.5% MgO.

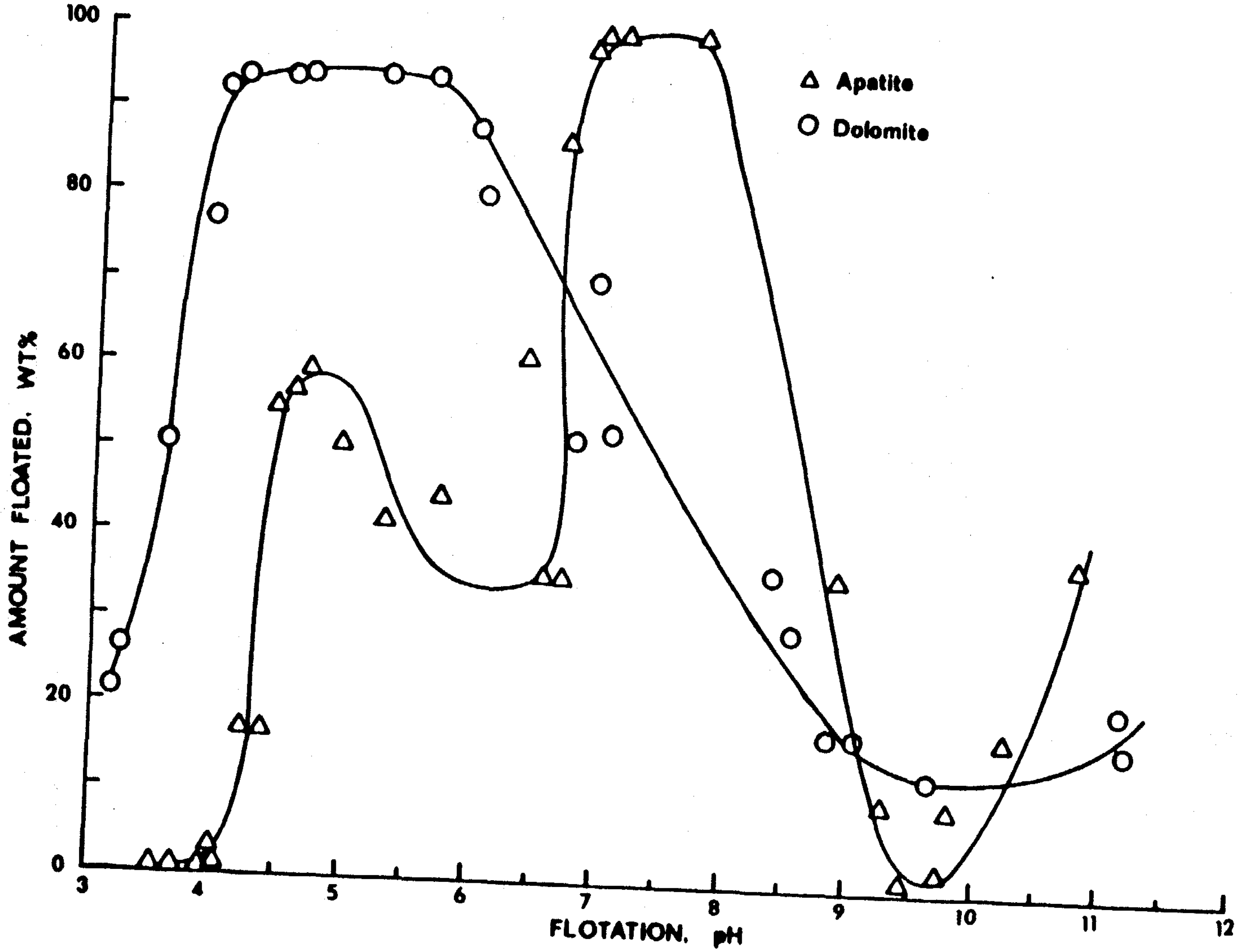

Figure 15. Apatite and dolomite flotation as a function of pH at NaCl concentration of 2.0×10^{-2} kmol/m^3. Sodium oleate concentration 4.0×10^{-5} kmol/m^3 (single mineral).

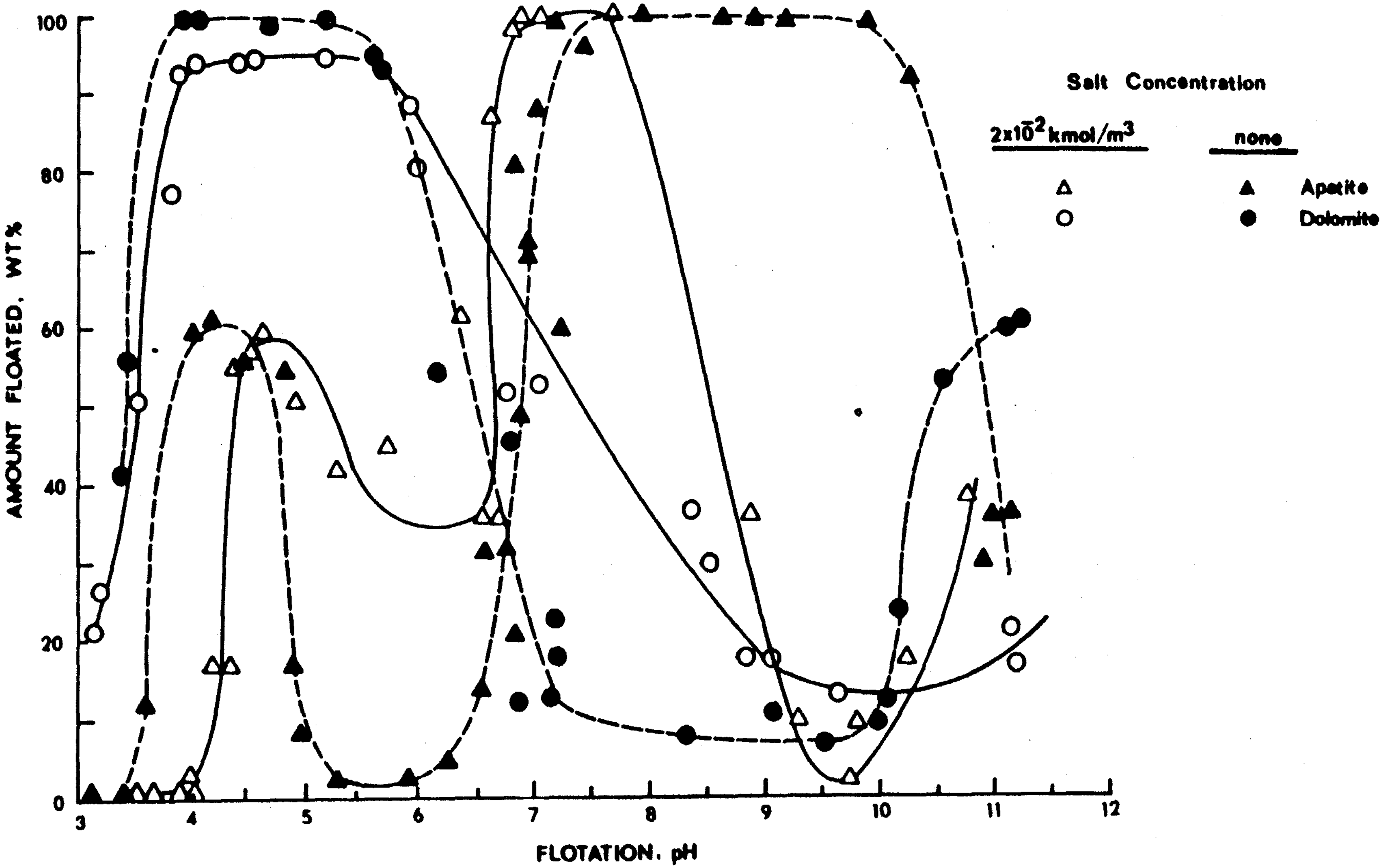

Figure 16. Flotation of apatite and dolomite as a a function of conditioning pH with and without added NaCl (single minerals).

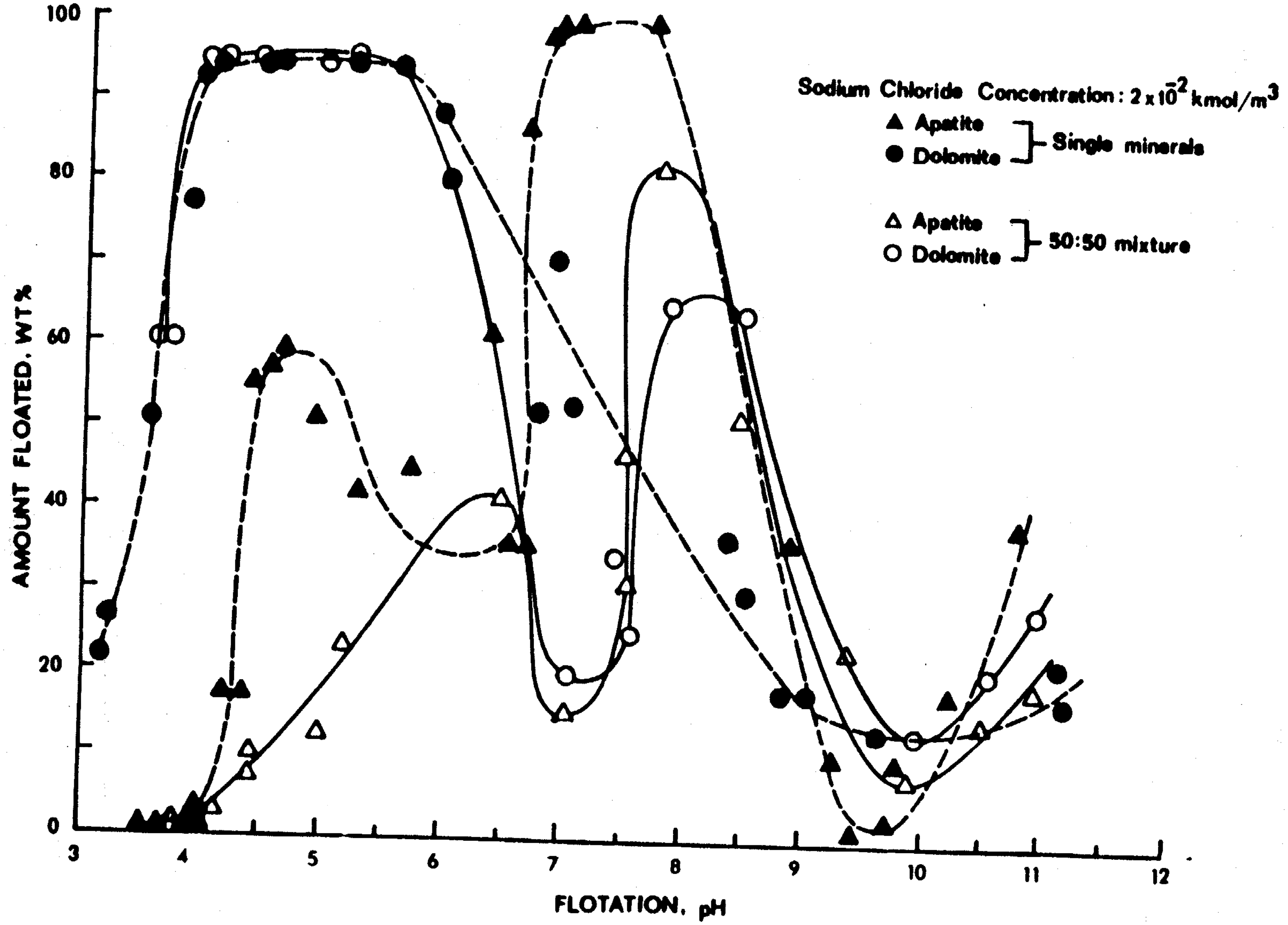

Figure 17. Flotation of apatite and dolomite (single and 1:1 mixture) as a function of pH at NaCl concentration of 2.0 x 10^{-2} kmol/m^3 using 4.0 x 10^{-5} kmol/m^3 sodium oleate.

Having established the conditions for selective separation of dolomite from apatite with sodium oleate in the acidic pH range, the electrokinetic behavior of apatite with and without salt additions was studied to understand the molecular mechanisms involved.

ELECTROKINETIC STUDIES

The objective of these studies was to determine surface charge behavior of apatite and dolomite with and without added salt.

Zeta Potential Behavior of Apatite and Dolomite

Zeta potential measurements of apatite and dolomite in triple distilled water are plotted in Figures 18 and 19, respectively. In the case of apatite an isoelectric point (IEP) at pH 5.4 is observed whereas dolomite exhibits two IEPs at pH 5.3 and 11.2. The second IEP at pH 11.2 is attributed to the precipitation of $Mg(OH)^+$ and its polynuclear complexes (8) on the dolomite surface.

Effect of Sodium Chloride on the Zeta Potential

The zeta potential of dolomite at a NaCl concentration of 2.0×10^{-2} $kmol/m^3$ is illustrated in Figure 20. These measurements indicate no significant change in zeta potential of dolomite below pH 5.3 (IEP), but a decrease in magnitude at all pH levels above 5.3 is observed. IEP of dolomite, however, remained unchanged in the presence of added salt. Zeta potential behavior of apatite in the presence of NaCl is illustrated in Figure 21. It is clear that in the entire pH range examined (3-11), apatite exhibits negative surface charge indicating that the IEP is shifted to a lower pH value. This can occur only if added ionic species act as the potential determining ions and/or if they exchange with the lattice ions.

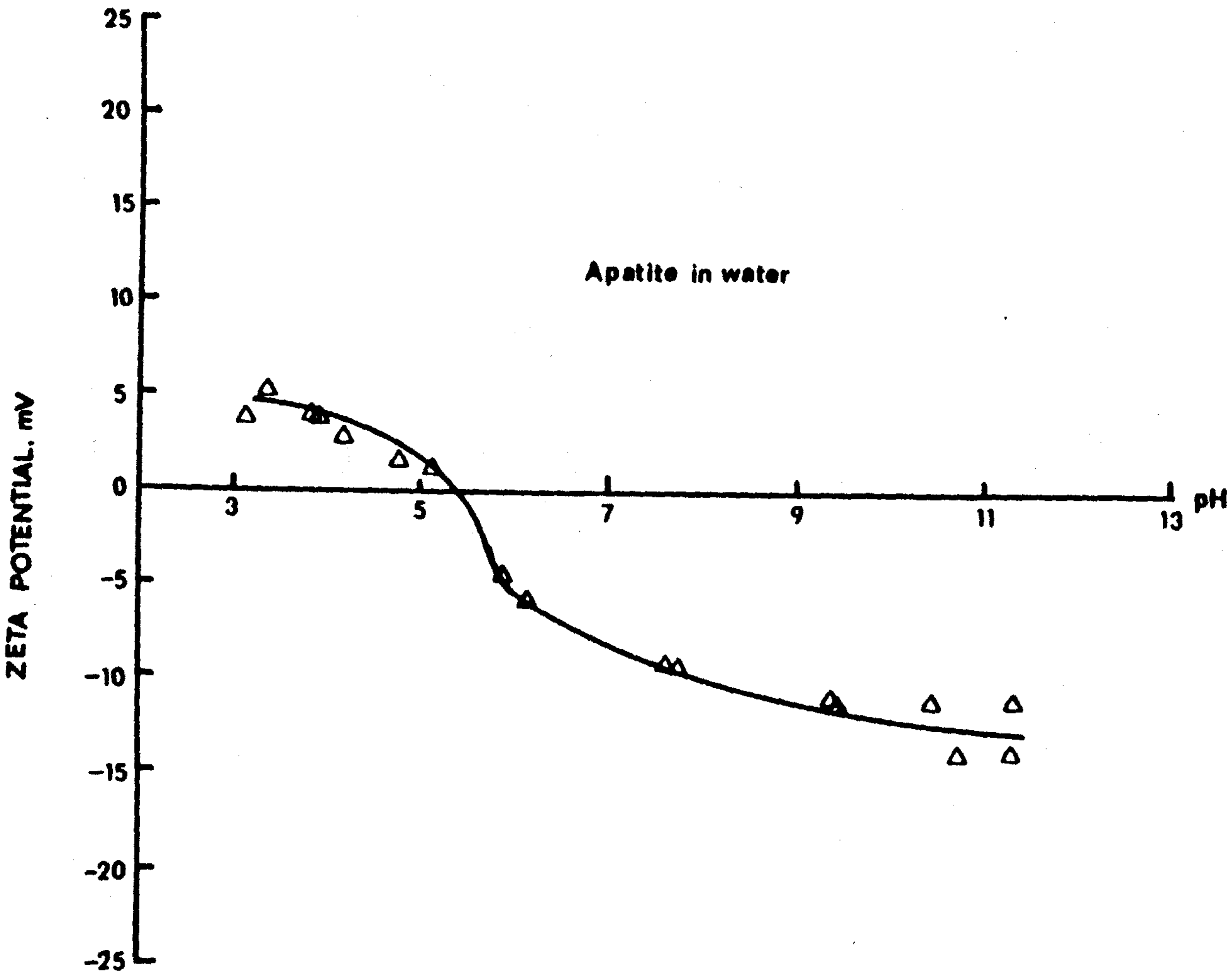

Figure 18. Zeta potential of apatite as a function of pH.

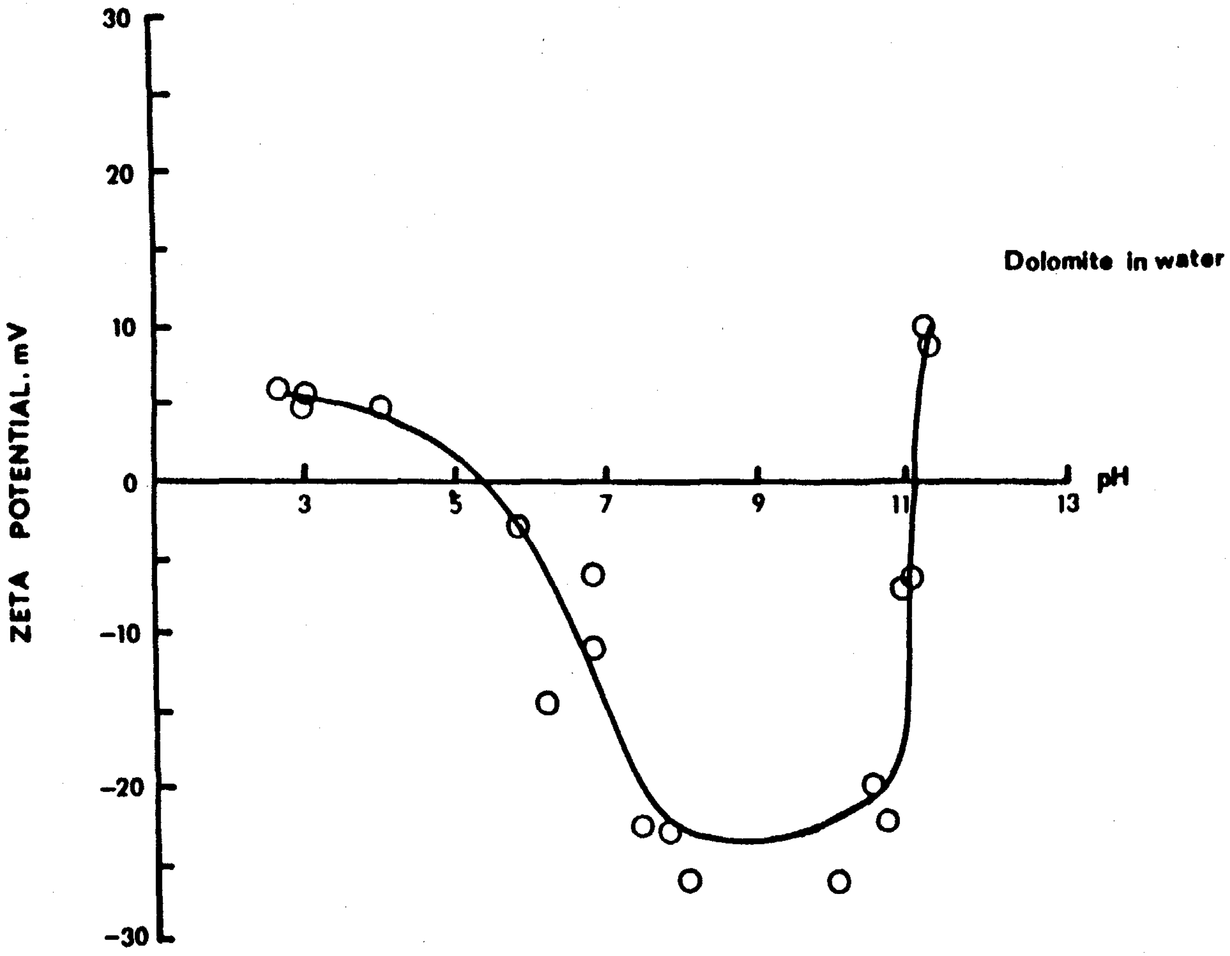

Figure 19. Zeta potential of dolomite as a function of pH with and without added NaCl.

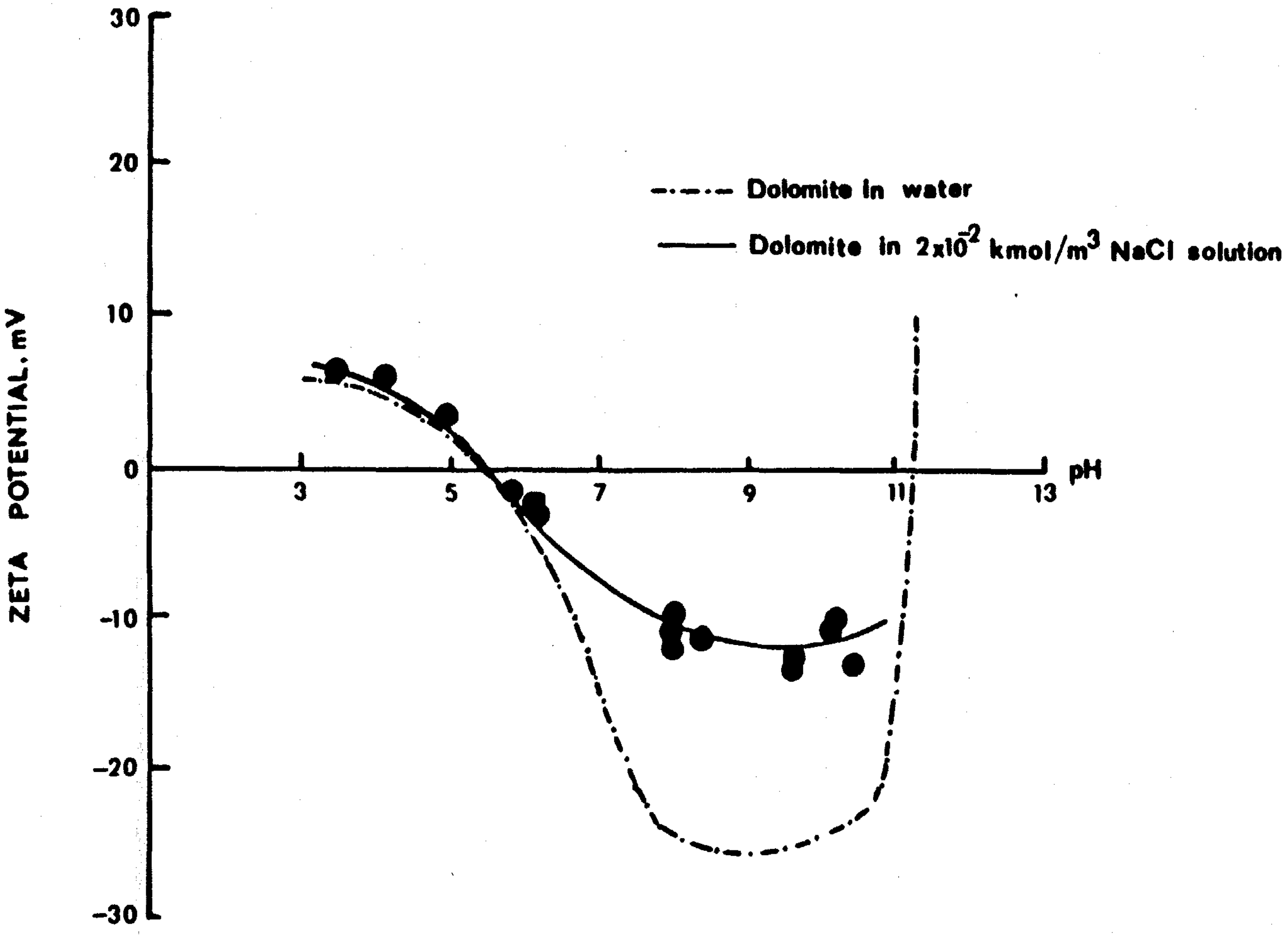

Figure 20. Zeta potential of dolomite as a function of pH in 2.0 x 10^{-2} kmol/m^3 NaCl solution.

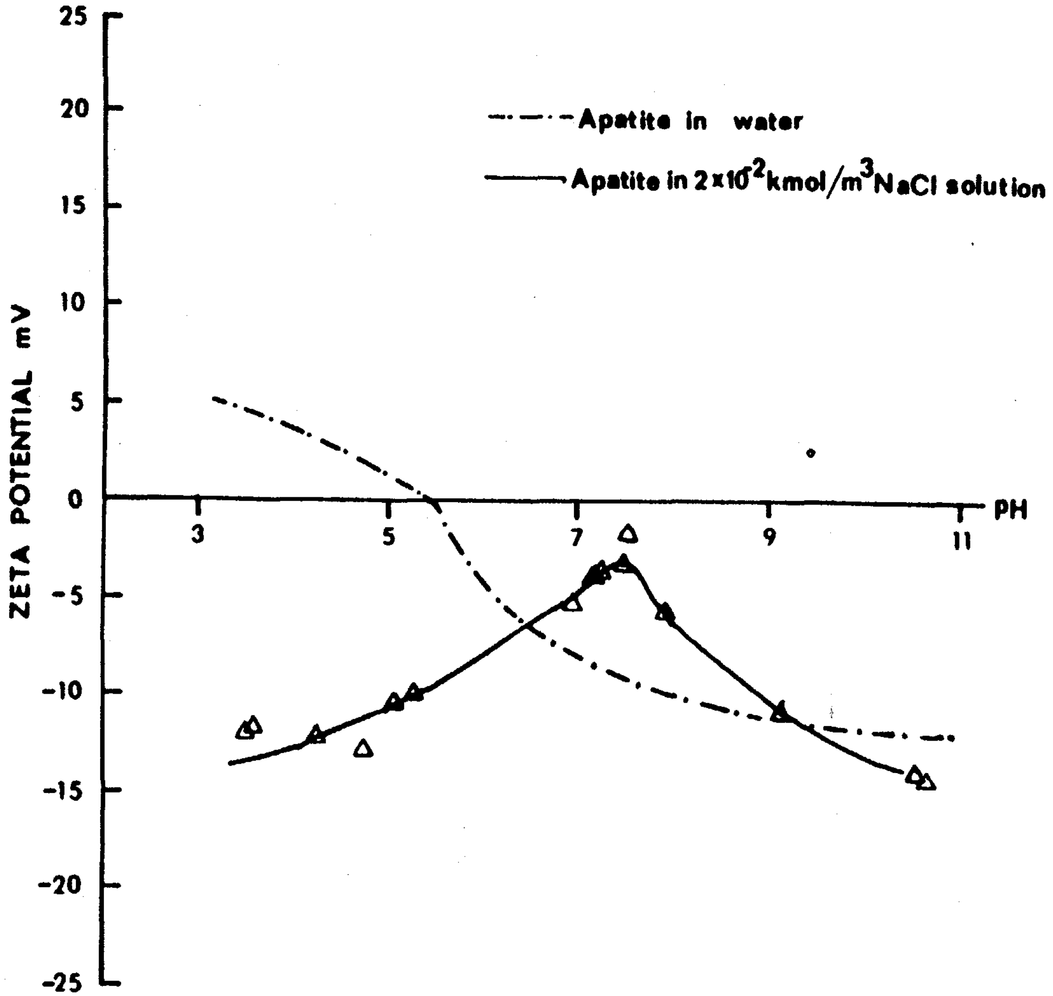

Figure 21. Zeta potential of apatite as a function of pH in 2.0 x 10^{-2} kmol/m^3 NaCl electrolyte.

Effect of Other Salts on the Zeta Potential Behavior of Apatite

Effect of other sodium and some potassium salts on the zeta potential behavior of apatite was examined next. Tests carried out using 2.0 x 10^{-2} kmol/m^3 solution of $NaNO_3$, NaF, KNO_3, and KCl as a function of suspension pH are presented in Figures 22-24 respectively. The zeta potential values for apatite in all of these cases were found to be negative between pH 3.0-11.0. The magnitude of the zeta potential was measured to be smaller for $NaNO_3$ and KNO_3 as compared to NaCl and KCl. On the other hand, NaF addition made the apatite surface more negative than any of the salts mentioned above. The absolute value of zeta potential in the presence of added electrolytes followed the order $NaF>NaCl>KCl>NaNO_3>KNO_3$. Since NaCl provided the best selectivity in flotation, further studies were conducted using this salt. In the first phase the possibility of Na^+ substitution for Ca^{++} ions in the apatite lattice was examined. Next, chloride depletion from the solution was monitored in order to investigate its adsorption on surface and/or substitution in the apatite lattice

ROLE OF SALT IN APATITE CHARGE REVERSAL

Calcium Dissolution from Apatite

The amount of calcium dissolved from apatite with and without NaCl addition was measured after 36 hours of aging. The results of these tests are summarized in Table 6. It should be noted that each figure for Ca^{++}

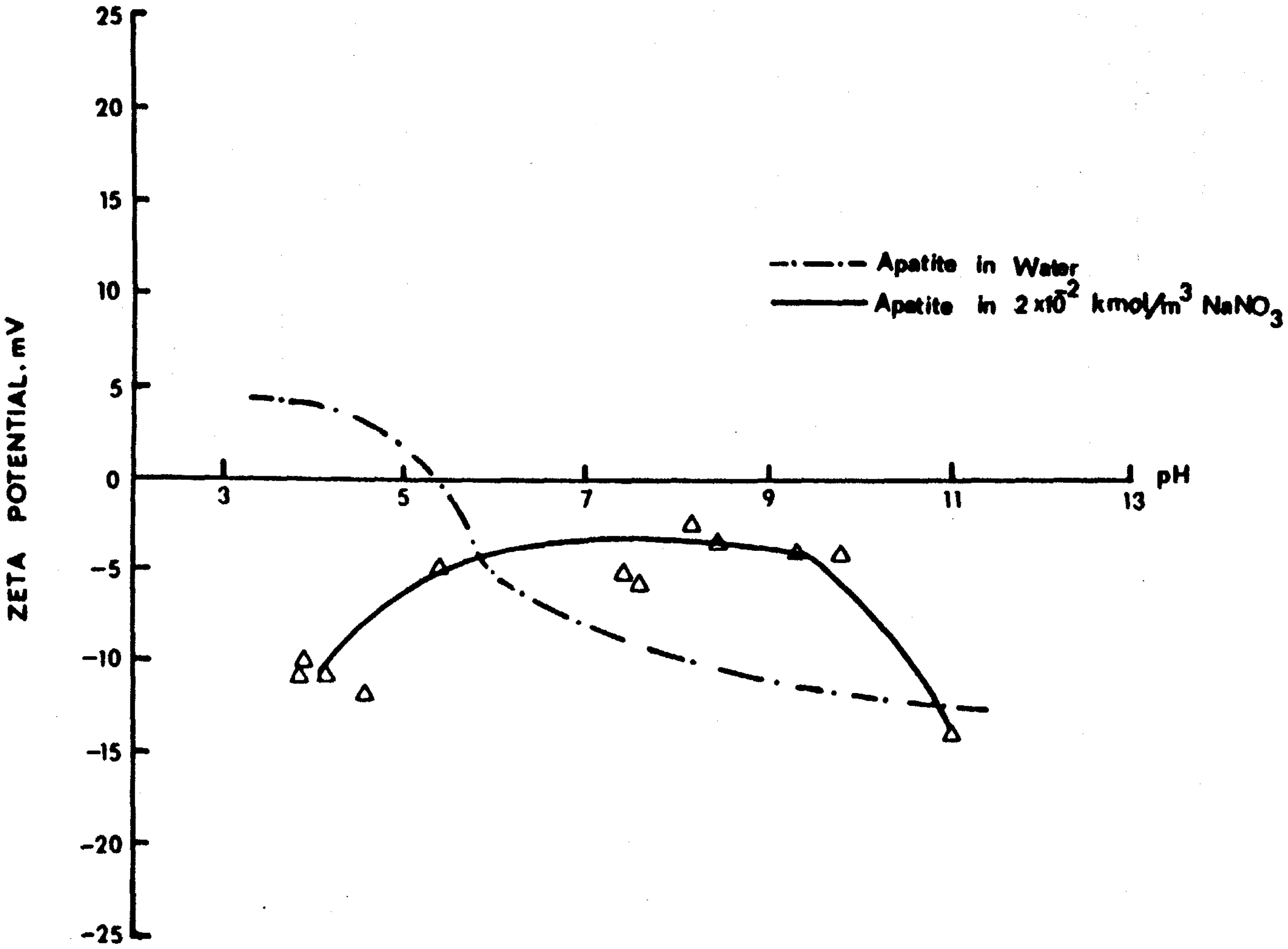

Figure 22. Zeta potential of apatite as a function of pH in 2.0 x 10^{-2} kmol/m^3 $NaNO_3$ solution.

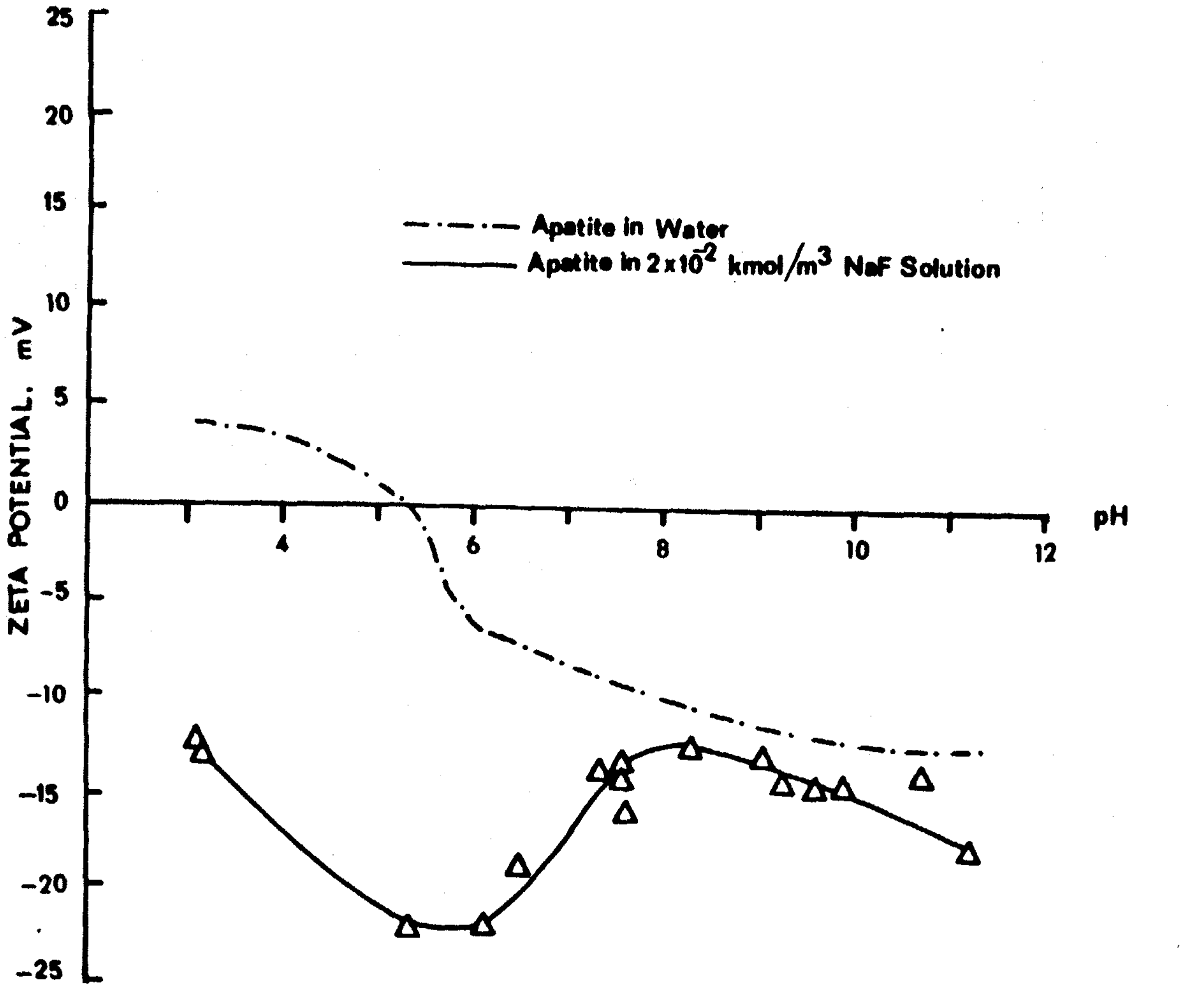

Figure 23. Zeta potential of apatite as a function of pH in 2.0 x 10^{-2} kmol/m^3 NaF solution.

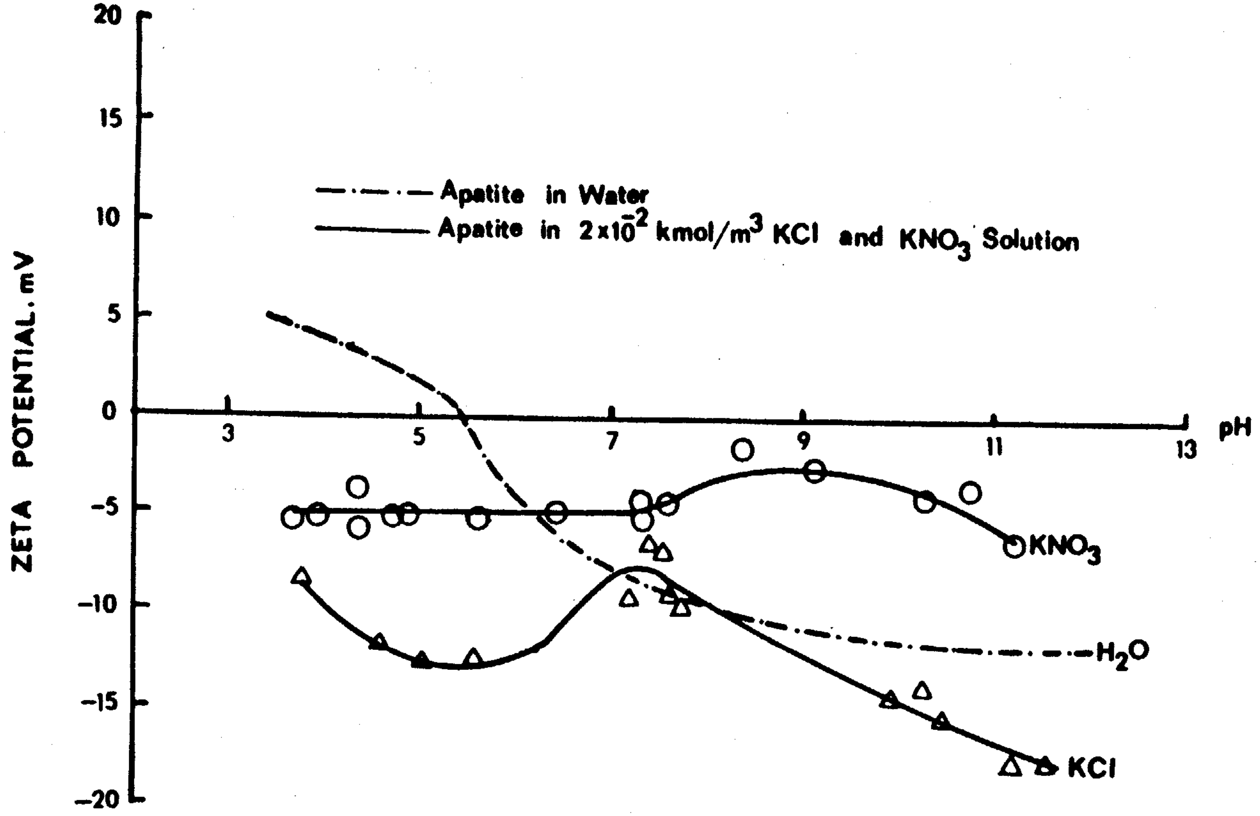

Figure 24. Zeta potential of apatite as a function of pH in 2.0 x 10^{-2} kmol/m^3 KNO_3 and KCl solutions.

Table 6

Calcium Dissolution from 65 x 100 Mesh Apatite

Aging: tumbled at 8 rpm for 36 hours

Suspension pH	Salt Conc. (kmol/m^3)	Amount of Ca^{++} Dissolved (kmol/m^3)	Measured Unit Cell Dimension "a" (Angstroms)
4.7 ± 0.1	----	9.71×10^{-4}	9.344
4.7 ± 0.1	7.5×10^{-4}	1.03×10^{-3}	9.340
4.7 ± 0.1	2.0×10^{-2}	1.17×10^{-3}	9.340

dissolution in the table represents an average of triplicate tests which were almost identical. More calcium dissolution was observed from the samples that were treated in salt solutions as compared to those aged in distilled water only. It is presumed that the dissolved calcium (Ca^{++}) ions are substituted by sodium (Na^{+}) ions from the solution. An attempt was made to monitor Na^{+} concentration after aging. No significant difference was observed, however. This was attributed to the small amount of Na+ depleted, which could not be detected using the analytical techniques employed in this study. The substitution of Ca^{++} with Na^{+} should lead to a more negative surface charge for apatite. To establish further evidence for this hypothesis, the treated samples were ground with elemental silicon (used as reference material), and powder X-ray diffraction patterns were obtained to study changes in lattice parameters of apatite unit cell. The results, presented in Table 6, Indicated no change in "c" direction of apatite's hexagonal unit cell, but some reduction was noticed in "a" dimension. This is not unexpected since the ionic sizes of Na^{+} (0.98Å) and Ca^{++} (1.06Å) are very close. In addition, due to the bonding of neighboring atoms with others in the unit cell, volume changes upon substitution of Ca^{++} with Na^{+} may not be detected, hence, the reduction in unit cell dimension would be small, as observed in this study.

Chloride Ion Depletion

The amount of chloride ions depleted from solution was determined using the ^{36}Cl labeled radionuclide. Chloride ion depletion as shown in Figure 25, ranged from 1.0×10^{-5} to 7.0×10^{-4} kmol/m^{3}. It is suspected that the Cl^{-} ions abstracted from the solution fill in the vacant anion sites and/or substitute for the anions in the apatite lattice. This is a reasonable

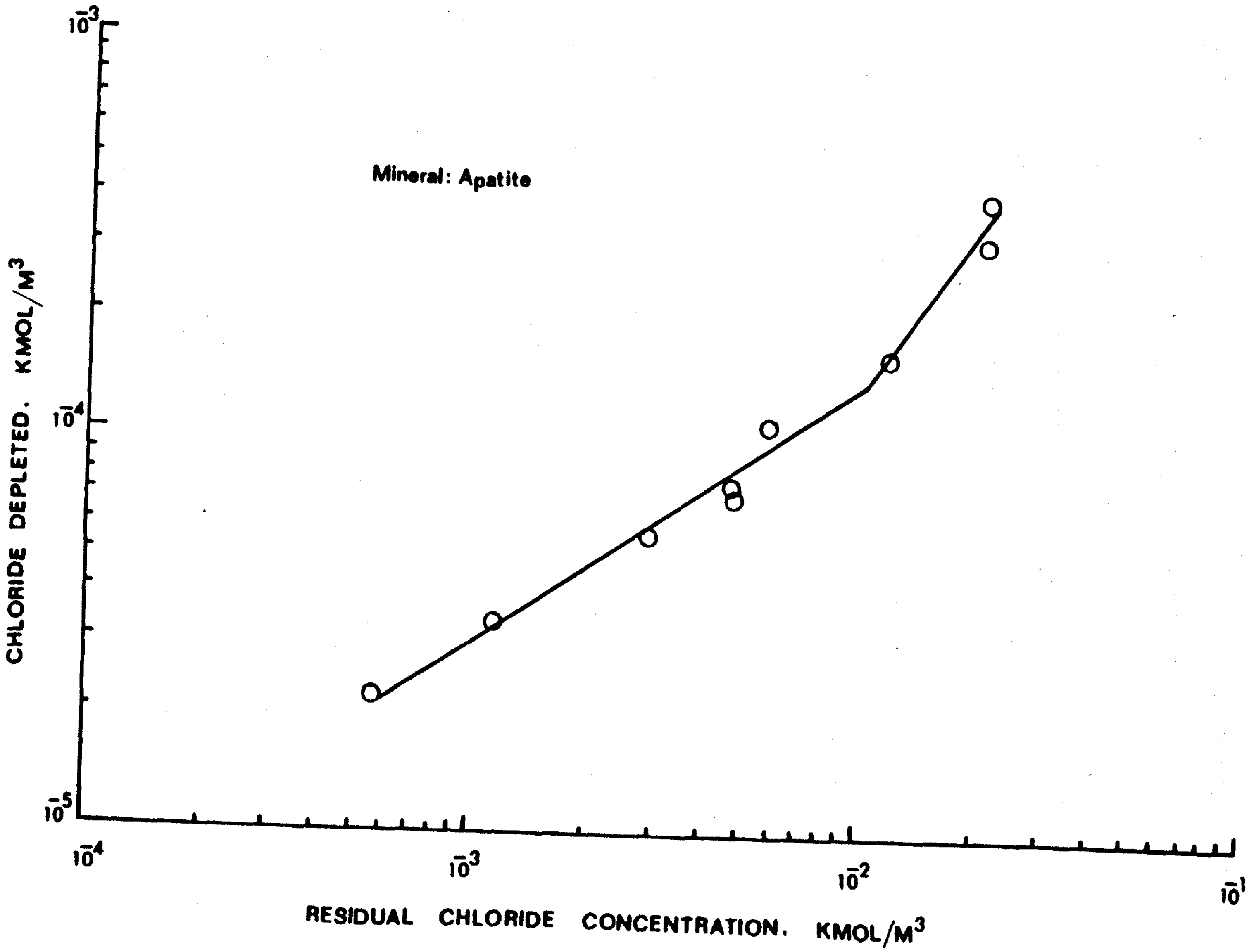

Figure 25. Chloride ion abstraction from solution as a function of total added chlorine at pH 5.5±0.2.

assumption in view of the fact that mutual substitution of F^-, Cl^-, and OH^- ions in the apatite structure makes it possible to form complete solid solutions between fluorapatite, chlorapatite, and hydroxyapatite (9). It should be noted that a stoichiometric substitution of Cl^- ions for OH^- or F^- (the last one being an unlikely event) would not change the surface charge of apatite. An increase in the negative charge is expected when vacancies are filled, along with Na^+ substitution for Ca^{++} in the apatite lattice.

BENCH SCALE TESTS

In the previous section it was demonstrated that it is possible to separate dolomite from apatite in the Hallimond cell. This was accomplished by floating the dolomite at an acidic pH using oleic acid in the presence of sodium chloride which acts as a depressent for apatite. In this section, results of bench scale flotation tests, with apatite dolomite mixtures and natural ore under experimental conditions of Hallimond Cell flotation studies are presented.

Materials

Minerals

Apatite: A high grade product provided by Agrico Chemical Company was prepared as described in the Appendix.

Dolomite: A dolomite sample from Cabbage Grove. Perry, Florida, was prepared as described in the Appendix. Some flotation tests were performed with a dolomite sample from Agrico Chemical Company. The pebble size material was hand-picked, washed from sand impurities, and dried. Then the sample was reduced in size first in a jaw crusher and then in a disc pulverizer to -48 mesh. The ground sample was dry sieved to eliminate the -150 mesh material and then deslimed by decantation after agitation in a Denver Conditioner. It was observed that slimes were produced during the agitation of Agrico dolomite in the conditioner. It was difficult to obtain a clear supernatant water even after 20 desliming steps. Analysis of this dolomite sample indicated 12% insolubles, 26% P_2O_5. and 16% MgO.

Natural Ore: A high MgO sample obtained from Agrico Chemical Company was used in this study. Details about the preparation and characteristics of this material are given in the Appendix.

Reagents: Analytical grade reagents such as sodium chloride, nitric acid for pH control, sodium oleate as collector, and sodium laurylsulfate used as frother, were provided by Fisher Scientific Company. Fuel oil, used as extender, was received from Westvaco.

Procedure

The desired amount of mineral (100-300 g) was conditioned for 5 minutes in a Denver flotation cell with 1200 ml deionized water containing different amounts of sodium chloride. pH was maintained at 4.0 by the continuous addition of HNO_3. After 5 minutes conditioning in the salt solution, sodium oleate. fuel oil, and sodium laurylsulfate were added and the pulp conditioned for 2 more minutes before opening the air valve. Froth was skimmed until it appeared free of mineral particles. When the natural ore was used, silica was first floated with dodecylamine. followed by conditioning and flotation using the procedure as described above.

RESULTS AND DISCUSSION

Mixed Mineral Flotation Tests

Effect of Sodium Chloride

It is clear from the results presented in Table 7 and Figure 26 that some natural selectivity is obtained with the Perry dolomite - Agrico apatite mixture. Flotation at pH 4.0 with oleic acid in pure deionized water resulted in MgO reduction from 5.0% MgO in the feed to an estimated 2.2-2.3% in the phosphate concentrate, at a P_2O_5 recovery above 90%. However, selectivity is

Table 7

Bench Scale Flotation of 48 x 150 Mesh Perry Dolomite:Agrico Apatite Mixture

Collector: sodium oleate, 2.0 lb/t
Extender: fuel oil, 0.9 lb/t
Frother: laurylsulfate, 1.0 lb/t
Salt: None

		Analysis, %		
	Weight, g	P_2O_5	MgO	P_2O_5 Recovery, %
Feed	100	25.7	5.0	100.0
Concentrate	78-80	30.0-30.5	2.3-2.2	94.0 92.0

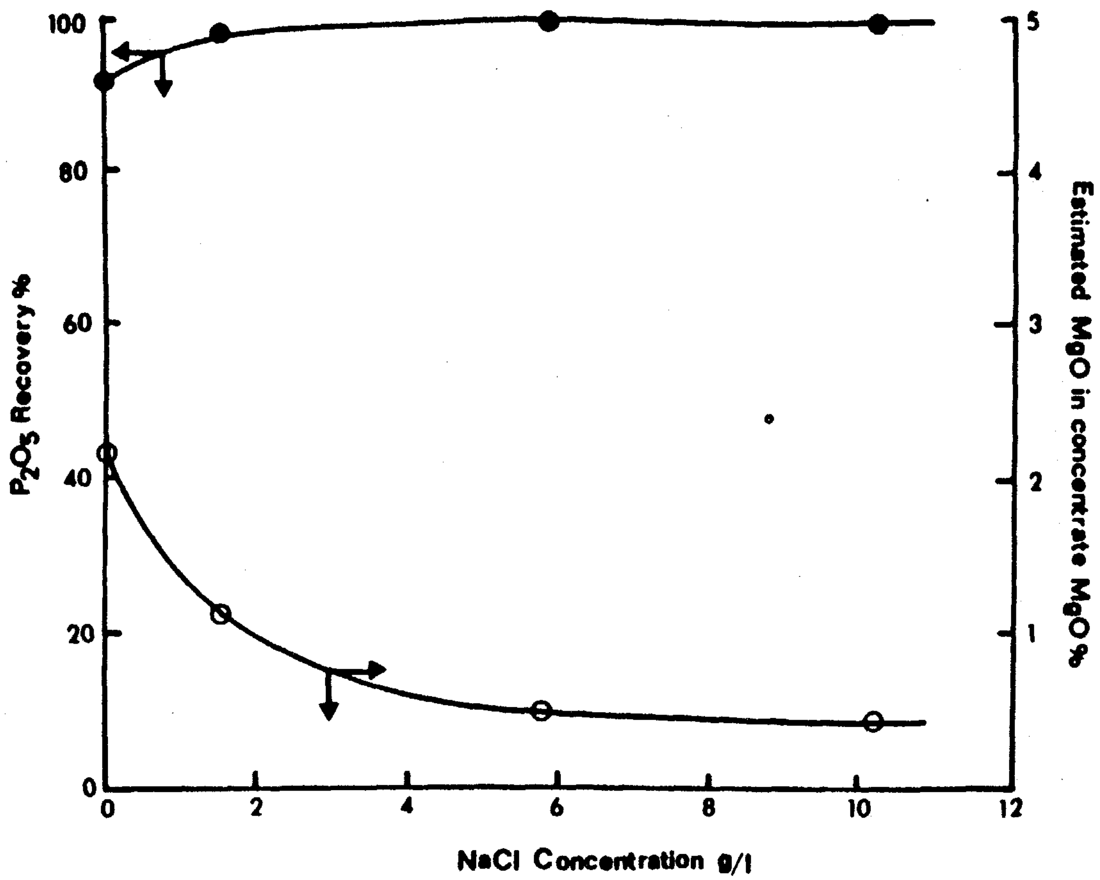

Figure 26. Flotation of mixture of Agrico apatite and Perry dolomite at pH 4.0 in Denver cell as a function of added salt. Collector: 1.0 lb/t oleic acid, 1.0 lb/t fuel oil.

greatly enhanced by the addition of NaCl. As shown in Figure 26, by adding just 1.5 g/l of sodium chloride, the MgO content of the sink is reduced to 1.1% MgO, and recovery increases to 99% P_2O_5. At a NaCl concentration of 5.8 g/l, the MgO content is reduced to 0.5% MgO with 99% P_2O_5 recovery (see Table 8). Similar results were obtained with larger amounts of sodium chloride.

Effect of Pulp Density

The above tests were conducted at 8% pulp density. Additional tests were carried out at increased pulp densities (up to 24% solids) with no deterioration of the flotation performance. For example, as shown in Tables 9 and 10, P_2O_5 recoveries of 99% were obtained with an estimated MgO content well below 1.0% MgO in the phosphate concentrate. No detrimental effect was observed when pulp density was increased to values similar to those used in the industrial practice. On the contrary, by increasing the pulp density it was possible to reduce the frother consumption from 1.0 lb/t at 8% solids to just 0.3 lb/t at 24% solids.

Effect of Particle Size

Selectivity of dolomite flotation in the presence of sodium chloride was found to decrease at particle sizes coarser than 48 mesh. For example, when a 35 x 150 mesh apatite:dolomite mixture was floated in a 1.5 g/l NaCl solution, most of the +65 mesh dolomite remained in the sink, while the -65 mesh dolomite was recovered in the froth. As shown in Table 11, the +65 mesh sink fractions contained essentially all the nonfloated dolomite, and the -65 mesh sink was practically pure apatite. Flotation test results obtained with a 35 x 48 mesh mixture are presented in Table 12. It was found that by

Table 8

Bench Scale Flotation of 48 x 150 Mesh Perry Dolomite:Agrico Apatite Mixture

Collector: 2.0 lb/t sodium oleate
Extender: 0.9 lb/t fuel oil
Frother: 1.0 lb/t laurylsulfate
Salt: 5.8 g/l

		Analysis, %		
	Weight, g	P_2O_5	MgO	P_2O_5 Recovery, %
Feed	100	25.7	5.0	100.0
Concentrate	75-76	33.5-33.8	0.5-0.8	98.0-99.0

Table 9

Bench Scale Flotation of 48 x 150 Mesh Perry Dolomite:Agrico Apatite Mixture

Collector: sodium oleate, 1.0 lb/t
Extender: fuel oil, 0.9 lb/t
Frother: laurylsulfate, 0.5 lb/t
Salt: 5.8 g/l

		Analysis, %		
	Weight, g	P_2O_5	MgO	P_2O_5 Recovery, %
Feed	200	25.7	5.0	100.0
Concentrate	154	33.2	0.6	99.7

Table 10

Bench Scale Flotation of 48 x 150 Mesh Perry Dolomite:Agrico Apatite Mixture

Collector: sodium oleate, 1.33 lb/t
Extender: fuel oil, 0.9 lb/t
Frother: laurylsulfate, 0.33 lb/t
Salt: 5.8 g/l

		Analysis, %		
	Weight, g	P_2O_5	MgO	P_2O_5 Recovery, %
Feed	300	25.7	5.0	100.0
Concentrate	229	33.5	0.6	99.7

Table 11

Bench Scale Flotation of 35 x 150 Mesh Perry Dolomite:Agrico Apatite Mixture

Collector: sodium oleate, 2.0 lb/t
Extender: fuel oil, 0.9 lb/t
Frother: laurylsulfate, 1.0 lb/t
Salt: 1.5 g/l

		Analysis, %		
	Weight, g	P_2O_5	MgO	P_2O_5 Recovery, %
Feed	100.0	25.7	5.0	100.0
Concentrate	71.8	29.8	2.5	83.4
Concentrate +65mesh	39.6	26.5	4.5	41.0
Concentrate -65 mesh	32.2	33.8	0.5	42.4

Table 12

Bench Scale Flotation of 35 x 48 Mesh Perry Dolomite:Agrico Apatite Mixture

Collector: sodium oleate, 2.0 lb/t
Extender: fuel oil, 0.9 lb/t
Frother: laurylsulfate, 1.0 lb/t
Salt: 11.6 g/l

		Analysis, %		
	Weight, g	P_2O_5	MgO	P_2O_5 Recovery, %
Feed	100.0	25.7	5.0	100.0
Concentrate	79.5	31.8	1.4	98.6

increasing the salt concentration selectivity increased, but it could not reach the level obtained with the finer 48 x 150 fraction (see Tables 8 and 12). Nevertheless, MgO content was reduced from 5.0% to 1.4% with 99% P_2O_5 recovery in a single stage flotation. It is possible that by optimizing the reagent additions or by using a cleaning flotation stage the MgO content can be reduced even further. The main conclusion from these tests is that it is difficult to float coarse dolomite particles (in this case, coarser than 48 mesh). Apparently, the coarser the dolomite particle, the larger the amount of collector necessary to float it. If larger amounts of collector are added to promote the coarse dolomite flotation, selectivity decreases because the extra collector tends to float the finer apatite particles. This problem is partially overcome by increasing the concentration of sodium chloride. It is, however, possible that the coarser dolomite particles along with the insoluble component of the phosphate ore will be rejected in the sink fraction.

Agrico Dolomite and Apatite Mixtures

Separation of Agrico dolomite and apatite mixtures was quite successful but required higher concentations of sodium chloride and collector (see Tables 13 and 14). Recoveries of P_2O_5 and rejection of dolomite were lower than that reported for the Perry dolomite mixtures. This may be attributed to the soft nature of the Agrico dolomite which resulted in the production of considerable amounts of slimes during conditioning and flotation. In turn, these slimes required a larger addition of acid to keep the pH at 4.0 and probably consumed a large portion of the collector. As a consequence, the coarser dolomite particles tended to remain in the sink fraction when larger dosages of collector and salt concentration were used.

Table 13

Bench Scale Flotation of 48 x 150 Mesh Agrico Dolomite:Agrico Apatite Mixture

Collector: sodium oleate, 2.0 lb/t
Extender: fuel oil, 0.9 lb/t
Frother: laurylsulfate, 1.0 lb/t
Salt: 17.5 g/l

	Weight, g	Analysis, %		P_2O_5 Recovery, %
		P_2O_5	MgO	
Feed	100	26.4	4.0*	100.0
Concentrate	78	31.8	1.2	94.0

* Estimated from P_2O_5 analysis.

Table 14

Bench Scale Flotation of 48 x 150 Mesh Agrico Dolomite:Agrico Apatite Mixture

Collector: sodium oleate, 2.0 lb/t
Extender: fuel oil, 0.9 lb/t
Frother: laurylsulfate, 1.0 lb/t
Salt: 11.7 g/l

		Analysis, %		
	Weight, g	P_2O_5	MgO	P_2O_5 Recovery, %
Feed	100.0	26.4	4.0	100.0
Concentrate	76.3	31.7	1.2	92.0

Beneficiaton of Natural High Dolomitic Phosphate Sample

In the application of the salt process to a natural ore where, in addition to dolomite, a considerable amount of quartz sand will be present, several alternative flotation schemes can be considered. The following is a discussion of some of those alternatives.

1. Flotation of sand with amines prior to salt addition.

   In this case the sand would be floated away at a slightly alkaline pH with an amine, and then sodium chloride would be added to the silica-free product to float dolomite with oleic acid. The major limitations associated with this route are large amounts of amine, a rather expensive collector, would be necessary; the apatite may adsorb part of the amine and float during dolomite flotation in the acidic pH range; finally, the coarser dolomite particles are likely to remain in the phosphate sink product.

2. Amine flotation of sand after dolomite flotation.

   In this case dolomite would be floated in the presence of salt ahead of the amine flotation of sand. Although this method would avoid the probable activation of apatite by amine, the other two problems pointed out above remain unsolved. In addition, the presence of sodium chloride would probably affect the flotability of quartz with amine.

3. Dolomite flotation followed by apatite flotation with oleic acid.

   In this case dolomite would be floated from the ore at pH 4.0 in the presence of salt, and then apatite floated from the sand by increasing the pH to 8.0-9.0. Although this alternative has the advantages of using only sodium oleate as the collector, and has the potential of leaving the coarse dolomite particles in the sink sand fraction, there are several problems that can be visualized. Flotation of apatite at alkaline pH may not be effective in the presence of salt. Also, the calcium dissolved from the ore during the conditioning stage in the acidic pH range would probably precipitate out with the collector in the alkaline pulp. This would increase collector consumption and/or cause difficulty in apatite flotation. These problems may be overcome by repulping the ore in fresh water.

4. Apatite flotation with oleic acid followed by dolomite flotation.

    In this case the apatite would be floated in a conventional way and the concentrate repulped in a salt solution where dolomite would be floated at acid pH. This route would eliminate the problems associated with the previous alternative, but instead may present the problem of depressing the apatite which has already been floated and, therefore, adsorbed collector. However, the antecedents given in Chapter IV referring to the two stage conditioning process allow us to think that by lowering the pH, apatite should be depressed thus yielding the desired separation.

It is indicated from the above discussion that all four alternatives have some merits and are worthy of further testing. So far, only the first alternative has been tested. In this case, the quartz was floated with 0.8 lb/t of dodecylamine and 0.9 lb/t fuel oil at natural pH. Then salt was added, pH lowered to 4.0 and the dolomite floated with 1.0 lb/t oleic acid and 0.45 lb/t fuel oil and 0.45 lb/t frother. Results presented in Table 15 indicate that the ore was up-graded from 13.2% P_2O_5 to 31.5% P_2O_5 with 87% recovery and the MgO content reduced from 1.7% to 1.1% MgO. In other words, the MgO/P_2O_5 ratio was reduced from 0.130 to 0.035.

Table 15

Bench Scale Flotation of 48 x 150 Mesh Agrico Ore (K6)

Amine: 0.80 lb/t
Sodium Oleate: 1.00 lb/t
Extender: 1.43 lb/t
Frother: 0.45 lb/t
Salt: 11.70 g/l

		Analysis, %		
	Weight, g	P_2O_5	MgO	P_2O_5 Recovery, %
Feed	200	13.2	1.7	100.0
Concentrate	72	31.5	1.1	87.0

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APPENDIX

Materials

Apatite

The high grade product from the Agrico Chemical Co. was screened to provide 35 x 65, 65 x 100, and for later tests, 35 x 150 mesh. These samples were then leached, deslimed 10 times, dried at 50°C, and stored in glass bottles. The BPL content of the composite sample was 74.6%, with an MgO content of 0.37%.

Dolomite

Agrico Dolomite: Large size pieces of hand picked bottom dolomite from the Agrico Chemical Co. were dried in an oven at 50°C and reduced in size with a hammer before grinding in a rod mill. Batch samples of one kg were ground in the rod mill for 12 seconds and then the material was dry screened on a Ro-Tap Siever to separate the 35 x 150 mesh and the oversize recycled to the mill. After using a hand magnet to remove iron impurities, the 35 x 150 mesh dolomite was wet sieved to remove the coating of fines on the particles, and then dried in an oven. Finally, a high tension separator from Carpco, Inc., Jacksonville, Florida, was used to remove the quartz, thus reducing the acid insoluble content to 3.1%.

Perry Dolomite: A pure dolomite sample obtained from Cabbage Grove in Perry, Florida, was ground in a Bico-Braun Chipmunk Crusher, pulverized in a Bico Pulverizer, and screened to the same size fractions as the apatite samples. The various size fractions were passed through a Carpco Magnetic Separator to remove any iron impurity. The samples were then deslimed 10 times, dried at 50°C, and stored in glass bottles. The MgO assay of the composite material was 19%.

<u>Natural Phosphate Ore</u>: A natural high MgO feed was obtained from the Agrico Chemical Co. The sample was dried at 50°C and screened to eliminate the +35 mesh material, and stored. During testing, the samples were deslimed in deionized water one time prior to use. The assay of the sample was 52.7% Insols, 28.84% BPL, (13.2% P_2O_5) and 2.4% MgO.

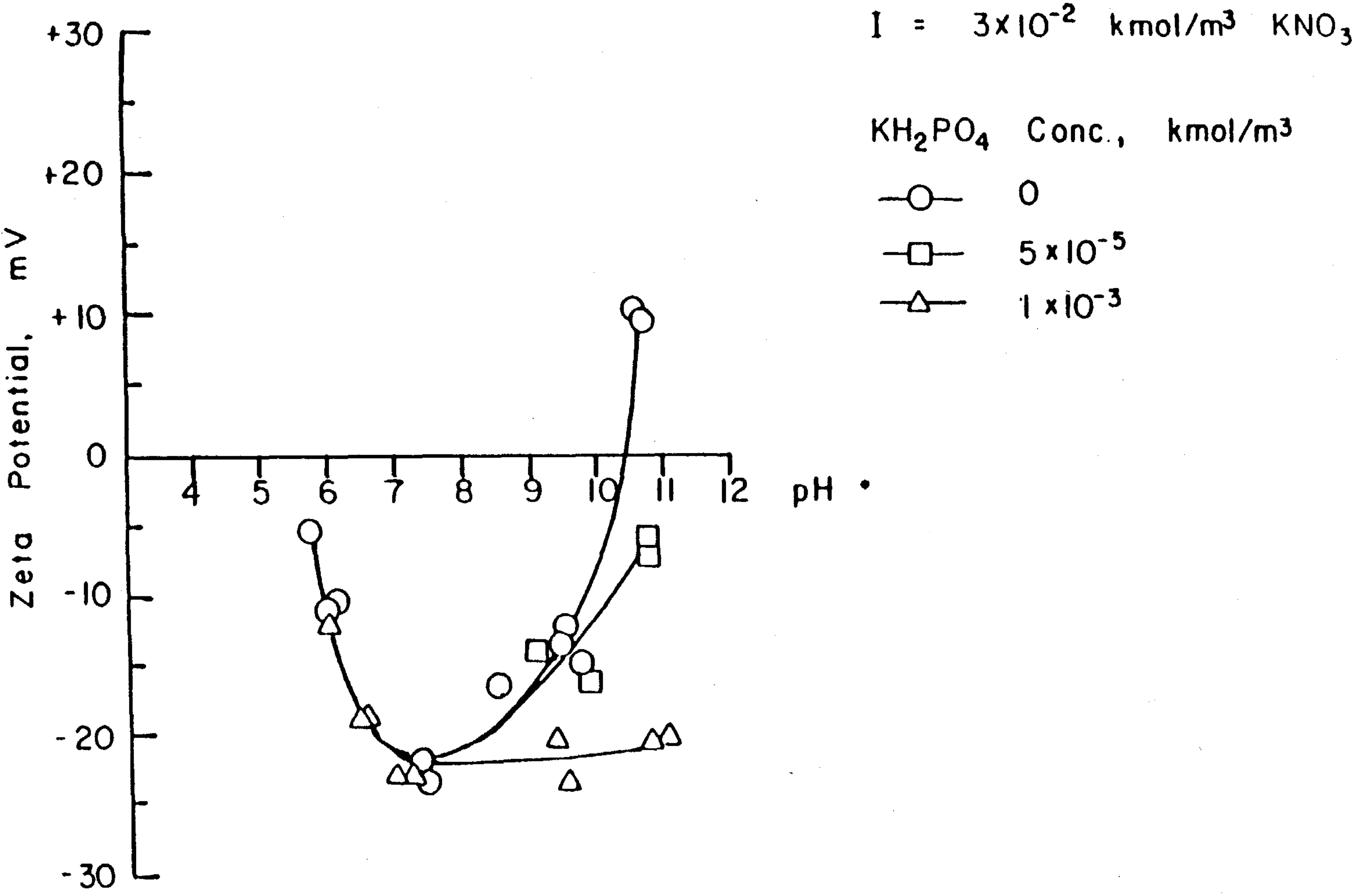

Figure 1. Effect of phosphate ions on the zeta potential of dolomite