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The Effect of Roasting on the Flotation Characteristics of "Paint Rock" and Associated Clay Minerals

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Abstract

The purpose of this work was to ascertain the surface properties of "paint rock" and to determine how these properties are affected by roasting, a method for the beneficiation of the low grade iron ore.

The properties of this sampl were compared with the properties of the pure standard samples, goethite, kaolinite, and montmorillonite.

The experimental results indicate that the flotation behavior of these samples is changed by roasting, due to the change of the crystal structure.

I. Introduction

In flotation of iron ore, it is known that clay minerals associated with the ore may have detrimental effects upon achieving a successful separation of the iron oxides from the gangue constituents. One detrimental effect is considered to be the excessive consumption of flotation reagents by clay minerals due to their high specific surface. Another effect, a slime-coating action, due to clay and other substances, interferes with, or prevents contact between the bubble and the particles of the iron oxide minerals.

Recent experimental data[1] have shown that the nature of the slime interference and the high consumption of reagents in the flotation of iron ore can be correlated with the clay mineralogy of the sample.

Whichever type of flotation, cationic or anionic, is to be employed, a knowledge of the mineralogy of the ore is essential and, consequently, warrants a thorough investigation.

If the original clay which causes so much difficulty can be changed structurally (for example, by roasting), a corresponding change in the flotation behavior of the ore should be expected. Grim[2] reported that the removal of water held by the clay minerals caused significant changes in structure. Correspondingly, the writer has found that roasting lowers the adsorption capacity of clay minerals toward cationic collectors.

The objective of this work was to ascertain the surface properties of some natural clay minerals and "paint rocks" and to determine how these properties, especially in respect to flotation, are affected by roasting. Furthermore, magnetic roasting, followed by magnetic separation, is a promising, commercial method for the beneficiation of "semi-taconites". Consequently, the results of the present study should be applicable to the utilization of the "paint rock" of the Mesabi range; both by flotation and magnetic roasting.

The mineralogical composition of the clay minerals investigated was obtained by differential thermal analysis, thermal balance analysis (hereinafter referred to

as DTA ane TBA, respectively), chemical analysis, and x-ray diffraction. The surface properties of both natural and roasted specimens of some typical clay minerals were investigated by electrophoretic measurements and by determining the adsorption of some typical collectors by the natural and roasted minerals.

An investigation of the specific surface of kaolinite, montmorillonite, and paint rock as a function of the roasting temperature was made, using the air permeability method for determination of the relative change of specific surface.

The flotation characteristics of natural and roasted samples of kaolinite, montmorillonite, and paint rock were investigated by measurements of their flotation recoveries as a function of pH in a Hallimond tube flotation unit.

Preparation of Samples

Since kaolinite and montmorillonite clays were regarded as being the most likely clay minerals to be encountered in the paint rock horizons of the Mesabi range, relatively pure samples of these two minerals were chosen as comparison standards, the montmorillonite being the variety known as bentonite. When the samples of paint rock were collected, care was taken to obtain various types and compositions, for example, kaolinite type, goethite rich etc. from the wide area of the Mesabi.

The sources and descriptions of the samples studied are listed below and their chemical analyses are given in Table 1.

"pure-standard" samples

Montmorillonite (Bentonite)
Obtained from Wards Natural Science Estab.
John C. Lane Tract.
Upton, Wyoming

Aqua gel Bentonite
Obtained from S. S. Goldich
Dept. of Geology, University of Minnesota

Kaolinite (china clay)
Obtained from S. S. Goldich
Department of Geology, University of Minnesota

Kaolinite (Georgia clay)
Obtained from Mines Experiment Station, Minnesota

"paint-rock" samples from the Mesabi range, Minnesota

Paint(1) rock 1.
Obtained from the Patrick Mine (The MA Hanna Co.)

(1) All "pain rock" samples were collected by J. N. Gundersen.

Paint rock 2.
Obtained from the Whiteside Mine (Snynder)
Paint rock 3.
Obtained from the North Shirvs Mine (Pacific Isles)
upper slaty paint rock
Paint rock 4.
Obtained from the Whiteside Mine (Snynder)
lower slaty paint rock

TABLE 1. Chemical Analyses of the Samples

	montmorillonite		kaolinite		paint rocks			
	aqua gel Bentonite	Bentonite Wyoming	Georgia clay	China clay	No. 1	No. 2	No. 3	No. 4
Total								
Fe	2.73	2.74	0.48	0.57	4.51	44.15	27.14	27.87
Fe^{++}	0.58	0.56	0.48	0.49	0.57	0.48	0.47	0.49
CO_2	0.48	0.14	nil	0.75	nil	nil	nil	nil
SiO_2	58.05	60.20	44.27	45.28	44.53	10.67	50.74	43.26
Al_2O_3	19.64	19.95	39.61	39.54	32.47	10.62	5.60	9.38
MgO	2.75	2.56	0.18	0.23	1.46	0.34	0.27	0.26
CaO	1.42	0.69	0.16	0.24	0.12	0.11	0.16	0.13
TiO_2	0.12	0.11	1.04	0.25	1.04	0.89	0.35	0.33
Na_2O	2.14	2.82	0.54	0.26	0.30	0.009	0.030	0.005
K_2O	0.37	0.36	1.03	0.82	2.35	0.013	0.016	0.007
H_2O (105°C)	5.14	3.52	0.25	0.32	1.90	2.33	0.51	0.95
H_2O (130°C)	0.41	02.0	0.07	0.13	0.08	0.02	0.03	0.05
H_2O (1000°C)	5.43	5.64	13.21	11.44	9.28	11.70	3.36	5.70

Theoretical compositions:

	SiO_2	Al_2O_3	H_2O
Kaolinite	46.54	39.50	13.96
Montmorillonite	66.7	28.3	5.0

From the results of the chemical analyses (Table 1) and DTA (as discussed in the following section) of the samplese of "paint rock", their mineralogical compositions are believed to be as follows:

paint rock No. 1: Kaolinite is the major constituent.

paint rock No. 2 : A mixture of goethite and kaolinite.
paint rock No. 3 : A mixture of goethite and kaolinite.
paint rock No. 4 : A mixture of goethite and kaolinite.

DTA and TBA

(a) Apparatus and Procedure

The sample holder of the DTA apparatus consisted of an inconel block 2.5 cm in diameter, in which three 0.6 cm diameter holes were drilled. The bottoms of the holes were plugged with porcelain insulating tubing through which the thermocouple wires were passed. Twenty four-gauge chromel and alumel wires were used for the thermocouples. The furnace was a standard vertical type with a heating chamber 6 cm in diameter and 15 cm deep. Power to the furnace windings was supplied from an auto-transformer driven by a small electric motor through a speed reducer. At the start of each test, the auto-transformer was positioned to give a heating rate of 10°C per minute. The differential and the temperature thermocouples were each connected to Brown Electronik Strip Chart recorders. Minus 120 mesh alundum was used as the thermally inert material.

A manually-controlled type of TBA apparatus was used to determine the weight loss of the samples as a function of temperature. The crucible containing the sample, 1.6 cm in diameter and 5.4 cm in depth, was suspended in a vertically disposed cylindrical type of electric furnace from one end of the balance. The temperature inside the furnace was adjusted by manual sitting of the variac-transformes in increments of 20° of arc every 5 minutes from an initial setting angle of 30°. This method of manual control of the furnace resulted in a sample heating rate of approximately 11°C per minute with only a small deviation from linearity. In each case the initial weight of the sample was about 5 grams.

During heating, the weight of the sample was measured every 5 minutes and the weights were plotted as a function of temperature to obtain the thermogravimetric curves that accompany the DTA curves in Figs. 2 through 7. This part of the investigation was performed by two persons, one controlling the temperature and the other balancing and recording the weight at that temperature.

(b) Discussion of DTA Results

Fig. 1 shows the DTA curves for four samples of paint rock, together with the curves for the pure standard clays (montmorillonite (Wyoming), kaolinite (Georgia clay)) and that for goethite. The curve for goethite is reproduced from I. Iwasaki's report[1].

From the chemical analysis and from the curves of Fig. 1, it can be

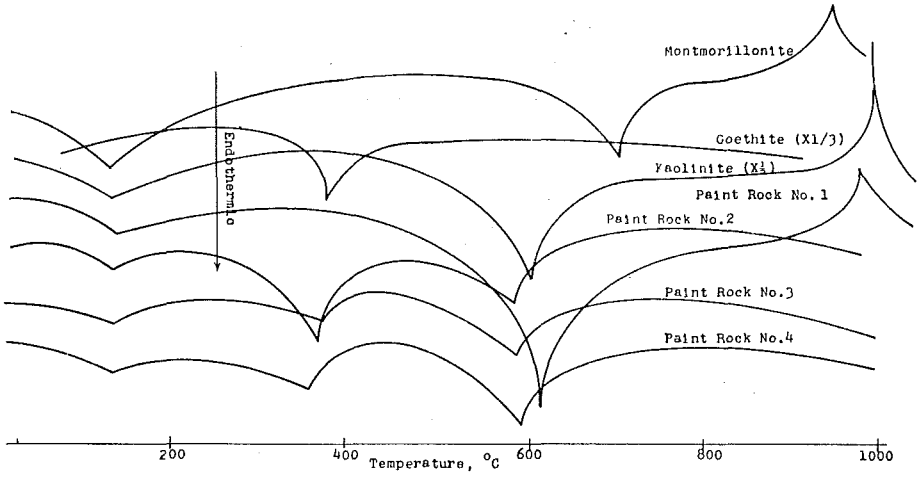


Fig. 1. DTA curves of montmorillonite, goethite, kaolinite and paint rocks

assumed that the major constituent of Paint Rosk No. 1 is kaolinite.

As shown in Fig. 1, Paint Rock No. 2 gave three endothermic peaks. The first peak at abnut 140°C apparently corresponds to the removal of 'adsorbed water' from the material. The second peak at about 360°C corresponds to the decomposition of goethite, and the third peak at 580°C to the decomposition of kaolinite respectively.

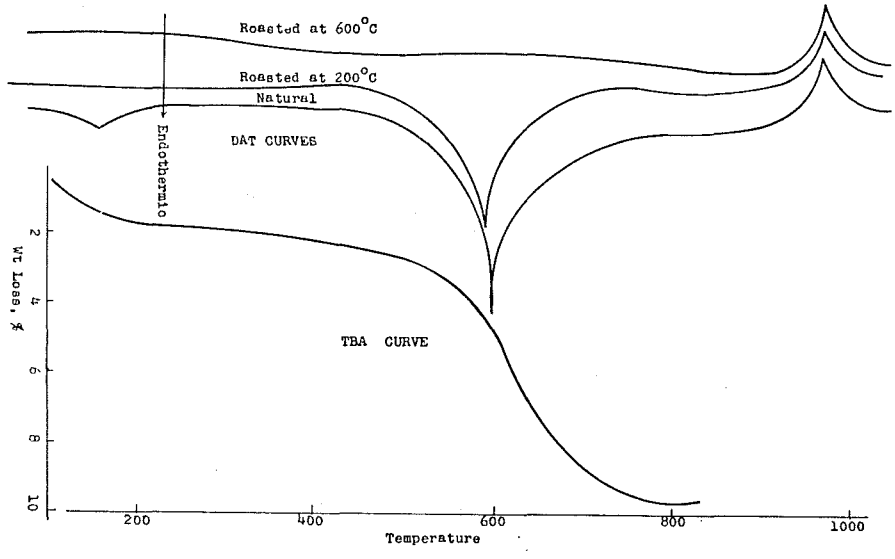


Fig. 2. The DTA and TBA Curves of Paint Rock No. 1

The DTA curves for paint rocks Nos. 3 and 4 appear to have shapes and peaks similar to those for paint rock No. 2, hence these three materials appear to be composed primarily of goethite and kaolinite.

Fig. 2 shows the DTA curve and the TBA curve of the sample of paint rock No. 1.

On the DTA curve in Fig. 2 the natural specimen of paint rock No. 1 exhibits two endothermic peaks, at 140°C and 600°C, and one exthothermic peak at 1000°C. This same natural specimen has inflection points on the TBA curve at about 145°C and about 600°C, corresponding to the peaks on the DTA curve.

In the case of a sample of paint rock No. 1 which had been roasted at 200°C for one hour, the peak at 140°C no longer appeared in the DTA curve, althongh the highest temperature peaks were still present.

Similarly, when a specimen of paint rock No. 1, roasted at 600°C, was tested, the 140°C, and 580°C peaks shown by the unroasted specimen were no longer present although the peak at 1000°C was unchanged. Similar statements can be made of all the other samples reported in Table 2 and Figs. 3, 4, 5, 6, and 7.

Fig. 3 shows the DTA and TBA curves of the samples of kaolinite (Georgia Clay). In the DTA curves, the peak at 600°C on natural kaolinite (curve 1) disappeared when the sample which had been preheated at 600°C for one hour, was tested (curve 2). In the TBA curve, the inflection point of natural kaolinite

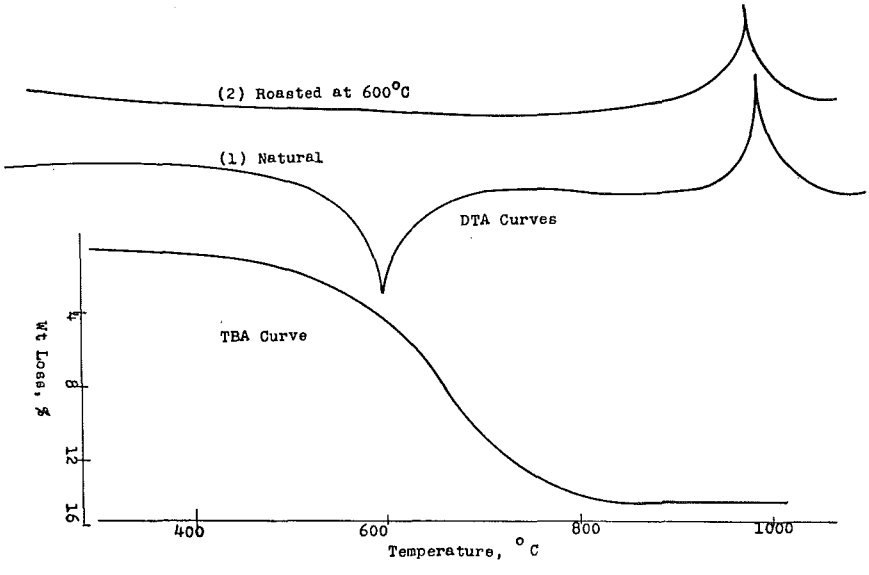


Fig. 3. The DTA and TBA Curves of Kaolinite (Georgia Clay)

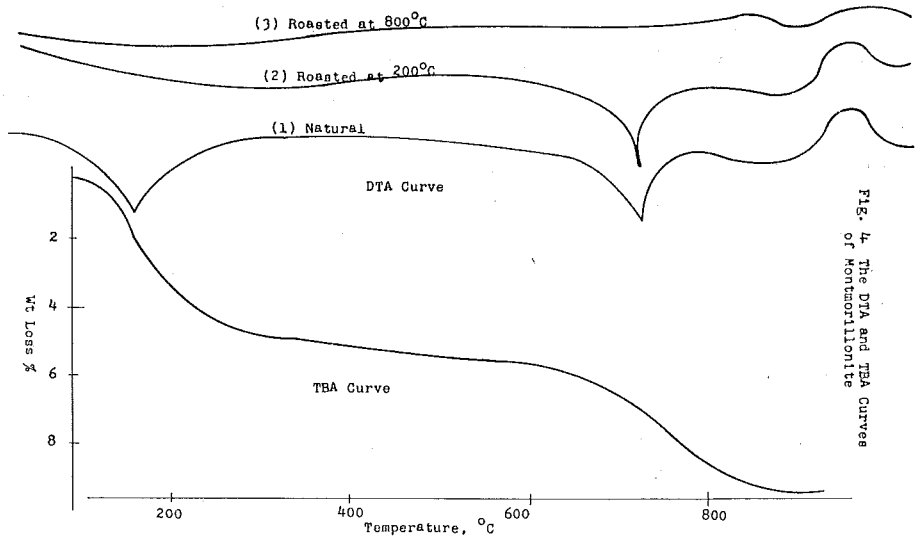


Fig. 4. The DTA and TBA Curves of Montmorillonite

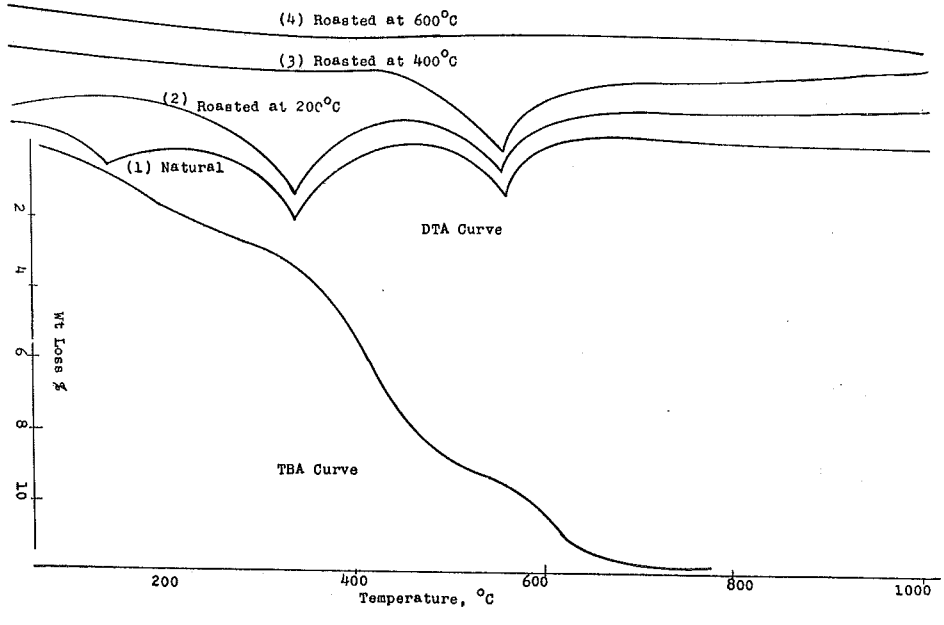


Fig. 5. The DTA and TBA Curves of Paint Rock No. 2

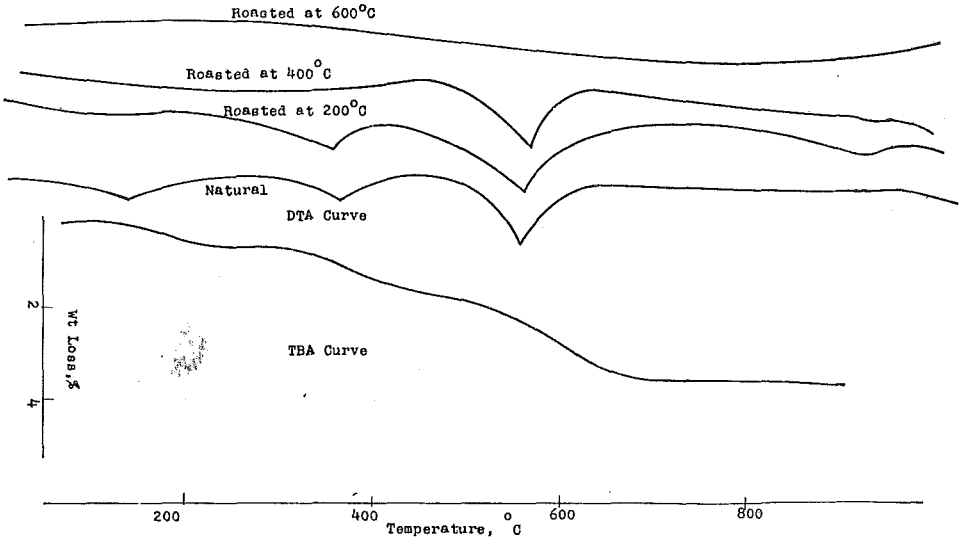


Fig. 6. The DAT and TBA Curves of Paint Rock No. 3

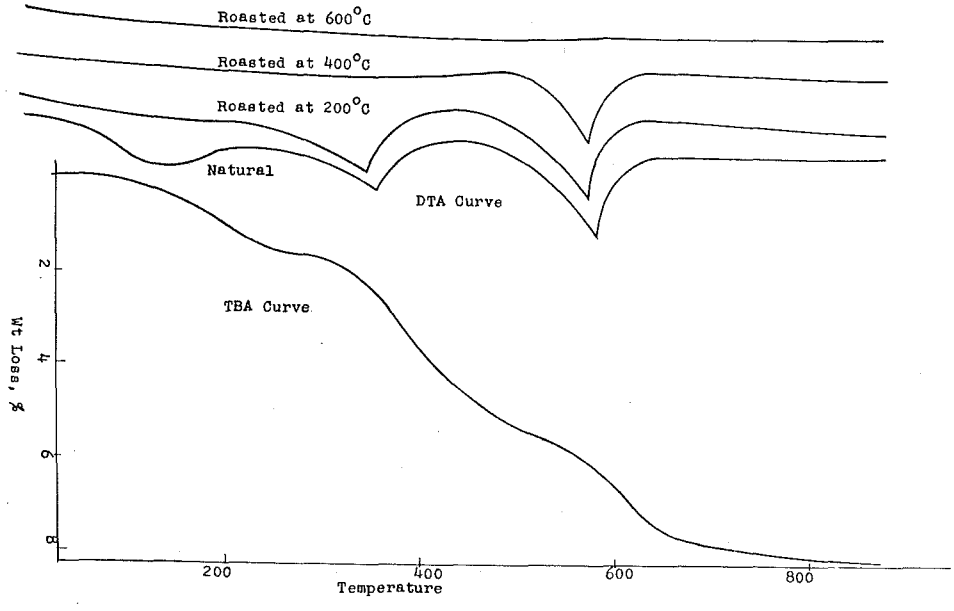


Fig. 7. The DAT and TBA Curves of Paint Rock No. 4

appeared to correspond approximately to the peak at 600°C in the DTA curve. As the temperature exceeded 800°C, the change in weight appeared to approach zero. Total weightloss at 900°C was about 14 Pct.

Fig. 4 shows the DTA ane TBA curves of the sample of montmorillonite (aqua gel bentonite). Similar statements made of the samples of paint rock No. 1 and kaolinite are also applicable in this case. The final loss in weight of montmorillonite was about 9.3 Pct.

Table 2 summarizes the results of the DTA and TBA.

(c) Discussion of TBA Results

In the TBA curve of Fig. 3, it is shown that natural kaolinite (Georgia clay) loses a few percent of weight before the endothermic reaction at 600°C occurs. This loss is undoubtedly due to removal of water. Therefore, the true loss, occurring only during the endothermic reaction at 600°C, may be regarded as a difference between the total loss (about 14%) and the initial loss (about 2%), i.e., about 12%.

If it is supposed that the true loss during the reaction resulted only from the removal of chemical water, a stoichiometric calculation can be made using the chemical formula of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). A calculated value of 14% should be compared with the experimental value of 12%. These two values are in fairly good agreement with the value of 13% obtained from the chemical analysis of this material given in Table 1.

If a similar calculation is applied to montmorillonite, the experimental value of 4.5% is comparable to the stoichiometric value of 4.7%. In this case the chemical formula of montmorillonite is taken as ($Al_{3.92}$ $Fe_{0.08}$ $Si_{6.92}$ $Al_{1.08}$) $O_{22} \cdot 2H_2O$[3]. The chemical formula, however, is quite variable and depends upon the impurities, as stated by Mackenzie[3].

This agreement between the experimental and theoretical results leads to the belief that the removal of water from the two minerals is fully responsible for the weight loss during the respective endothermic reaction. Thus it seems probable that the first weight loss at about 140°C, less than 2 persent, was due to the absorbed water in the clay minerals. This is unrelated to the crystalline structure of the minerals. However, the endothermic reaction at 580°C for kaolinite and 715°C for montmorillonite are due primarily to the removal of combined (or 'chemical') water, mineralogically an important part of the materials. Therefore, once the definite internal atomic arrangement of the respective structures has been destroyed, by the removal of the water, the product must be different from the original. Grim[2] has suggested that amorphous material is formed by the loss of OH from the crystalline lattice.

TABLE 2. DTA and TBA of Samples

Material	DTA				TBA				Fig. No.
	Peak Point, °C				Inflect. Point. °C				
	Endotherm.			Exotherm.				Total	
	1st	2nd	3rd		1st	2nd	3rd	loss %	
Kaolinite									
natural	140	600		1000		550-650		14	3
roast. at 200	×	×		1000					
Montmorillonite									
natural	140	715		1000	140	710		9.3	4
roast. at 200	×	715		1000					
roast. at 800	×	×		1000					
Paint Rock 1									
natural	140	600		1000	145	610		9.6	2
roast. at 200	×	600		1000					
roast. at 600	×	×		1000					
Paint Rock 2									
natural	140	360	580	1000	150	350	600	11	5
roast. at 200	×	360	580	1000					
roast. at 400	×	×	580	1000					
roast. at 600	×	×	×	1000					
Paint Rock 3									
natural	140	360	580	1000	160	370	600	4	6
roast. at 200	×	360	580	1000					
roast. at 400	×	×	580	1000					
roast. at 600	×	×	×	1000					
Paint Rock 4									
natural	140	360	580	1000	150	370	600	8	7
roast. at 200	×	360	580	1000					
roast. at 400	×	×	580	1000					
roast. at 600	×	×	×	1000					

Note: The mark of × indicates the disappearance of the peak as a result of previous roasting.

Upon further heating, up to about 1000°C, mullite is produced. This reaction gives an exthothermal curve, the so-called 'mullite formtion' curve. The reaction which leads to the formation of mullite is given as follows:

$$\underset{\text{kaolinite}}{3\{Al_2O_3\cdot 2SiO_2\cdot 2H_2O\}} \xrightarrow[\text{Reaction}]{\text{Exthothermic}} \underset{\text{mullite}}{3Al_2O_3\cdot 2SiO_2} + 4SiO_2 + 6H_2O$$

This exthothermic peak at about 1000°C is shown in Fig. 1 for the samples of kaolinites, montmorillonites, and paint rocks Nos. 1 through 4.

The endothermic reaction of goethite occurring at abnut 360°C is regarded as being due to the following reaction:

$$\underset{\text{goethite}}{2FeO\cdot OH} \xrightarrow[\text{Reaction}]{\text{Endothermic}} \underset{\text{hematite}}{Fe_2O_3} + H_2O$$

This peak for goethite appears for the samples of paint rocks Nos. 2, 3 and 4 shown in Fig. 1.

Electrophoretic Mobilities

In the case of some oxide minerals the mechanism of adsorption of a collector at the mineral-solution interface has long been considered as being governed by the electrokinetic potential of the mineral. By considering the "electrical double layer" as a simple condenser at the mineral-solution interface, the zeta potential (Z) has been defined as the potential drop in the diffuse layer. It has been found that the zeta potential is related to the electro-phoretic velocity of a particle by the following equation:

$$Z = \frac{4\pi nm}{D} \qquad (1)$$

where m is the electrophoretic mobility of the mineral particle in cm per second under a potential of 1 volt per cm, and n and D are the viscosity and the dielectric constant, respectively, of the liquid medium.

Equation (1) shows that the zete potential is directly proportional to m, the electrophoretic mobility provided that the viscosity (n) and the dielectric constant (D) of the modium remain constant: hence, the greater the mobility, the greater the zeta potential.

The zeta potential itself is significant as indicating the strength of attraction (or adsorption) of the electrolyte in the bulk solution by the soid surface. Therefore, a high value of the zeta potential, either positive or negative, and correspondingly a high value of the electrophoretic mobility, indicates a strong tendency toward adsorption of the electrolyte.

When the zeta potential falls to low values, as a result of the addition of excess electrolyte, the repulsion between the particles is reduced to such an extent that coagulation occurs, and measurements of mobility can not be made. This coagulation was observed in all the experiments at pH velues less than approximately 2.0 and greater than approximately 12.0.

(a) Experimental Apparatus and Procedure

Electrophoretic mobility was measured in a thin, rectangular, vertical micro-electrophoretic cell constructed from microscope slides. A 16 mm objective and an ocular (10 X) with micrometer (1 div=1/10 mm) were used withe a microscope to measure particle travel. By means of a stop-watch, particle velocity was determined. The rectangular glass cell, filled with water, was inserted between the light source and the microscope, and a piece of glass plate was attached to the stage of the microscope to minimize convection currents due to heating in the cell. Two No. 22 gauge platinum wire electrodes were set at opposite ends of the cell and the potential was applied to these. The cell dimensions and the experimental set-up are shown in Fig. 8.

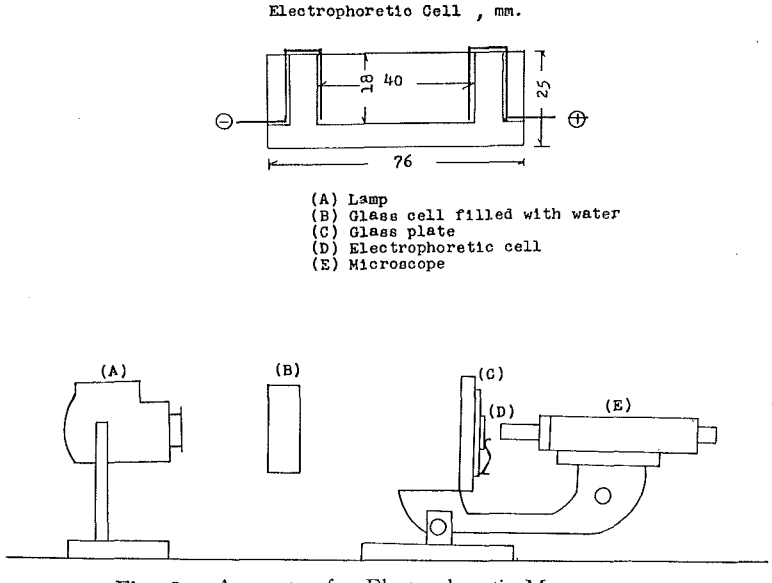


Fig. 8. Apparatus for Electrophoretic Measurement

To prevent liquid movement due to electro-osmotic and hydrodynamic flow in the cell from affecting the electrophoretic mobility, the microscope was focused at a point which was 0.2 times the internal width of the cell from the front plante of the cell.

A pulp of the mineral suspension having the desired pH was prepared by agitating the sample with a magnetic stirrer for more than 2 hours. The cell was filled with the conditioned suspension. When the electric potential (ranging from 21.5 to 21.8 volts) was applied, the time necessary for a particle to travel a certain distance (ranging from 26.6 μ to 133 μ) was determined. About ten measurements were usually made to obtain an average mobility, expressed in terms of cm/sec per volt/cm.

A difficulty arose in measurement at about pH 3 or less as a result of electrolysis accompanied by the formation of hydrogen gas bubbles at the anode.

To get good reproducibility, it was necessary to maintain the cell temperature constant at 25°C.

As mentioned previously, another difficulty occurred in the measurement of mobility in solutions below pH 3 and above pH 10 because of coagulation

TABLE 3.

Fig.	Sample	Roasting Temp.	Isoelectric Point	Max. average mobility	
		°C	pH	cm/sec/volt/cm	pH
9	Montmorillonite (aqua gel)	natural	1.8–2.0	-3.8×10^{-4}	6.5
	"	800	2.0–2.5	-4.7×10^{-4}	10
10	Montmorillonite (Wyoming)	natural	2.0–2.5	-4.5×10^{-4}	9
	"	800	2.0–2.5	-3.8×10^{-4}	10
11	Kaolinite (china clay)	natural	3.0–3.3	-5.0×10^{-4}	10
	"	600	4.0–4.5	-4.2×10^{-4}	10
12	Kaolinite (Georgia clay)	natural	3.0	-4.8×10^{-4}	6
	"	600	4.0	-5.5×10^{-4}	9
13	Paint Rock No. 1	natural	3.0–3.5	-4.2×10^{-4}	10
	"	600	3.5–4.0	-4.0×10^{-4}	9.5
14	Paint Rock No. 2	natural	5.5	-3.8×10^{-4}	7.5
	"	600	4.5	-4.0×10^{-4}	3.0
15	Paint Rock No. 3	natural	3.5–4.0	-3.8×10^{-4}	8.5
	"	600	4.5–5.0	-4.0×10^{-4}	9.0
16	Paint Rock No. 4	natural	5.0	-3.2×10^{-4}	10
	"	600	5.0	-3.8×10^{-4}	10

between particles.

The electrophoretic mobilities were measured in the range of pH 3 to 12 for the all clay minerals and paint rocks both in the natural and in the roasted conditions. For the montmorillonite sample, both aqua gel bentonite and montmorillonite from Wyoming were measured. For the kaolinite sample, both Georgia clay and china clay were tested.

(b) Experimental Results

Figures 9 through 16 show the electrophoretic mobilities for the natural and roasted samples throughout the pH ranges investigated.

In Table 3 the maximum average mobilities are given together with the pH value at which they occurred.

Within the limit of experimental error, Figs. 9 and 10 show that the isoelectric pointes (extrapolated) for both the natural montmorillonites and the montmorillonites roasted at 800°C occur at almost the same pH. In the case of kaolinite, the isoelectric points of roasted kaolinites (600°C) fall at definitely higher pH value than natural kaolinites (Figs. 11 and 12).

The isoelectric point and the shape of the mobility curve of paint rock No. 1 (Fig, 13) appears to be very similar to that of kaolinite. This is in accord with the DTA determination that the major constituent of Paint Rock No. 1 is kaolinite.

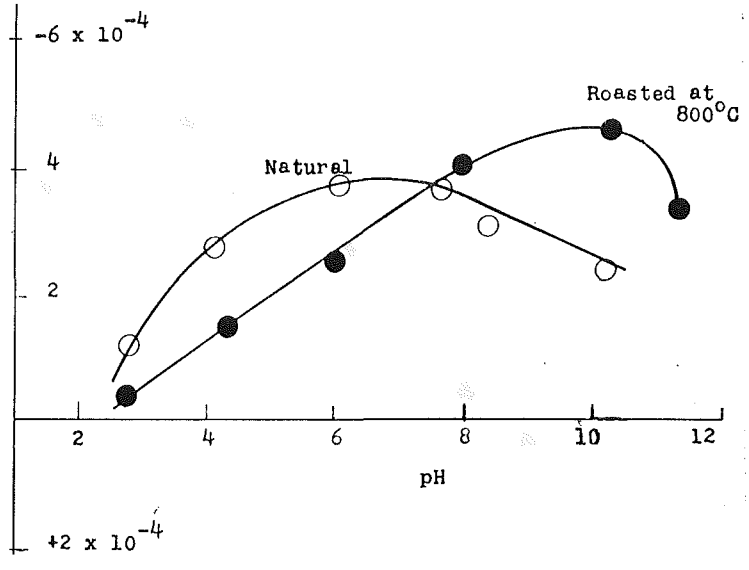


Fig. 9. Electrophoretic Mobility of Montmorillonite (aqua gel bentonite)

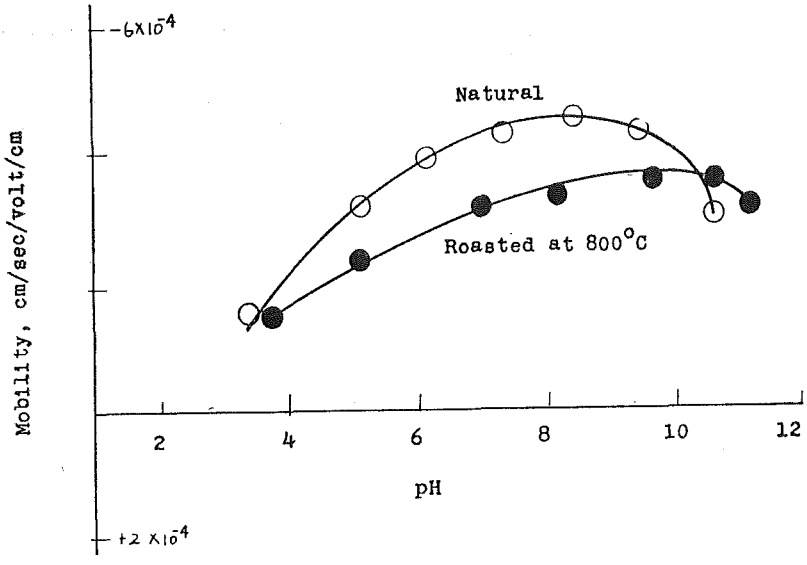


Fig. 10. Electrophoretic Mobility of Montmorillonite (Wyoming Clay)

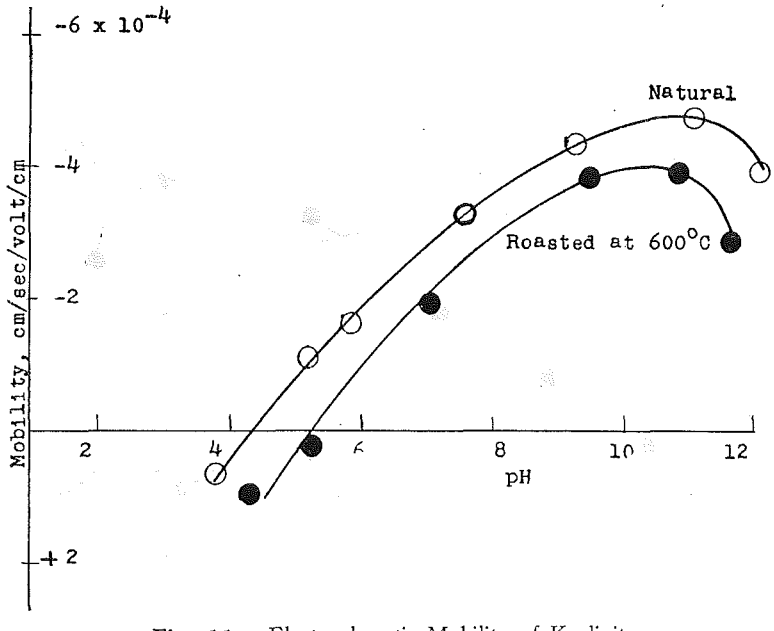


Fig. 11. Electrophoretic Mobility of Kaolinite (China Clay)

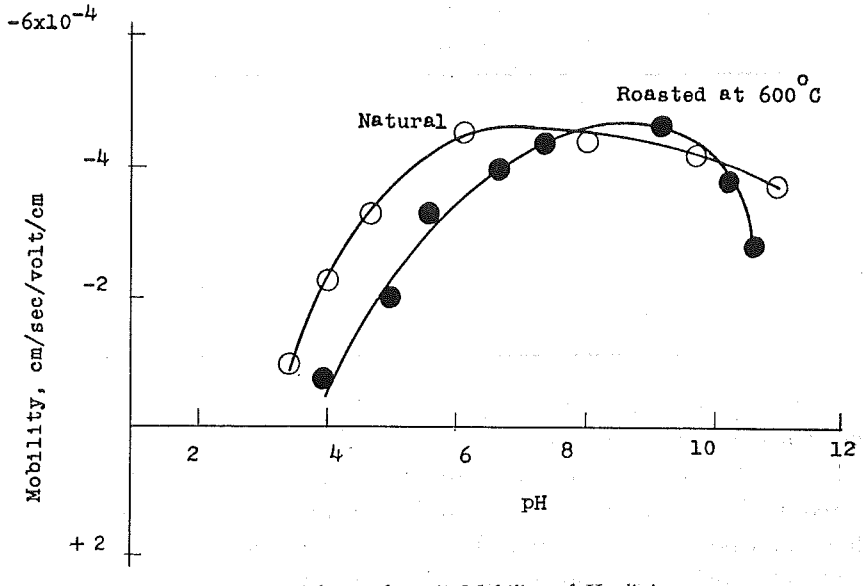


Fig. 12. Electrophoretic Mobility of Kaolinite (Georgia Clay)

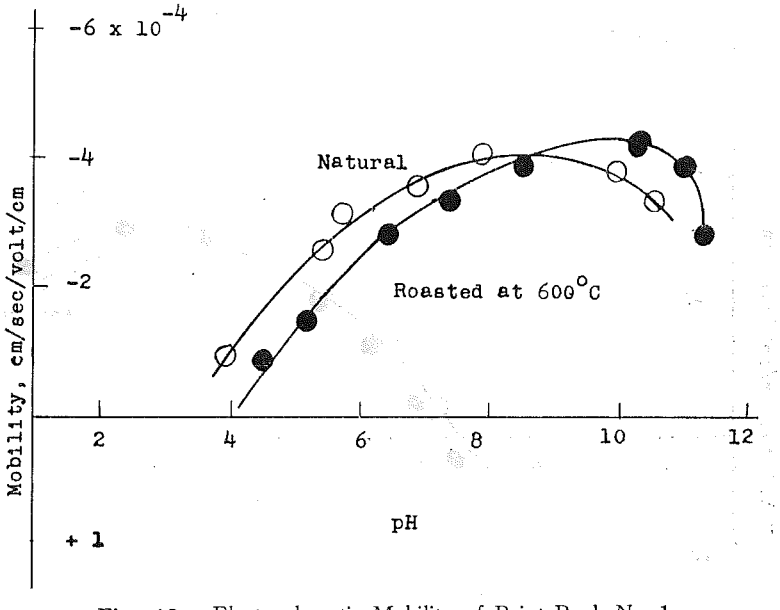


Fig. 13. Electrophoretic Mobility of Paint Rock No. 1

TABLE 4. The Isoelectric Points (IEP) of Kaolinite, three Paint Rocks, and Goethite

Mineral	IEP
Kaolinite	3.0
Goethite	6.7
Paint Rock No. 2	4.5
Paint Rock No. 3	3.5-4.0
Paint Rock No. 4	5.0

Table 4 gives the isoelectric points of kaolinite and Paint Rocks No. 2, 3 and 4 and also the isoelectric point of goethite as determined by Kim[5].

The isoelectric points of paint rocks No. 2, 3 and 4 shown in Table 4 appeared to be similar to and intermediate between, the isoelectric points of kaolinite and goethite. This may be altogether coincidental.

The electrophoretic mobilities of paint rocks No. 2, 3 and 4 in their natural and roasted states are given in Figs. 14, 15 and 16, respectively.

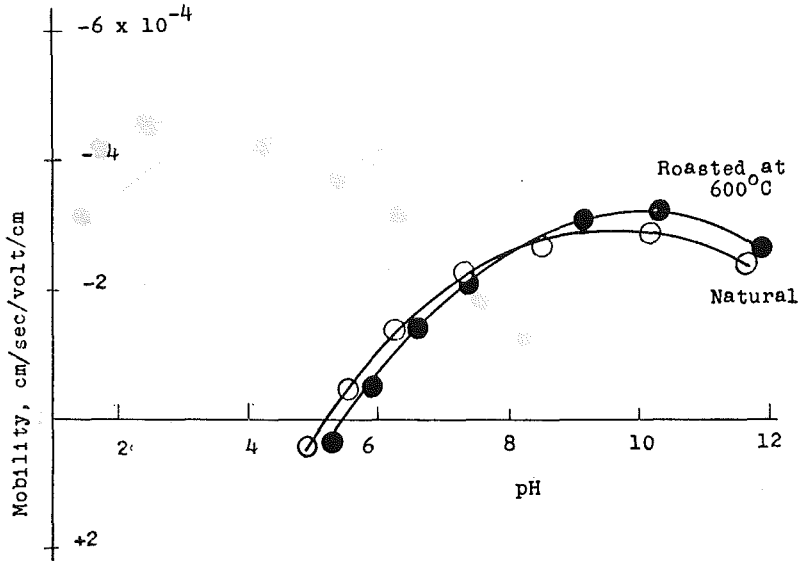


Fig. 14. Electrophoretic Mobility of Paint Rock No. 2

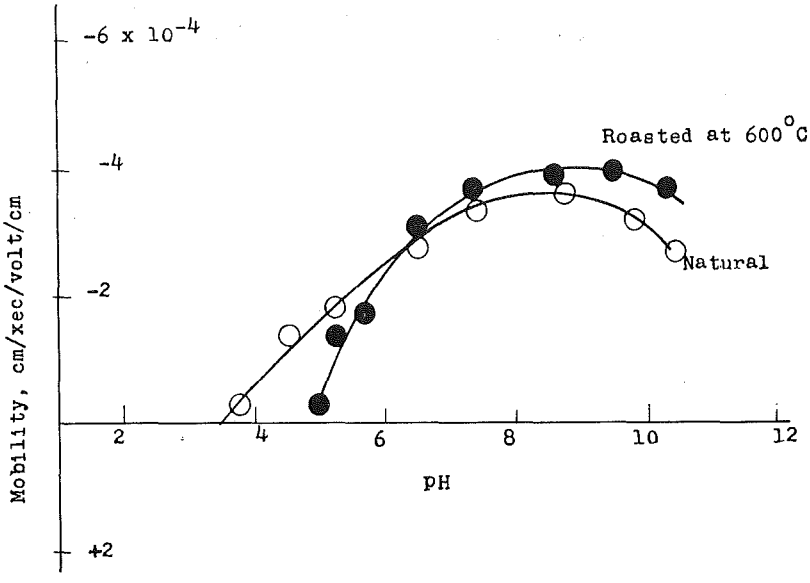


Fig. 15. Electrophoretic Mobility of Paint Rock No. 3

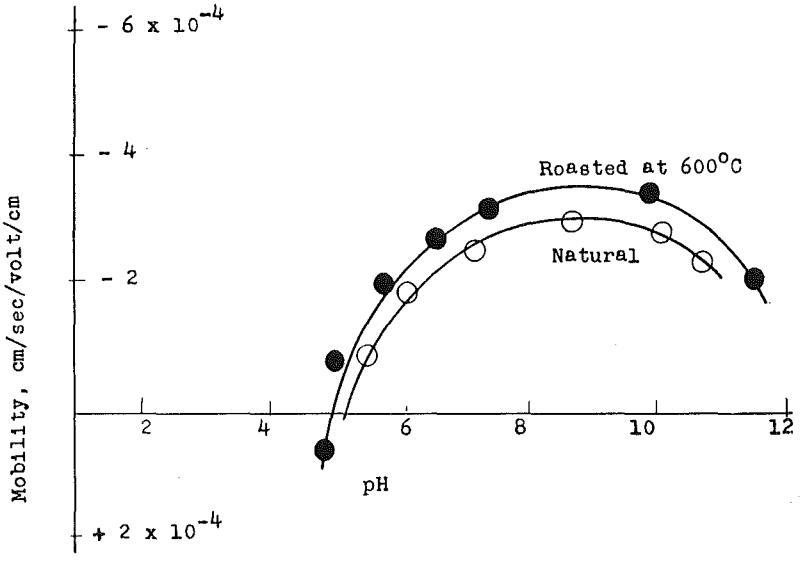


Fig. 16. Electrophoretic Mobility of Paint Rock No. 4

Adsorption Characteristics of Flotation Collectors on Kaolinite and Montmorillonite

(a) Procedure for Measurement of Adsorption

The adsorption characteristics of the clay minerals were measured in terms of moles of the collector adsorbed per gram of the clay. The cationic collectors, dodecylammonium chloride, and the anionic collectors, sodium dodecylsulfate and potassium ethyl xanthate, were used in these experiments.

The experiments were made in a pyrex glass jar of about 500 ml total volume. Normally 300 ml of suspension containing up to 5 g of solid was used in each test. The suspension was agitated by means of a magnetic stirrer. The adsorption of each of the organic electrolytes as a function of concentration was determined by adding known quantities of electrolyte, withdrawing 5 ml samples of the equilibrium solution, centrifuging out the suspended solids and then analyzing colorimetrically for the residual concentration of electrolyte in the solution. For the clay, equilibrium was usually attained in less than two hours. For the cationic collector, the pH range of 3 to 9 was investigated. For the anionic collectors, adsorption was measured at pH 7 or close thereto.

Dodecylammonium chloride in aqueous solution was analyzed colorimetrically by precipitating it as amine picrate, extracting the precipitate with chloroform and then measuring the transmittancy at 510 mμ[4].

Concentrations of sodium dodecylsulfate were determined in a similar manner by precipitating with rosaniline hydrochloride and extracting the precipitate with a 1 : 1 chloroform-ethyl acetate mixture[4]. The transmittancy measurements at 556 mμ showed that Beer's law was applicable up to 10^{-7} moles/liter.

Concentrations of potassium ethyl xanthate were determined without extraction of the aqueous solution and making transmittancy measurements at 301 mμ.

All the collectors used in this investigation, namely dodecylammonium chloride, sodium dodecylsulfate and potassium ethyl xanthate, were of high purity[1]. Demineralized water with an equivalent conductivity of less than 0.1 ppm sodium chloride was used throughout the work.

(b) Experimental Results

The results of adsorption measurements on natural kaolinite using dodecylammonium chloride at pH 9, 5 and 3 are shown in Fig. 17. At a fixed pH the amout of adsorbed dodecylammonium chloride increased with increase in equilibrium concentration of collector in solution. At a constant concentranion, the adsorption of dodecylammonium chloride increases with increase in pH.

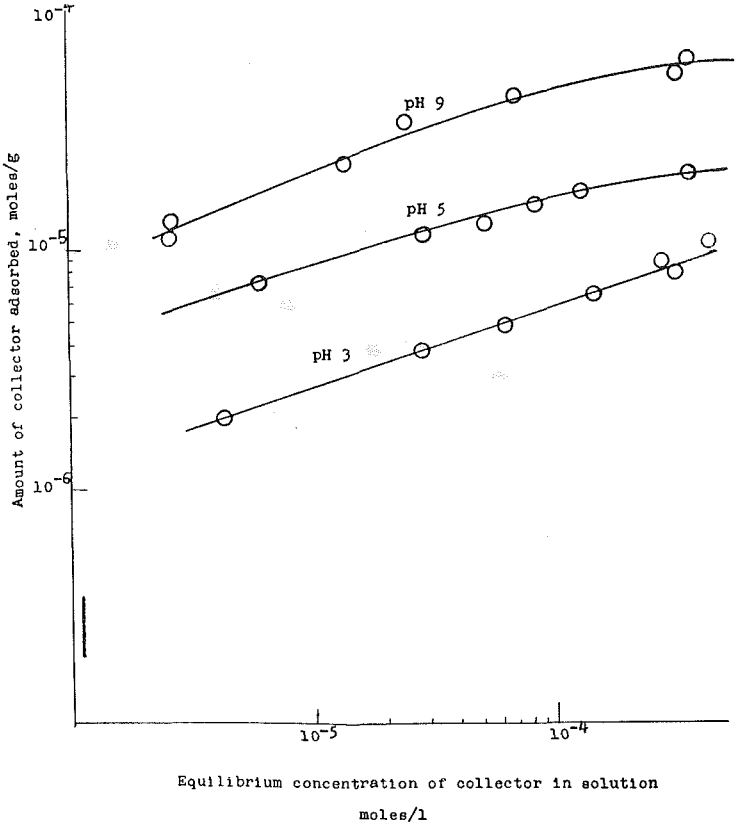


Fig. 17. Adsorption Characteristics of Dodecylammonium Chloride on Natural Kaolinite (China clay) at pH 9, 5 and 3

The saturation capacities of kaolinite for dodecylammonium chloride at pH 9, 5 and 3 are 10^{-4} moles per gram and 3×10^{-5} moles per gram and 2×10^{-5} moles per gram, respectively. Those values, converted to the usual unit in terms of milli-equivalent of adsorbed reagent per 100 grams of clay in dry weight, are respectively 10 meq/100 g, 3 meq/100 g and 2 meq/100 g at pH 9, 5 and 3.

The results of adsorption measurement of dodecylammonium chloride, at pH 5, on kaolinite roasted at 600°C are presented in Fig. 18. This shows the difference of adsorption compared with the corresponding results for the natural specimen at the same pH, as reproduced from Fig. 17.

It is evident that roasting kaolinite decreases the adsorption capacity at identical pH values. The ratio of saturation capacities for natural and roasted kaolinites is about 3 meq/100 g to 1.5 meq/100 g, or 2 to 1. This considerable

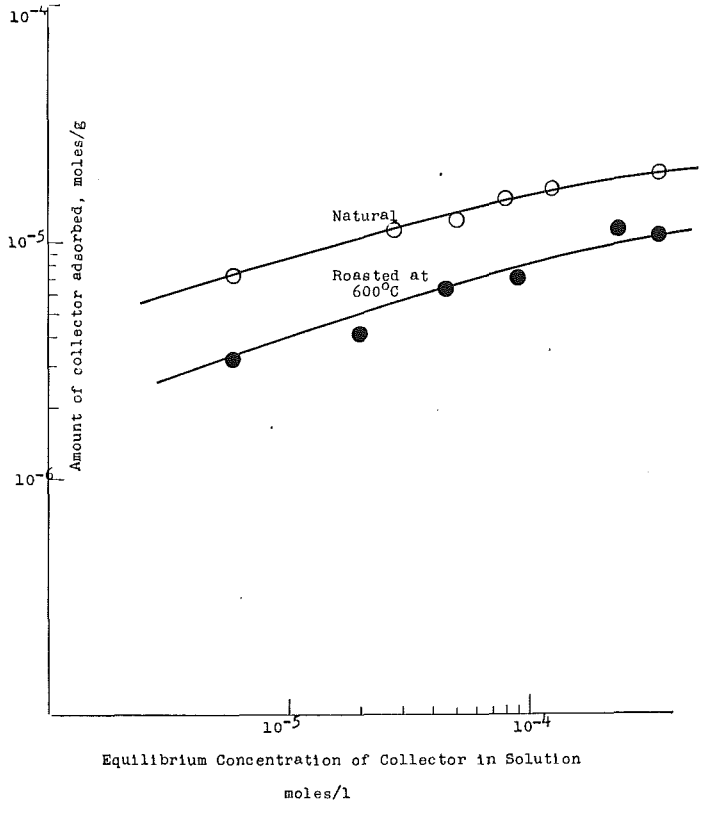


Fig. 18. Adsorption Characteristics of Dodecylammonium Chloride at pH 5 on Kaolinite in the Natural and Roasted States

reduction in adsorption of the collector after roasting may favorably affect flotation of iron ore dy decreasing the detrimental effects of kaolinite.

Fig. 19 shows the result of measurement of adsorption of dodecylammonium chloride at pH 7 and 3 on natural montmorillonite (aqua gel bentonite). At a fixed pH the amount of adsorption increased gradually with increase in equilibrium concentration. In contrast with the behavior of kaolinite, the adsorption of dodecylammonium chloride at a constant concentration, did not materially increase with increase in pH. The saturation capacity of montmorillonite, however, appeared to be extremely high as compared with that of kaolinite, namely about 10^{-3} moles/g. or 100 meq/100 g. The most probable reason for this is that montomorillonite contains constituent and exchangeable cations such as Ca^{++}, Na^{+}, Mg^{++} etc. (Table 1). Grim[2] has stated, with regard to the exchangeable cations of montmorillonite, that Ca^{++} is the most abundant ion in

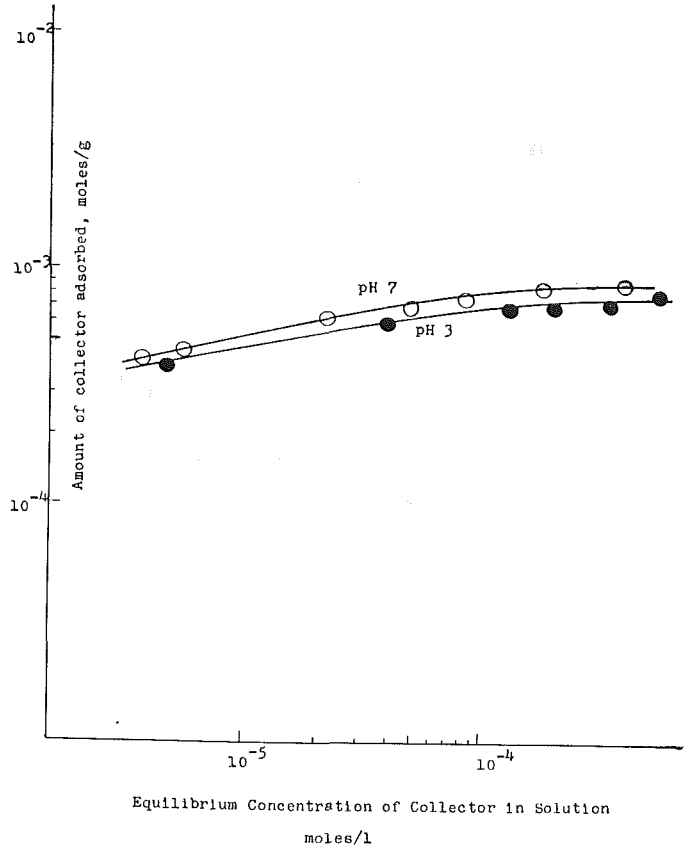


Fig. 19. Adsorption Characteristics of Dodecylammonium chloride on Natural Montmorillonite (aqua gel bentonite) at pH 7 and 3

montmorillonite and that Na^+ is the dominant ion in Wyoming montmorillonite. He also has stated that Mg^{++} is frequently present as an exchangeable ion. The amount of such exchangeable ions in montmorillonite seems to be large enough to permit the exchange adsorption of a cationic collector to such extent that changes in the surface properties, such as electrophoretic mobility, pH etc., became insensible.

Fig. 20 shows the result of measurements of the adsorption of dodecylammonium chloride, at pH 7, on natural montmorillonite, and on the same mineral roasted at 180° and 800°C. Fig. 20 shows that the adsorption capacity of montmorillonite roasted at 180°C is nearly identical with that of the natural mineral, whereas the adsorption capacity of the specimen roasted at 800°C differs markedly and is very much less than for the former. This may suggest that

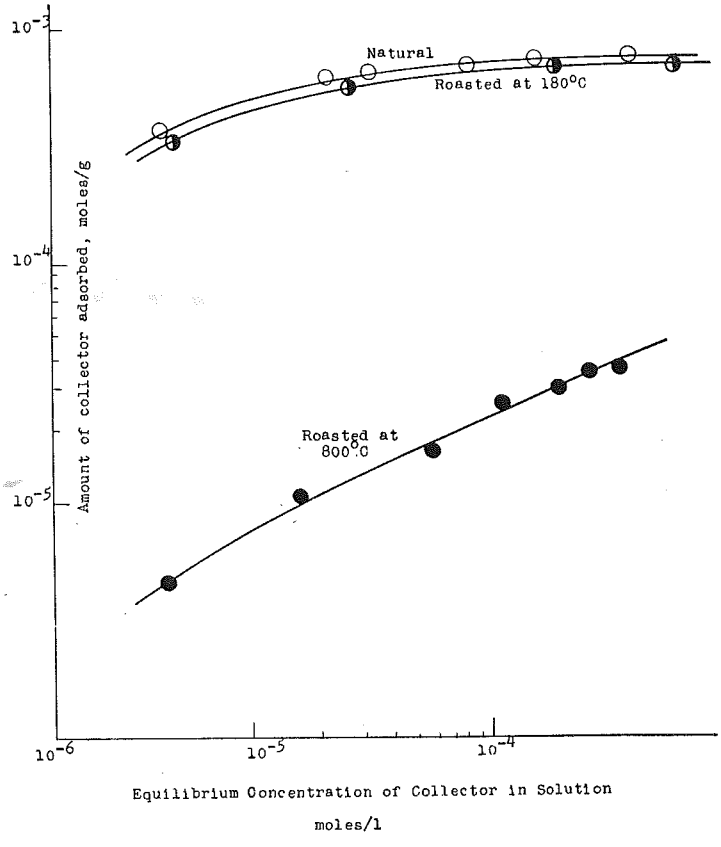


Fig. 20. Adsorption Characteristics of Dodecylammonium Chloride at pH 7 on Montmorillonite in the Natural and Roasted States

the removal of adsorbed water from the mineral body has no influence on the original atomic arrengement and so does not change the adsorption characteristics of this mineral significantly.

An attempt was made to determine the adsorption characteristics of the clay minerals for anionic collectors for comparison with the foregoing results. Potassium ethyl xanthate and sodium dodecylsulfate were used. The results are given in Fig. 21 and show that at a constant equilibrium concentration, the anionic collectors are adsorbed more by kaolinite than by montmorillonite at the same pH, or a reversal of the situation using the cationic collector. A van der Waals type of attraction[16] between the particle and the collectors seems to be responsible for the weak adsorption exhibited.

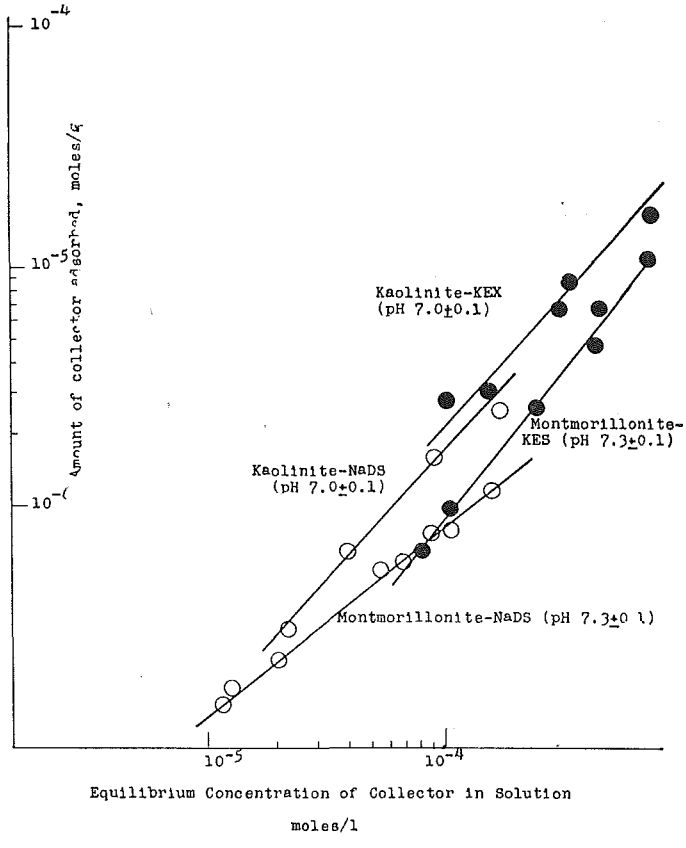


Fig. 21. Adsorption Characteristics of Kaolinite and Montmorillonite for Anionic Collectors, Potassium Ethylxanthate and Sodium Dodecylsulfate

Effect of Roasting Temperature on Surface Area of Clay Minerals and Paint Rock

It was found in an investigation of the adsorption characteristics of kaolinite and montmorillonite with respect to a cationic collecter, that the saturation capacities of these minerals are greatly reduced when the minerals are roasted at temperatures, slightly above the endothermic peak temperatures, or 600°C for kaolinite and 800°C for montmorillonite. Lattice water is removed from both minerals by the heat treatment described.

It was not clear, however, how the adsorption characteristics as modified by roasting were related to the surface exposed to the cationic collctor. An investigation was made of the effect of the roasting temperatures on the specific

surfaces of kaolinite and montmorillonite and of one paint rock from the Mesabi Range. The specific surface was measured by the air permeability method[6].

Kaolinite (China clay) and montmorillonite (aqua gel bentonite), the same materials as those used for measurements of adsorption capacities, were chosen for this investigation. Paint rock No. 4 was arbitrarily chosen from four samples which were rather similar mineralogically and chemically. Each sample was prepared by grinding through 200 mesh and was stored in a bottle.

(a) Apparatus and Procedure

The Swedish-made apparatus used for the measurements of surface area consisted of a permeability cell in which the powder bed was packed, an aspirator by means of which air could be sucked through the bed, a kerosene manometer, which measured the pressure drop across the bed caused by the air flow, and a flowmeter by means of which the volume rate of the air flow through the bed could be measured. The volume flow-rate of the air was measured by means of a stop watch, and and a soap film in a burette. The amount of the powder required for forming a bed 2 to 5 cm thick was weighed out and transferred by a spatula to the cell, which was then placed in the apparatus. The needle valve was opened and adjusted so as to give a pressure drop of about 50 cm in the manometer reading. When equilibrium was reached, the volume flow rate was determined and the manometer reading was taken. A sketch of the apparatus is shown in Fig. 22.

The equation for the calculation consisted of two terms, which were respectively the Kozeny-Carman term[7] and the slip correction term[6]. The equation for the calculation of the specific surface (S) in terms of cm^2 per cm^3 or cm^2 per gram was simplified by the fixed conditions, and the following equation was derived:

$$S^2-188.6\frac{\varepsilon^2}{1-\varepsilon}\alpha^2\cdot S-8.34\times 10^6\frac{\varepsilon^3}{(1-\varepsilon)^2}\alpha^2=0$$

in which ε is a porosity factor and α is the reciprocal value of the flow rate. The simplified equation given above is based upon assumption of the following conditions:

air pressure	760 mm Hg
Temperature	20°C
viscosity of the air	1815.5×10^{-7} poise
cross-sectional area of the cell	9.67 cm^2
specific gravity of the karosene	0.7820 g/cm^3
pressure drop across the bed	about 50 cm manometer reading
constant	$K_0=2.0$, $K_1=2.5$

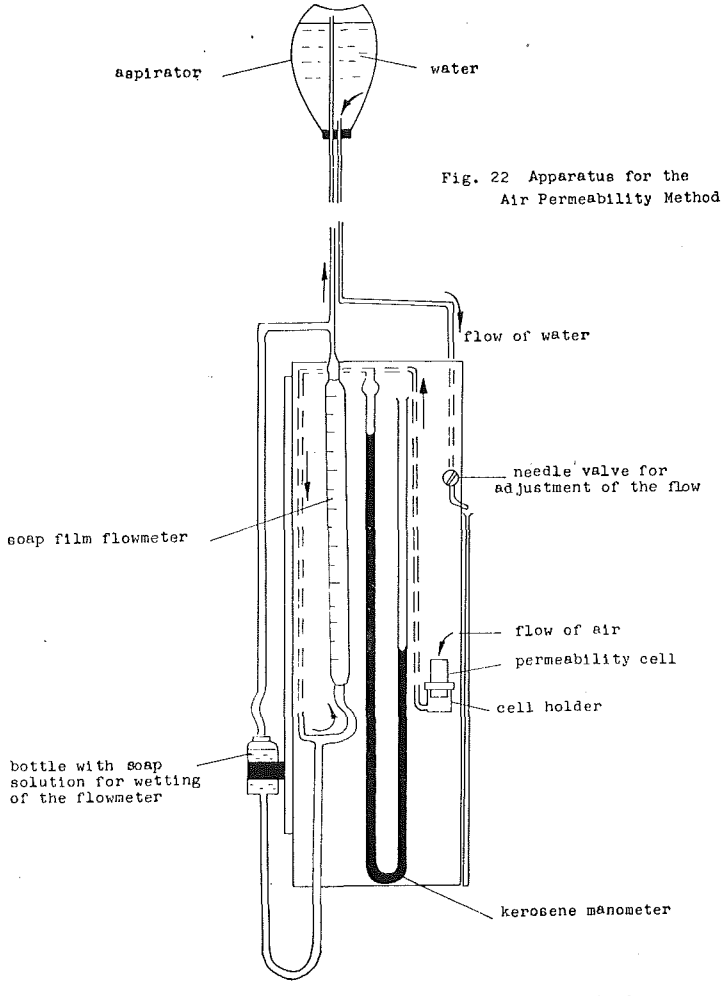


Fig. 22. Apparatus for the Air Permeability Method

Before calculating the specific surface, the true density had to be determined accurately to the second decimal place. This was done by using a 10 ml pycnometer with benzene as a liquid. The specific gravity of the benzene was previously determined as a function of the temperature.

The porosity, ε was obtained from the following equation:

$$\varepsilon = \frac{\text{vol. of void}}{\text{vol. of total}} = 1 - \frac{W}{AL\rho}$$

in which W=wt of the sample; ρ=the density of the sample; and A= the

cross sectional area of the cell ($=9.67\ cm^2$).

The reciprocal value of the flow rate of the air, α, was obtained from the following equation:

$$\alpha = \sqrt{\frac{h}{Q \cdot L}}$$

in which $h=$ the pressure difference across the bed in cm manometer reading, and $Q=$ the volume rate of the flow through the bed in cm^3/sec as measured with the flowmeter.

With compact beds of very fine powders the size of the voids becomes small in comparison with the mean free path of the gas.

It has long been known that when this condition prevails in capillary tubes, the rate of gas flow is greater than that given by Poiseuille's law. The effect is regarded as a "slip" at the capillary wall.

When permeability measurements of specific surface were corrected for slip, Carman[7] and Halherbe (1950–51) obtained fairly satisfactory results in comparison with the gas adsorption method. Zavaritskaya and Grigorov (1953) found agreement in results obtained by permeametry and by direct microscopy for relatively uniform polystyrene beads within the size limits of 10 to 15, 15 to 20 and 40 to 60 μ.

(b) Experimental Results and Discussion

(1) The Effect of Roasting Temperature on Specific Surface

The following procedure was followed for each of the three samples:

Approximately 100 gm of each sample was weighed out and its specific surface was determined by the air permeabillity method.

The sample was then heated in air to 200°C for 60 minutes. A two-gram sample was taken for specific gravity determination, and the specific surface was again measured. This same procedure was repeated at 400°C, 500°C, 600°C, 700°C and 800°C. The reasons for following the procedure given were (a) to eliminate any sampling error resulting from the use of fresh samples, and (b) to minimize change-of-shape factors. All surface area measurements were repeated twice, and the average specific surface computed. The specific surface of kaolinite in cm^2/g is given in Fig. 23 as a function of the roasting temperature. The specific surface of the natural kaolinite was 24,500 cm^2/g, a value which naturally varies with particle-size distribution, particle shape, and the presence of cracks and pores in the sample. Fig. 23 shows that a sharp drop in the specific surface continues until 500°C is reached. Above this temperature the curve flattens out until 600°C is reached, but becomes steeper between 600° and 800°C. Since 600°C corresponds to the second endothermic point for

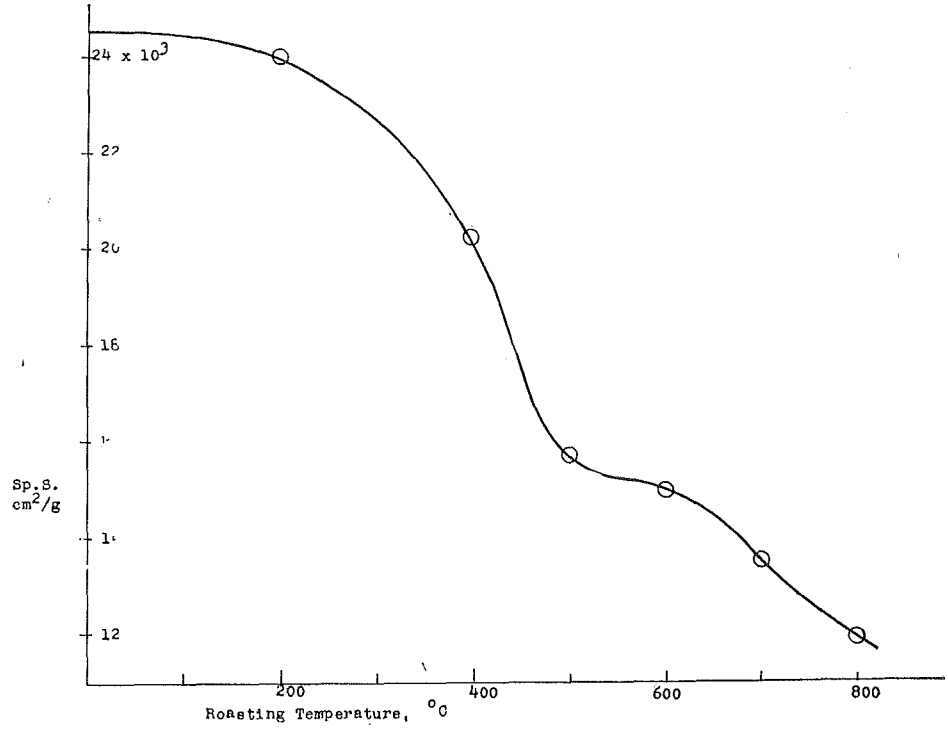


Fig. 23. The Specific Surface of Kaolinite as a Function of the Roasting Temp.

kaolinite, the apparent reduction of the specific surface which resulted from roasting seems to be associated with the loss of the water molecules.

Fig. 24 shows the specific surface of montmorillonite as a function of the roasting temperature. Upon heating, a sharp drop in the specific surface continus until 500°C is reached.

Above this temperature the curve flattens until 700°C is reached, and then steepens between 700° and 800°C. Since the second endothermic point for montmorellonite occurs at 715°C, the apparent reduction of the specific surface at this point is probably associated with the loss of the chemically combined water from the material. Comparison of Figs. 23 and 24 shows that the general slope of the curve for kaolinite is much steeper than for montmorillonite.

In the case of the paint rock (Fig. 25), the general slope is flater than for either montmorillonite or kaolinite, due probably to the existence of the iron oxide, which seems to stabilize the specific surface of the paint rock against the change of temperature.

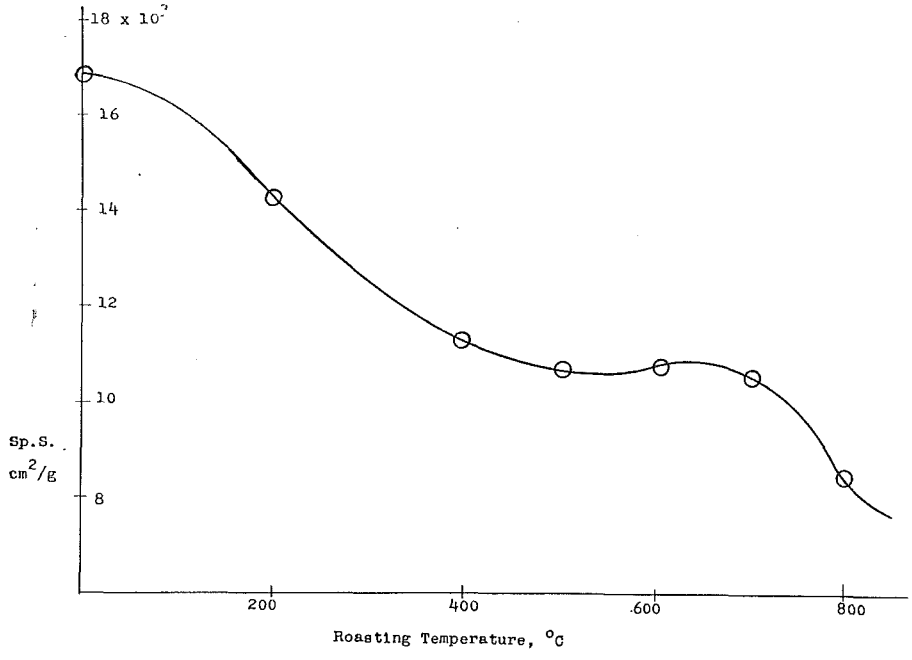


Fig. 24. The specific Surface (Sp. S.) of Montmorillonite as a Function of the Roasting Temperature

As the roasting temperature is increased, changes both in "feel" and colour of the sample are very obvious:

(1) The initial soapy (or smooth) feel changes to a sandy (or gritty) feel.

(2) The observed colour changes for the three samples are as follows;

Kaolinite, light yellow ⟶ yellow
Montmorillonite, greyish white ⟶ light pink
Paint Rock, brown ⟶ dark brown.

The colour changes of kaolinite and montmorillonite can be attributed to the oxidation of ferrous iron. That of the paint rock is undoubtedly due to the conversion of the goethite to hematite.

(2) Effect of Roasting Temperature on Specific Gravity

The specific gravities of the three samples in both the natural and roasted conditions were measured. The results given in Table 5 are the averages of three independent determinations for each material and for each roasting temperature.

It should be noted that the specific gravity attained a maximum at certain temperatures and thereafter decreased gradually. The temperatures for the

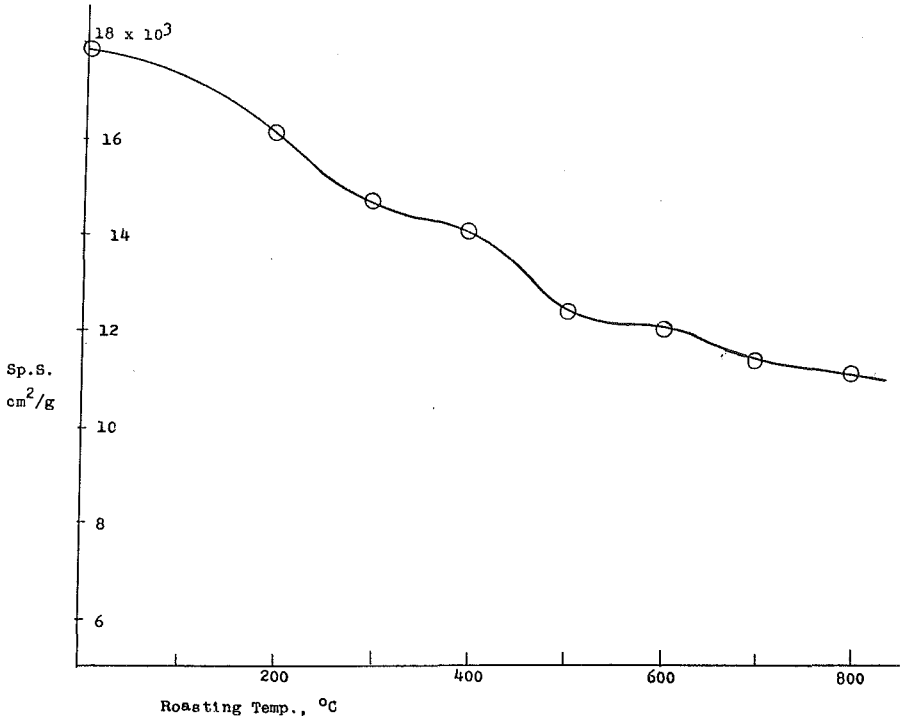


Fig. 25. The Specific Surface of Paint Rock as a function of the Roasting Temperature

maximum specific gravity of kaolinite, montmorillonite and paint rock are 500°, 600° and 500°C respectively, and there is a rather broad agreement with the results obtained with the DTA and TBA works.

TABLE 5. Change in Specific Gravity with Roast. Temp.

Mineral	Temperatures Roasted, °C							
	natural	200	300	400	500	600	700	800
Kaolinite	2.59	2.61	nd	2.62	2.67	2.54	2.53	2.53
Montmorillonite	2.52	2.65	nd	2.67	2.80	2.82	2.56	2.54
Paint Rock	3.10	3.27	3.32	3.34	3.46	3.45	3.39	3.29

The removal of the lattice water during roasting causes changes both in the mass and in the volume of the specimen. The change in specific gravity is not a linear function of temperature. The rate of change in specific gravity appears to greatest at temperatures corresponding roughly to the endothermic

peaks of the minerals involved. After the endothermic peak temperatures are exceeded there seems to be a general decrease in specific gravity in each case. This may be due to loosening of the crystal structure due to loss of lattice water.

Flotation Characteristics of Clay Minerals and Paint Rock from the Mesabi Range

(a) Experimental Apparatus and Procedure

The Hallimond[8] tube flotation unit, originally designed by Hallimond and modified by Fuerstenau et. al.[9] and later by Kim[5], was employed for the present experiments. Not only is this method quite simple and rapid, but it also permits close control of operating conditions and yields highly reproducible results.

In the present experiments, the lower part of the Hallimond tube was modified by replacing the stirring mechanism with a vibrating mechanism in order to eliminate a magnetic effect on the sample. The modified Hallimond tube flotation system is schematically shown in Fig. 26. Part (A) is fixed by

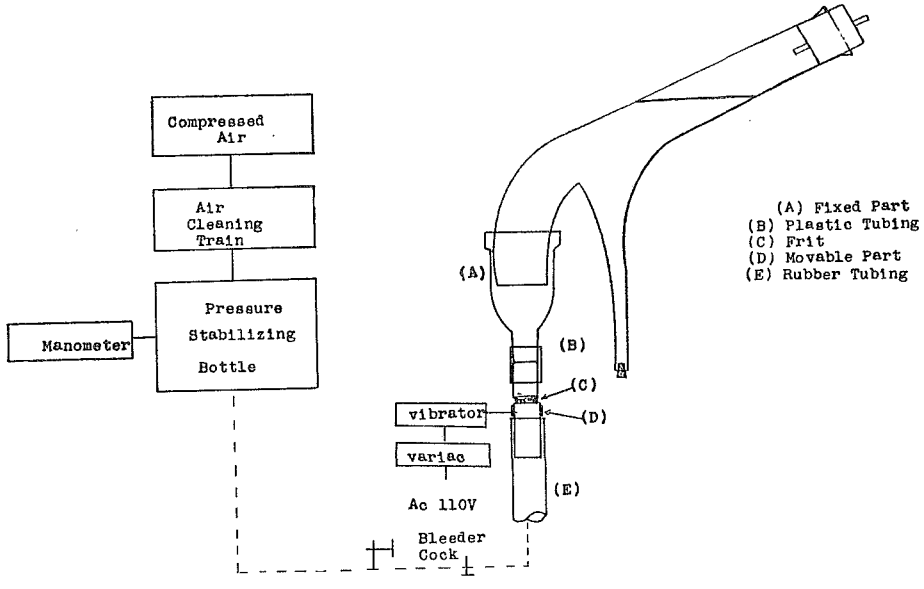


Fig. 26. Hallimond Tube Flotation Unit

means of a clamp and holds the entire upper part of the Hallimond tube. The lower end of part (A) is connected with part (D) by a short length of rubber tubing (B) so that part (D) can be readily vibrated. Part (D) has a coarse-pored, fritted glass disk for gas introduction.

The air used for aeration was filtered through a column of glass wool to

remove any greasy material, then passed through a 30 pct potassium hydroxide solution to remove carbon dioxide, and finally washed by bubbling through water. The cleaned air then flowed into a 20-liter pressure stabilizing bottle which was connected to a water manometer. The air finally passed through the flotation cell and was released to the atmosphere.

The procedure for the Hallimond tube tests was standardized by determining the optimum amount of vibration, flow rate, and flotation time. After a series of preliminary tests the optimum flotation time was standardized at 3 minutes for 0.5 grams sample at a gas flow rate of 20 ml per minute.

A sample of 150/200 mesh material weighing about 0.5 grams was transferred from a storage bottle to a 100 ml test tube and filled with a prepared solution of collector. The test tube was sealed carefully to avoid entrapment of gas bubbles and then rotated 60 minutes at a speed of 100 rpm to condition the sample. After conditioning, the sample and solution were transferred to the Hallimond tube and the pH of the solution was measured. At the conclusion of a test, the flow of air was stopped, both float and nonfloat products were collected, dried, and weighed in order to calculate the recovery.

(b) Experimental Results

The percent recovery of the sample as a function of pH was obtained under various flotation conditions. To find the effect of roasting on the floatability, both the natural and the roasted specimens were tested and compared. The concentration of the collector, as well as the type of collector used, was an important factor in the investigation of the flotation characteristics.

(1) Effect of Roasting

Fig. 27 shows the percent recoveries of natural and roasted montmorillonite as a function of pH when using 10^{-3} m/l of dodecylammonium chloride. It is clearly shown that natural montmorillonite is essentially nonfloatable through the entire pH range, whereas roasted montmorillonite is quite floatable. The flotation characteristics of roasted montmorillonite appears to be strongly controlled by pH. In the pH range 4 to 10, recoveries of over 90 pct of the roasted montmorillonite are obtained. Below pH 3 the recovery decreases rapidly until only 20 pct is recovered at pH 1. This is in accord with the isoelectric point of about pH 2.5 for the material. This means that, below the isoelectoric point for roasted montmorillonite, the positively charged surface of the material tends to repel electrically the cationic collector, to reduce rapidly the flotation recovery. Above pH 10 the recovery again decreases rapidly to a recovery of zero at pH 12 due to the precipitation of free amine.

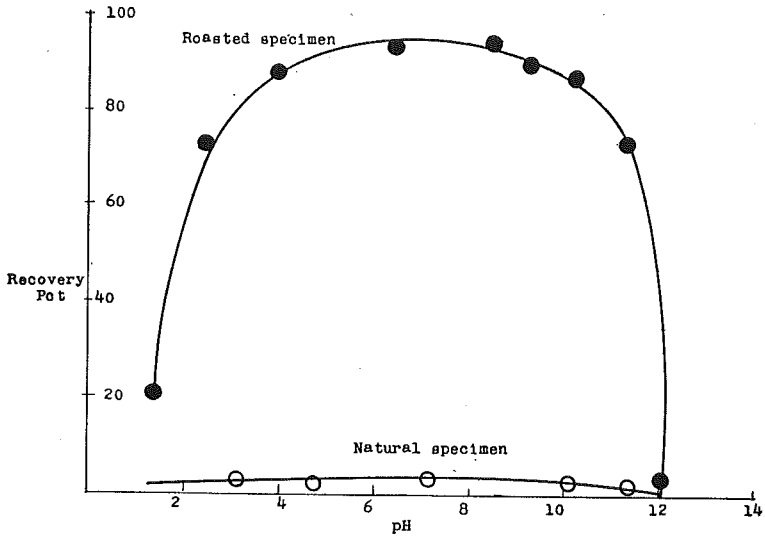


Fig. 27. Flotation of Montmorillonite with 10^{-3} m/l of DACl

Fig. 28 shows the percent recoveries of natural and roasted kaolinite as a function of pH when using 10^{-3} m/l of dodecylammonium chloride. It shows that high recoveries of natural kaolinite are obtained in the pH range from 2 to 6. Above pH 6 the recovery decreases gradually to zero at pH 12. High recoveries of roasted kaolinite are obtained through the entire pH range until

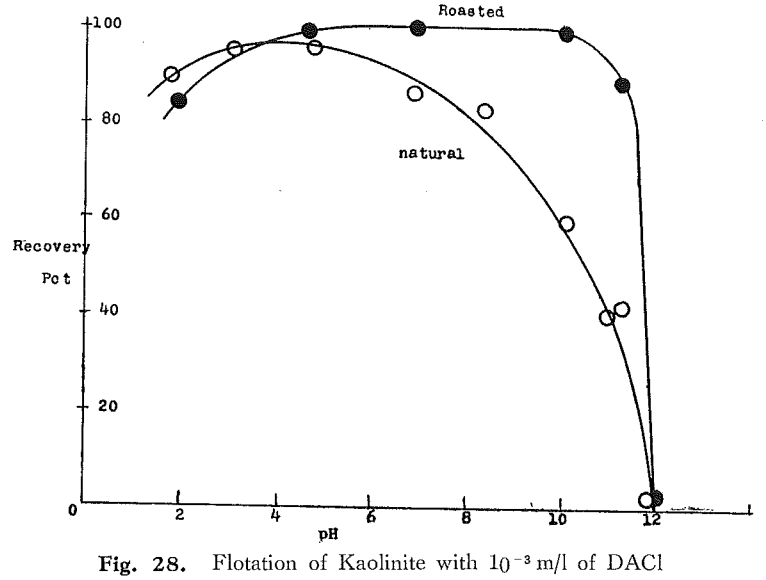


Fig. 28. Flotation of Kaolinite with 10^{-3} m/l of DACl

free amine precipitates at pH 12.

Fig. 29 shows the percent recoveries of a paint rock (Paint Rock No. 2) in the natural and the roasted states as a function of pH when using 10^{-3} m/l of dodecylammonium chloride. About 90 pct of natural paint rock is recovered in the pH range 5 to 9, but the recovery decreases rapidly above pH 10 to about zero at pH 12. The recovery also sharply decreases below pH 5 to about 20 pct at pH 2. Below pH 5, the isoelectric point of the paint rock, the repulsion of the cationic collector by the positively charged surface may be

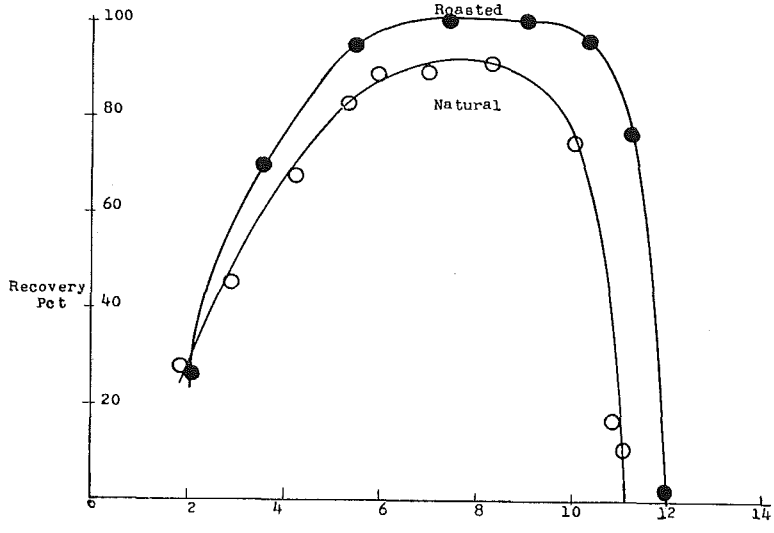


Fig. 29. Flotation of Paint Rock with 10^{-3} m/l of DACl

responsible for the sharp reduction in recovery which was observed. About 100 pct of roasted paint rock is recovered in the pH range 6 to 10, ie. no selectivity is exhibited. The recovery decreases below pH 6 and above pH 10.

(2) Effect of concentration of collectors

About 0.5 grams of natural kaolinite and natural paint rock were tested in the Hallimond tube at different pH values and using various concentrations of collectors.

Fig. 30 shows the percent recoveries of natural kaolinite (China clay) as a function of pH when using 10^{-3}, 10^{-4}, and 10^{-5} m/l of dodecylammonium chloride. With 10^{-3} m/l of the collector the recovery decreases rapidly with increase in pH, from 77 pct at pH 9 to zero at pH 12. When the collector concentration is decreased to 10^{-4} m/l, maximum recoveries occur in the pH range 3 to 6, then the recovery decreases rapidly with increase in pH to about

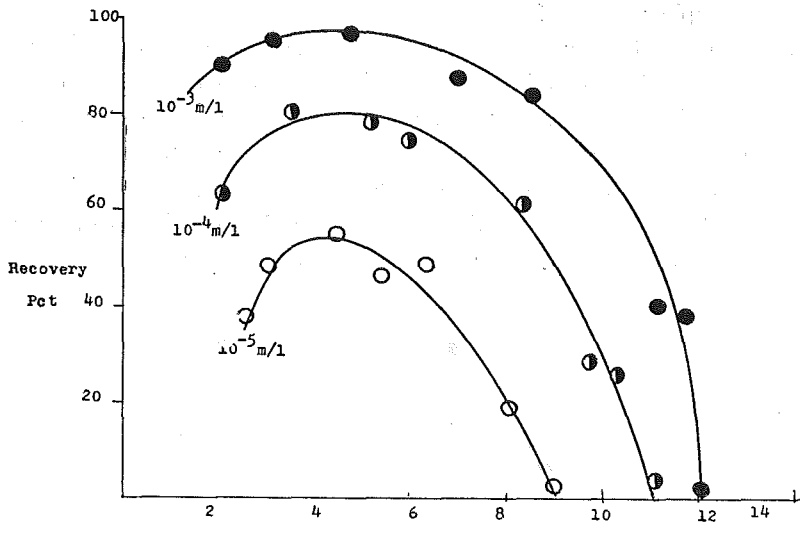


Fig. 30. Flotation of Kaolinite at Different Concentration of DACl

zero at pH 11. When the concentration is further decreased to 10^{-5} m/l, a maximum recovery of about 55 pct is obtained in the pH range 4 to 5 and then decreases very rapidly with increase in pH to about zero at pH 9.

Fig. 31 shows the percent recoveries of natural paint rock as a function of pH when using 10^{-3} and 10^{-4} m/l of dodecylammonium chloride. With

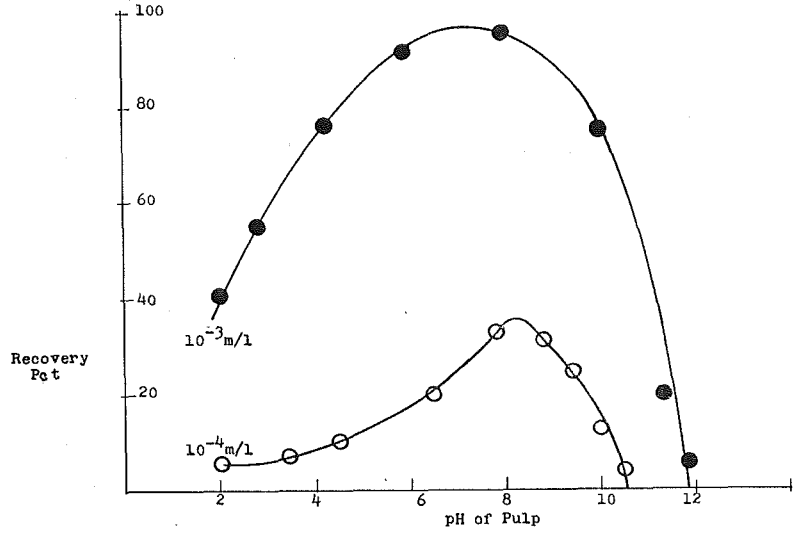


Fig. 31. Flotation of Paint Rock at Different Concentrations of DACl

10^{-3} m/l of the collector, the recovery sharply increases with increase in pH from 40 pct at pH 2 to nearly 100 pct at pH 7. Above pH 7 the recovery decreases rapidly to zero at pH 12. With 10^{-4} m/l of the collector, a maximum recovery is about 35 pct at pH 8.

Fig. 32 shows the percent recoveries of natural paint rock as a function of pH when using 10^{-2} and 10^{-3} m/l of oleic acid, an anionic collector. With 10^{-2} m/l of oleic acid, maximum recoveries of about 60 pct are obtained in the pH range 4 to 8. With 10^{-3} m/l of the collector, maximum recoveries of about 40 pct are obtained in the pH range 6 to 8.

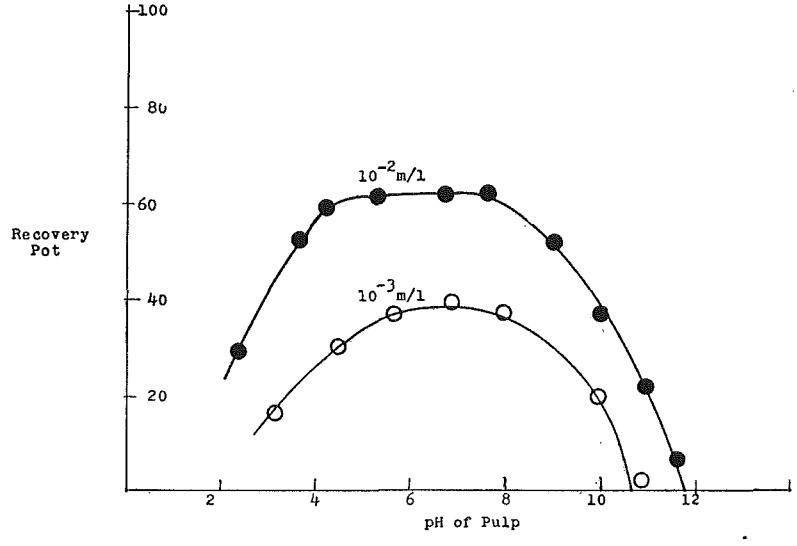


Fig. 32. Flotation of Paint Rock at Different Concentrations of Sodium Oleate

Discussion of Experimental Results

The Adsorption of Dodecylammonium Chloride on Kaolinite and the Ion Exchange Theory

The structure of kaolinite[10] is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedrons and one of the layers of the octahedral sheets form a common layer. Fig. 33 shows a diagrammatic sketch of this mineral. The charge distribution in the unit layers is as follows:

$60^{=}$	12^{-}	
$4Si^{4+}$	$16+$	
$40^{=}+2(OH)^{-}$	10^{-}	(Layer common to tetrahedral and octahedral sheets)
$4Al^{3+}$	$12+$	
$6(OH)^{-}$	6^{-}	

The net charges within the structural unit are balanced. The layers are continuous in the *a* and *b* directions, and are stacked one above another in the *c* direction.

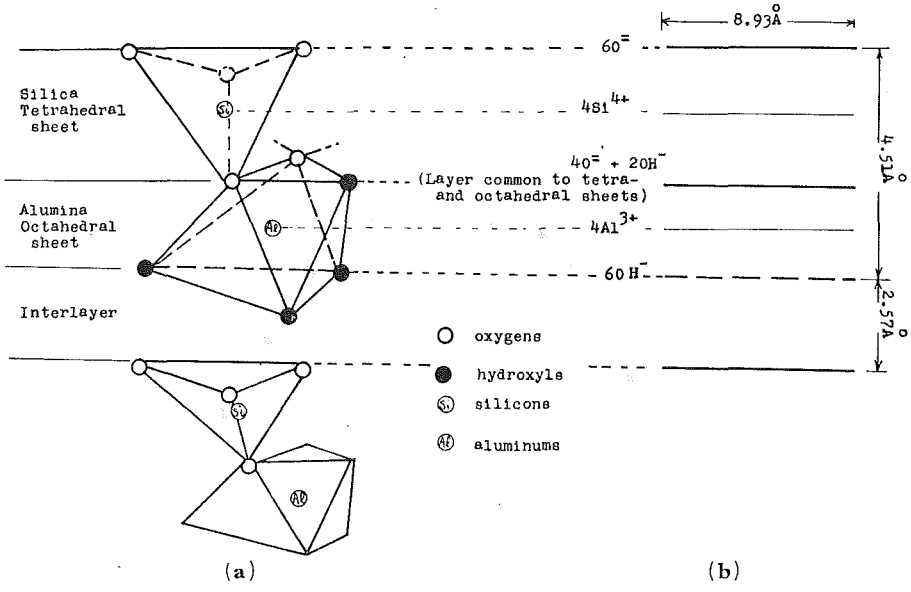


Fig. 33. Diagrammatic Sketch of the Structure of the Kaolinite Layer
(a) Diagrammatic Sketch of the Kaolinite Structure after Grumer[10]
(b) Arrangement of layers, after Bates et. al.[11]

When the mineral particles of kaolinite are dispersed in water and an ionic equilibrium is reached, it is observed that the particles migrate under the influence of an electric field. This migration of the mineral implies the existence of an electric charge at the mineral-solution interface. The ionic equilibrium reactions between the mineral and the solution can be expressed by the following equations:

For the oxygen ions in the silica tetrahedral sheet (Fig. 33 (a)),

$$O^{=}\ (\text{mineral}) + H_2O \rightleftharpoons 2OH^{-}\ (\text{solution})$$

and for the hydroxyl ions in the alumina octahedral sheet

$$OH^- \text{ (mineral)} \rightleftharpoons OH^- \text{ (solution)}.$$

In both equations, an increase in hydroxyl ion concentration of the solution should drive the reaction toward the left, making the mineral surface more negative. Thus the mineral surface relative to the solution will be influenced by the concentration of hydroxyl ions, and accordingly also by hydrogen ions. These ions are generally called the potential determining ions[12]. Electrophoretic measurements made on kaolinite in water (Fig. 11) has verified that the above-mentioned ions are the potential determining ions. Above pH 3.3 (the isoelectric point of kaolinite), the surface of the mineral is charged negatively by the potential determining ions (OH^-) and is adjacent to the counter ions (H^+) in a plane called the Stern plane, to form an electrical double layer at the mineral-solution interface. When a cationic collector, for example, dodecylammonium chioride, is added, the amine ions replace the hydrogen ions at the surface of the kaolinite, a process known as exchange adsorption. If the assumption is made that there is a stoichiometric ion exchange detween H^+ and RNH_3^+ at the surface of kaolinite, the following equation may be proposed;

$$\overline{M-}|-H^+ + RNH_3^+ \rightleftharpoons \overline{M-}|-RNH_3^+ + H^+ \qquad (2)$$

in which $\overline{M-}|-$ is the site of exchange on the mineral and RNH_3^+ the dodecyl-ammonium ion. In equation (2), the reaction is driven to the left with increase in (H^+), or decrease in pH. In other words, the adsorption density of dodecyl-ammonium ion decreases with decrease in pH. This is clearly shown in Fig. 34, derived from Fig. 17, in which is plotted, as a function of pH, the adsorption of the amine ion in terms of moles per cm^2 at each constant concentration of the collector in solution. For the calculation of the adsorption density, the measured specific surface of the kaolinite was used (24.5×10^3 cm^2/g). If the further assumption is made that the activities of the reacting ionic species at the surface and in the solution are equal to their respective concentration, the equilibrium constant (K) of Eq. (2) becomes;

$$K = \frac{\overline{|RNH_3^+}}{\overline{|H^+}} \times \frac{(H^+)}{(RNH_3^+)} \qquad (3)$$

in which $\overline{|RNH_3^+}$ and $\overline{|H^+}$ are the adsorption densities of the amine and hydrogen ions, respectively, and (RNH_3^+) and (H^+) are the concentrations of the respective ionic species. If $\overline{|_0}$ is the total exchange capacity, Eq. (3) may be rewritten to

$$\frac{(RNH_3^+)}{(H^+)} = \frac{\overline{|RNH_3^+}}{K \cdot \overline{|H^+}} = \frac{\overline{|RNH_3^+}}{K(\overline{|_0} - \overline{|RNH_3^+})} \qquad (4)$$

If $\overline{|RNH_3^+}$ is small compared to $\overline{|_0}$, Eq. (4) can be rewritten to

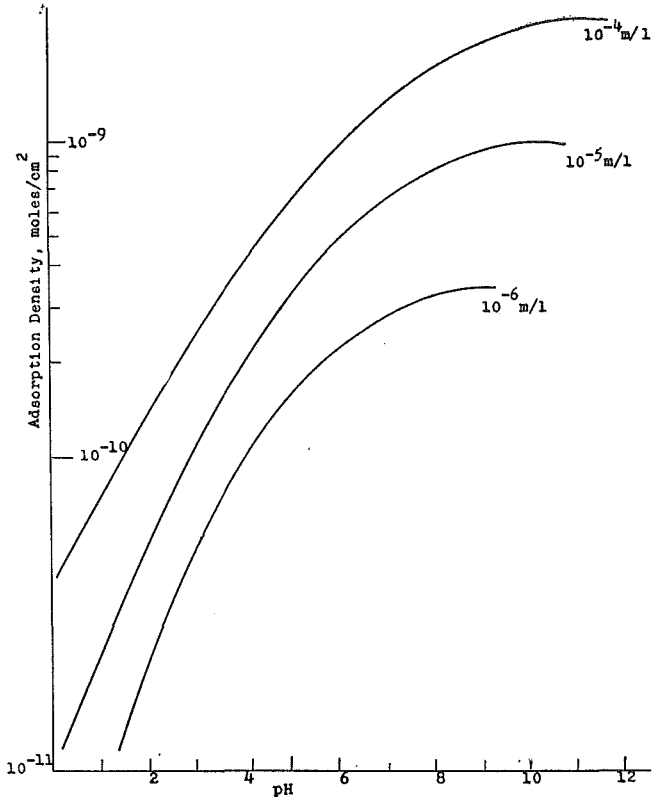


Fig. 34. Adsorption Density of Dodecylammonium Chloride (DACl) at Different Concentration of DACl in the Pulp as a Function of pH

$$\overline{|RNH_3^+} \fallingdotseq K \overline{|_0} \frac{(RNH_3^+)}{(H^+)} = K^1 \frac{(RNH_3^+)}{(H^+)} \qquad (5)$$

Taking logarithms of both sides of Eq. (5,)

$$\log \overline{|RNH_3^+} = \log \frac{(RNH_3^+)}{(H^+)} + \log K^1 \qquad (6)$$

If $\log \overline{|RNH_3^+}$ is plotted against the log ratio of $\frac{(RNH_3^+)}{(H^+)}$, a straight line with a slope of 45° degree can be expected. Fig. 35 shows the resulte of the experimental data so plotted.

Fig. 35 shows that at a low $\frac{(RNH_3^+)}{(H^+)}$ ratio, $\overline{|RNH_3^+}$ is a linear function of that ratio and is independent of the ion concentration. As shown by the

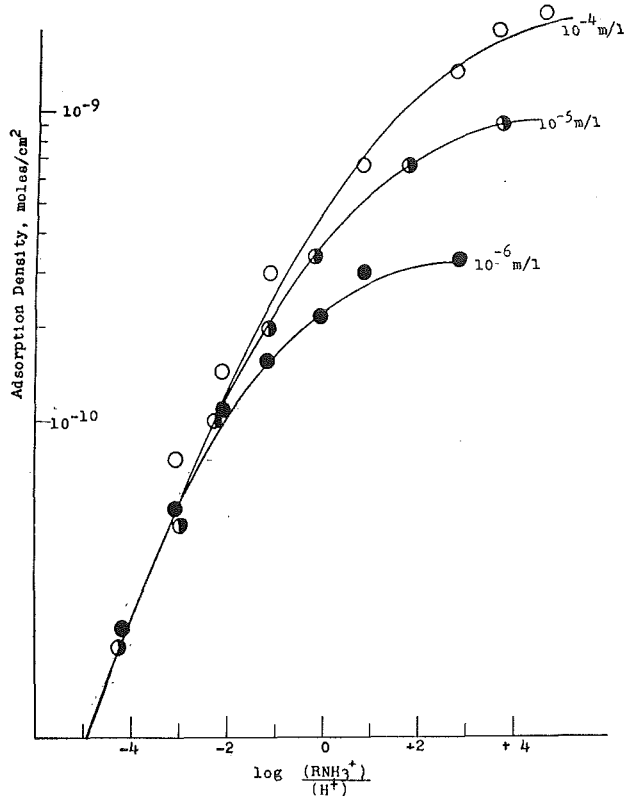


Fig. 35. Adsorption Density of Dodecylammonium Chloride as a Function of the Ratio of Amine and Hydrogen Ion Concentration

divergence of the curve in the upper part of Fig. 35 this is not true at high $\frac{(RNH_3^+)}{(H^+)}$ ratios. This means that at low $\frac{(RNH_3^+)}{(H^+)}$ ratios, amine and hydrogen ions are competitive at the adsorption sites, but this is not true when the ratio is large.

It is noteworthy that the calculated slope of the linear portion of the curve is about 0.4, ie, $\overline{|RNH_3^+}$ varies as $\left(\frac{(RNH_3^+)}{(H^+)}\right)^{0.4}$ instead of as the first power. Accordingly, either the assumption regarding the value of the activity coefficients is not reasonable, or the competitive ion exchange mechanism is not as simple as here assumed. A similar conclusion has been reported[13] from an investigation of the adsorption of ethyl xanthate on pyrite, in which the slope of the curve expressing the competition of xanthate and hydroxyl ions has been determined

to be 0.4.

It is concluded from the preceding work that the adsorption of the amine takes place on the surface of natural kaolinite by replacing the hydrogen ions initiating the formation of the electrical double layer at the mineral-solution interface. The replacement, or the exchange between the hydrogen ions and the organic cations, is competitive at the adsorption site at low ratios of $\frac{(RNH_3^+)}{(H^+)}$, but is not stoichiometric, if the activities on the reacting ionic species are assumed to be equal. At high ratios of $\frac{(RNH^+)}{(H^+)}$, the adsorption depends on the amine ion concentration in the solution, i.e., the higher the amine concentration, the greater is the adsorption.

The ion exchange theory, the most widely accepted theory of adsoption, is, therefore, not definitely applicable in this case.

Flotation Characteristics of Roasted Montmorillonite

According to Maegdefran and Hofman[14], natural montmorillonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The layers are continuous in the *a* and *b* directions, and are stacked one above another in the *c* direction.

Fig. 36 is a diagrammatic sketch of the structure of montmorillonite.

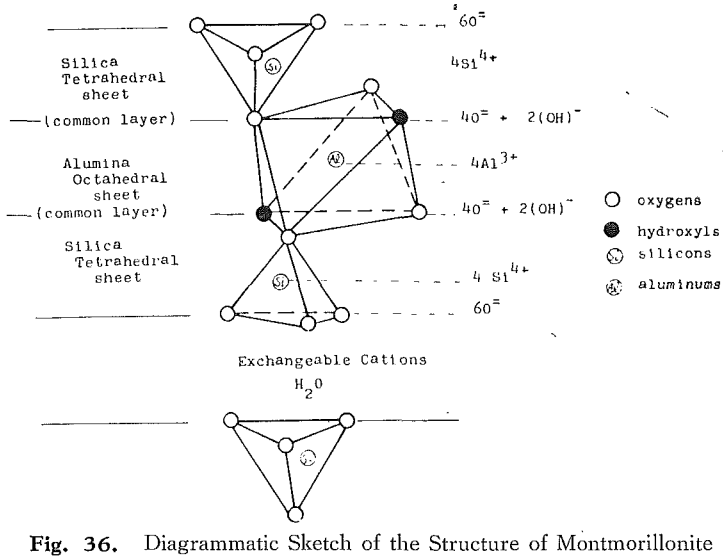


Fig. 36. Diagrammatic Sketch of the Structure of Montmorillonite

The theoretical charge distribution, without considering lattice substitutions within the layer, is as follows:

$60^{=}$	12^{-}	
$4Si^{4+}$	$6+$	
$40^{=}+2(OH)^{+}$	10^{-}	(Layer common to tetrahedral and octahedral sheets)
$4Al^{3+}$	$12+$	
$40^{=}+2(OH)^{-}$	10^{-}	(Layer common to tetrahedral and octahedral sheets)
$4Si^{4+}$	$16+$	
$60^{=}$	12^{-}	

Thus the net charges within the layer are balanced. However, montmorillonite always differs from the theoretical formula because of unbalancing by the substitutions, such as Mg^{++} for Al^{3+}, Al^{3+} for Si^{4+}, etc. The unbalancing may result from substitution of ions of different valence in the tetrahedral and/or octahedral sheets. It is significant that the substitutions in the montmorillonite lattice, with the internal compensating substitutions, always result in about the same net charge on the lattice. This net-charge deficiency is balanced by exchangeable cations adsorbed between the unit layers and around their edges. Grim[2] states that the outstanding feature of the montmorillonite structure is that water and other polar substances (such as amine salt) can enter between the unit layers, causing the lattice to expand in the *c* direction.

According to Conley[15], a Wyoming bentonite swells in water until it occupies about 18 times the actual volume of the bentonite dried at 105°C and having an average specific gravity of 2.75.

Hendricks[16] has indicated that introduced organic substances occur as ions and are held by van der Waals forces in addition to the coulombic forces. He found that the organic ions he studied were so oriented between the montmorillonite layers that minimum expansion occurred. Thus, flat-shaped ions were found to lie with their flat surfaces parallel to the besal surface of the montmorillonite plate. Jordan[17] has shown that for some organic ions more than one molecular layer may be adsorbed on the basal surfaces of the montmorillonite planes by an accompanying shift in the *c*-axis spacing of the unit layers. He determined the *c*-axis spacing of Wyoming montmorillonite when treated with aliphatic amines of increasing chain lengths. His results, shown in Fig, 37 (a), indicate that when the amine chain contains more than 12 carbon atoms, the amount of separation of the montmorillonite plates approaches 8 Å, which is the thicknese of two such hydrocarbon chains. Bradley, Grim, and MacEwan[18] suggest that the polar molecules are also held to the clay surface

through a C–H·····O (clay-mineral surface) bond in addition to the two forces mentioned above. MacEwan has explained multiple-layer adsorption by montmorillonite as follows: Each of the surfaces of the montmorillonite sheets is formed by a layer of oxygen ions (Fig. 36), and thus they behave rather like sheets with a uniform diffuse-negative-charge. Each sheet of montmorillonite will tend to collect a layer of dipoles on both its surfaces, so that between such sheets will be two layers as shown in Fig. 37 (b). According to MacEwan, the number of layers in montmorillonite appears to increase with the function u/p, in which u is the molecular dipole moment and p is molecular size.

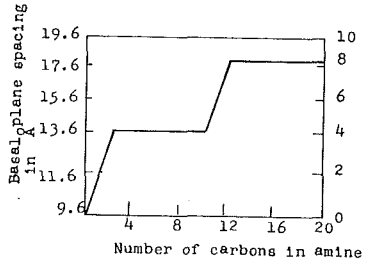


Fig. 37 (a) Ionic type of adsorption; Effect of amine chain length on montmorillonite basal spacing, modified after Jordan (17)

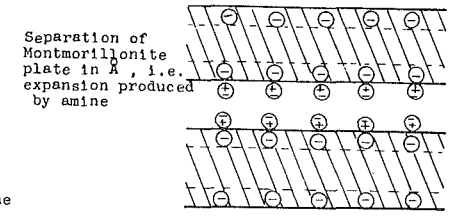


Fig. 37(b) Polar types of adsorption; The process of complex formation of montmorillonite, after MacEwan (18)

Fig. 37. Ionic and Polar Types of Adsorption on Montmorillonite

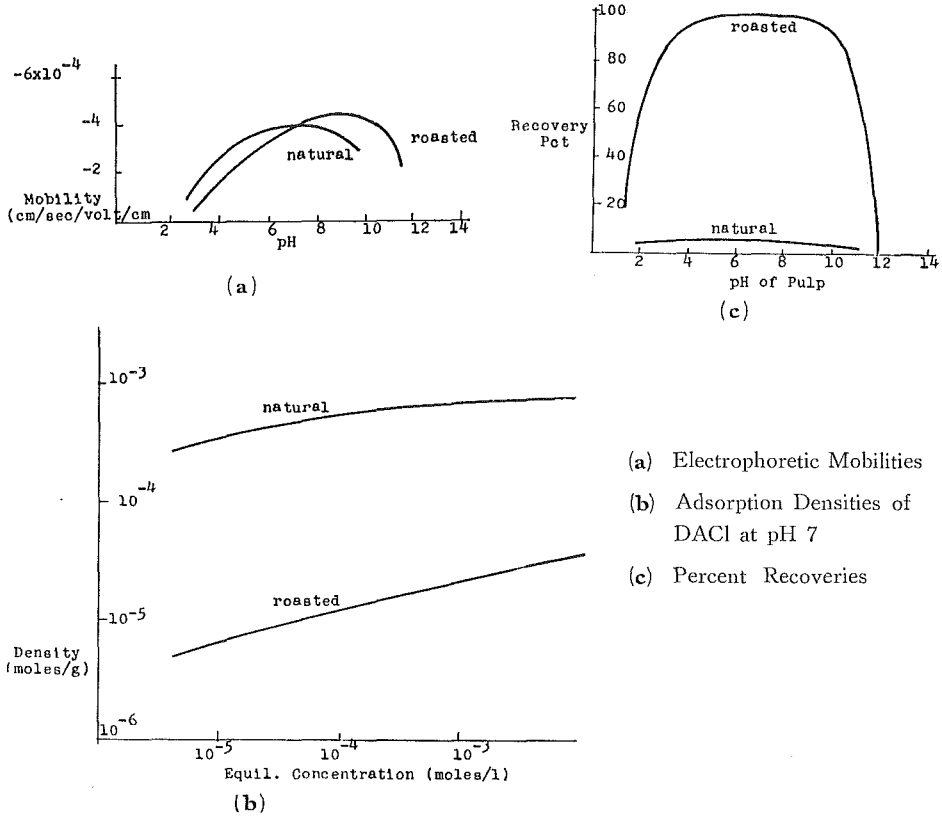
Grim[2] has also compared the difference between the ionic and polar types of adsorption. He states that, in the case of the ionic type, enough organic molecules must be present to neutralize the charge on the montmorillonite, and if the molecules are large, this will require more than two layers (Fig. 37 (a)). In polar adsorption, Grim believes that the number of layers is determined by the energy of adsorption, which decreases as the nonpolar part of molecule becomes large.

Fig. 38 summarizes the result obtained during the present investigation of montmorillonite. In Fig. 38 (a) it is shown that the electrophoretic mobilities at pH 7 for the natural and the roasted specimens are approximately the same. If the adsorption of dodecylammonium chloride (Fig. 20) is to be explained by the double layer theory, the adsorption densities for both specimens should be very similar, because the electrophoretic mobility is proportional to the zeta potential (Eq. 1), which provides the force for adsorption. Fig. 38 (b), giving adsorption density curves at pH 7, shows that the double layer theory is not applicable because the adsorption density of natural montmorillonite is markedly lowered by roasting. It is also interesting to note, in spite of the high apparent

adsorption of the amine ions on natural montmorillonite, that the flotation curve (see Fig. 38 (c)) indicates that the mineral is essentially nonfloatable.

It seem probable that in this case ionic and polar types of adsorption are taking place and limited, if any, double layer formation. If the dodecylammonium ions are lying between the sheets of the montmorillonite (Fig. 37 (b)), the sheets of the montmorillonite should interfere with the attachment of the air babble to the collector and thus the mineral should remain nonfloatable as observed.

When roasted, however, montmorillonite becomes floatable (Fig. 38 (c)). According to Grim and Bradley[19], Wyoming bentonite roasted at 800°C for 1 hr., (i.e., the same material and the same conditions used in the present work) showed no pickup of interlayer water at the end of 268 days. The same authors[20] have stated that the removal of hydroxyl water involves the expulsion of about one-sixth of the oxygens of the octahedrally coordinated portion of the structure. It would therefore be expected that the adsorption of the collector



(a) Electrophoretic Mobilities

(b) Adsorption Densities of DACl at pH 7

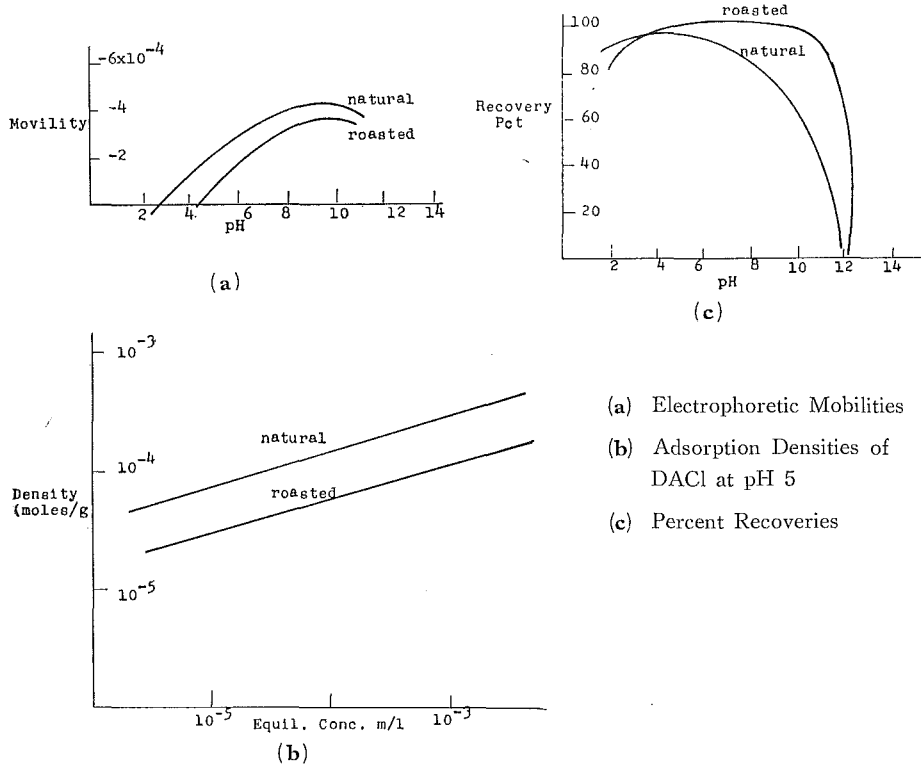
(c) Percent Recoveries

Fig. 38. Natural and Roasted Montmorillonite

on roasted montmorillonite differs in mechanism from adsorption on natural montmorillonite. Therefore, it is probable that the adsorption of the collector by roasted montmorillonite occurs on the surface of the individual sheets of the mineral rather than between the sheets, and hence the adsorption is controlled by the surface condition of the single sheets of the substance. In Fig. 38 (c), it is shown that the sharp drop of the floatability of roasted montmorillonite occurs at pH 2.5, the isoelectric point of the material, apparently substantiating the above conclusion.

Flotation Characteristics of Roasted Kaolinite

Because of the low cationic-exchange capacity of natural kaolinite, the quantity of organic cations adsorbed is small. Bradley[21] has pointed out that the adsorption of polar molecules would take place on the surface of the mineral and that the organic molecules do not penetrate between the unit layers of kaolinite as they do in montmorillonite, and therefore would be retained only around the edges and exterior surfaces of the particles. Grim and Bradley[19]



(a) Electrophoretic Mobilities

(b) Adsorption Densities of DACl at pH 5

(c) Percent Recoveries

Fig. 39. Natural and Roasted Kaolinite

has stated that on dehydration of well-crystallized kaolinite at 600°C, some structure remains which has sufficient regularity to take up at least minor amounts of hydroxyl water. Therefore, it could be expected that there would be little difference between the flotation characteristics of natural kaolinite and roasted kaolinite.

In Fig. 39 the electrophoretic mobilities, the adsorption densities, and the flotation recoveries of natural and roasted kaolinites have been summarized.

In Fig. 38 (a) the electrophoretic mobility of natural kaolinite at pH 5 is higher than that of roasted kaolinite at the same pH. This is also true of the adsorption densities of dodecylammonium chloride on the minearl (Fig. 39 (b)). However, these relationships are reversed when the floatability at pH 5 is determined (Fig. 39 (c)). In spite of the higher adsorption of the amine upon natural kaolinite, its recovery by flotation appears to be somewaht less than that of roasted kaolinite. This suggests that some detrimental effects, such as excessive consumption of reagent, slime coating action etc., are occurring during the flotation of the natural material. These tendencies increase with increase in pH.

Flotation Characteristics of Roasted Paint Rock

In addition to the fact that goethite is dehydrated to hematite by roasting, the effect of roasting on the floatability of paint rock is quite complex because

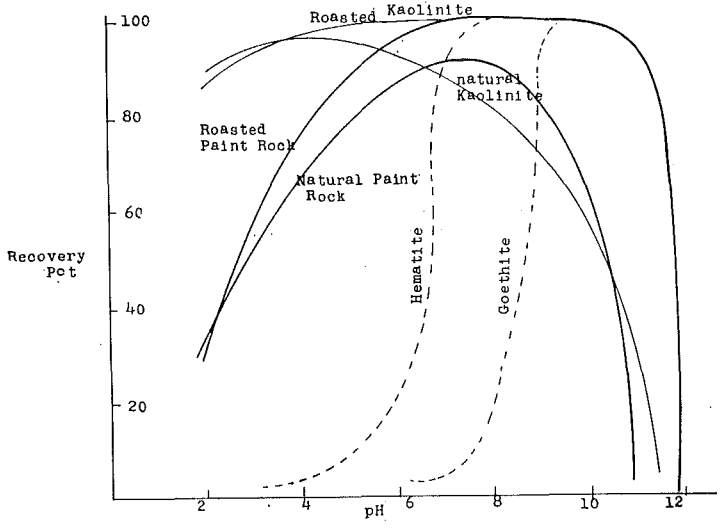


Fig. 40. Flotation of Natural and Roasted Paint Rock, Natural and Roasted Kaolinite, Goethite and Hematite with DACl. Data for Hematite from Iwasaki et. al.[23] and for Goethite from Colombo[22]

it is an intimate mixture of goethite and kaolinite. It is known that the isoelectric points of both goethite[22] and hematite[23] occur at pH 7 ± 0.5, and that hematite floats over a broader pH range at a collector concentration of 10^{-4}m/l of dodecylammonium chloride than does goethite.

Fig. 40 shows the percent recoveries, as a function of pH, for natural and roasted kaolinites, natural goethite and roasted goethite (or hematite), and natural and roasted paint rocks. From this figure the enhanced yet non selective floatability of roasted paint rock seems to be the result of the combination of the superior floatabilities of roasted kaolinite and hematite.

Summary and Conclusions

Differential thermal analysis, thermal balance analysis, chemical analysis, and x-ray diffraction were employed to determine the effect of roasting temperature upon the two clay minerals, kaolinite and montmorillonite. The first three methods were used to investigate four samples of paint rock from the Mesabi Range.

The adsorption characteristics of the natural and roasted clay minerals with respect to three common flotation collectors were investigated by measurements of their electrophoretic mobilities and of their saturation capacities. To obtain information for a study of the flotation of the paint rock samples, electrophoretic measurements were also made on all paint rock samples.

An investigation was made of the specific surface of kaolinite, montmorillonite, and paint rock as a function of the roasting temperature, using the air permeability method for determination of their relative change of specific surface.

The flotation characteristics of natural and roasted samples of kaolinite, montmorillonite, and paint rock were investigated by measurements of their flotation recoveries as a function of pH in a Hallimone tube flotation unit.

The experimental results lead to the following conclusions:

(1) Any endothermic reaction appearing on the DTA curve is due primarily to the removal of water molecules from the materials. For the first peak at about 140°C, which occurred with kaolinite, montmorillonite, and all paint rock samples, is undoubtedly due to the removal of adsorbed water. However, for the characteristic peaks at the higher temperatures, between 600° and 800°C, depending upon the material used, the endothermic peak is due to the removal of chemically combined water, which mineralogically is an important part of the materials.

When montmorillonite is roasted at temperatures slightly above 140°C, (the temperature of the first endothermic peak), or above 715°C the temperature of

the second endothermic peak), a subsequent DTA test shows that the corresponding endothermic peaks have completely disappeared. When kaolinite is roasted at temperatures above 140°C (the temperature of the first endothermic peak), or above 580°C (the temperature of the second endothermic peak), a subsequent DTA test shows that the corresponding peaks have completely disappeared. When paint rock is roasted at temperatures above 140°C (the first endothermic temperature), 360°C (the second endothermic temperature), or 580C° (the third endothermic temperature), a subsequent DTA test shows that the corresponding peaks have completely disappeared.

(2) The adsorption characteristics of natural kaolinite with respect to a cationic collector dodecylammonium chloride are controlled strongly by pH. The flotation characteristics of natural kaolinite with respect to the same cationic collector are also controlled by pH, and by the collector concentration used, but are little affected by roasting. However, the exchange between the hydrogen ion on the surface of kaolinite and the cation in the solution is not stoichiometric, and therefore the ion exchange theory does not appear applicable in this case. Roasting of kaolinite slightly modifies its behavior to flotation by dodecylammonium chloride, but the saturation capacity of kaolinite is considerably reduced by roasting.

(3) The adsorption characteristics of natural montmorillonite for dodecylammonium chloride are only slightly affected by pH. Although the saturation capacity of natural montmorillonite toward this cationic collector is very high, it is lowered markedly by roasting.

In spite of the high apparent adsorption of dodecylammonium chloride by natural montmorillonite, the flotation tests indicate that this mineral is essentially nonfloatable. This is probably due to the micaceous structure of the montmorillonite, the collector being adsorbed between the sheets of the mineral. The montmorillonite swells during adsorption, and the outer tetrahedral silica sheets then interfere with the attachment of the air bubble to the collector so that the mineral remains nonfloatable. However, roasting will render natural montmorillonite floatable by the cationic collector. It seems probable that the adsorption of the collector then takes place on the surfaces of the individual sheets of the montmorillonite structure. The flotation characteristics of roasted montmorillonite are strongly governed by pH.

(4) The two anionic collectors, potassium ethyl xanthate and sodium dodecyl sulfate are adsorbed only slightly by either natural kaolinite or natural montmorillonite. The adsorption in these cases seems to be due to a van der Waale's type of attaction between the particles of the minerals and the collector.

(5) In cationic flotation of natural paint rock with dodecylammonium chloride,

the flotation characteristics are governed by pH and by the collector concentration. The mineral association occurring in paint rock is at such a fine size that it is doubtful if such material will respond to flotation as a method of concentration.

(6) The specific surfaces of kaolinite, montmorillonite, and paint rock, measured by the air permeability method, decrease with increase in the roasting temperature. A sharp drop in the specific surface of three materials continues until 500°C is reached. The observed decrease in reagent consumption may be due in part to the decreased specific surface effected by roasting.

(7) Through DTA tests it was determined that three samples of paint rock from the Mesabi Range consisted of mixtures of goethite and kaolinite and that the fourth sample consisted essentially of kaolinite alone.

(8) The isoelectric points of all clay and paint rock samples, in both the natural and roasted conditions, were determined by measurement of their electrophoretic mobilities.

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