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A STUDY OF THE REACTION OF HYDRATED LIME WITH PURE CLAY (KAOLIN) IN CLAY STABILIZATION

BY

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A
THESIS
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Approved by

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E. D. Fisher C A Johnson

ABSTRACT

The work presented is the investigation of the reaction of pure Kaolinite clay with hydrated lime in clay stabilization. Pure Kaolin clay, ranging from one micron to five microns in size, was mixed with calcium hydroxide in the form of a paste. These mixtures were permitted to react for varying periods of time. An attempt was made to separate the lime from clay lime mixture by density separation using a mixed solution of carbon tetrachloride and tetrabromoethane. Since the above method failed because of the formation of a yellow gelatinous suspension, the lime was removed by washing the clay lime mixture in a concentrated solution of ammonium chloride and finally in water. Electron photographs of clay before and after the treatment were compared for changes in edge sharpness or corner erosion. No notable changes were observed by comparison of the photographs. The clay lime mixtures were also tested in the Geiger counter X-ray spectrometer. These tests gave no indication of formation of new products of reaction between the clay and lime additives. It is concluded that the reaction is a surface phenomenon only.

ACKNOWLEDGEMENTS

The author wishes to express his indebtedness to Mr. John B. Heagler Jr., Associate Professor of Civil Engineering, Missouri School of Mines and Metallurgy, for the exhaustive guidance and help he gave throughout the course of this investigation and in the preparation of this report.

The author also wishes to express his gratefulness to Dr. Planje, Chairman of the Ceramic Engineering Department, Missouri School of Mines and Metallurgy, for his suggestion of the problem, his valuable guidance at each phase of the investigation, and for materials which he supplied for the experiment. He was very kind to allow the free use of the X-ray diffraction equipment which helped this work very much.

Sincere thanks are also expressed to Mr. James Jensen, solid state physicist, Bureau of Mines, and Mr. Parker Martin, physical chemist, Bureau of Mines, for their encouragement and kind cooperation in taking the necessary photographs with the electron microscope.

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I. INTRODUCTION

The discovery that the workability of a clayey soil would be greatly improved by the addition of lime, $Ca(OH)_2$, dates back to the remote past. Highway and Airport Engineers have observed that when lime is applied to subgrade soils, which are otherwise difficult to stabilize due to their high percentage of clay, the bearing capacity of subgrade soil is considerably increased, with due reduction in their plasticity indices. Thus, lime is recognized as a good stabilizing agent in many parts of the world, because of its capacity to improve properties at a reasonable cost.

Many engineers have done research on the addition of calcium hydroxide to expansive clays, which contributed increased resistance of the material to deformation under load, as well as beneficial reduction in swelling characteristics. Nevertheless, the reaction of hydrated lime with clayey soil is still for the most part a mystery. There are ever so many opinions about the nature of reactions between the clay crystal and the hydrated lime. Many investigators have attempted to find out the nature of this beneficial reaction with pure clay crystals also.

The literature contains many reports describing the benefits of the lime additions and gives various explanations for the results obtained. The nature of the reaction due to the lime treatment has been variously explained as 1) aggradation caused by flocculation of dispersed clays, 2) exchange of calcium ions for other absorbed ions such as hydrogen, sodium, or potassium, 3) pozzolanic reactions which were thought to be the formation of calcium silicates from the reaction of lime with free silica in the soil, 4) the gradual reaction of the lime and carbon dioxide from the atmosphere and the soil to form calcium carbonate and thereby cementing the soil particles together. While some of the above may simply be different ways of stating the same idea, it is certainly possible that, with sufficient time, any or all of the phenomena might occur.

Many engineers have questioned the permanency of lime stabilization. Thus, if it were only a matter of flocculation or ion exchange, fluctuations of ground water levels or percolating ground waters might replace the calcium ion and reduce the beneficial effect of the added lime. There appears to be scant information on this subject. It is for this reason as well as others that data are needed concerning the true nature of the reactions of lime and soil under stabilization conditions.

The results of previous work showed that it would be almost impossible to study the reactions of small percentages of lime and soils, because of the complexity of soils from the standpoint of the mineral composition, particle size gradation, degree of crystallinity of the clay fraction, and the differences in the absorbed ions. In many cases it is extremely difficult to identify all the mineral components of an unfractionated soil sample by X-ray diffraction or other means of analysis. It is even more difficult to identify the reaction of lime and soil components.

Ralph E. Grim (1), in 1940, showed that clay minerals which form the components of soil control largely their physical properties. Therefore, in order to study the reaction of lime with soils more closely, it was believed that reactions with pure clay minerals of the types which occur in soils should be studied first. Then if all clay minerals did not react with lime, a clay mineral analysis could serve as a quick test to determine if lime would react with soil. Further, the analytical data for clay mineral lime reactions are more closely interpreted so that a start could be made for the interpretation of the more complex data for soil lime reactions.

The investigation presented in this thesis is confined to the effects of hydrated lime on a pure Kaolinite clay.

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(1) All references are in the bibliography.

II. REVIEW OF LITERATURE

In 1952, Messrs. Irving Goldberg and Alexander Klein (2) undertook a series of experiments on the effects of treating expansive clays with calcium hydroxide. The approach used in their investigation consisted of treating different samples of clays with calcium hydroxide in varying amounts and after curing for an adequate period of time, evaluating the effects of the given treatment by several types of analysis, including chemical analysis, X-ray diffraction and differential thermal analysis. The changes in the mechanical properties of the clays with increase in moisture content were determined and compared.

In their investigation they collected representative samples of soils and crushed them to about 14 mesh size, and dry calcium hydroxide from freshly opened containers were added to a predetermined weight of soil, and the two materials were blended. Distilled water was then added to make it a stiff paste. The additions of calcium hydroxide were by percentages by weight of soil in the oven dried state, in increments of 2, 4, 6, and 8 percent.

The prepared samples of air dried clays and clay-lime mixtures were initially ground in a ball mill, tested in the Geiger-counter and X-ray spectrometer. The X-ray diffraction patterns obtained were used to determine the changes in structure, if any, in the clay or in the calcium hydroxide after prolonged contact with each other in presence of water. They expected that the X-ray diffraction patterns of the clays containing 8 percent of calcium hydroxide would reveal the excess of calcium hydroxide, the presence of calcium carbonate if carbonation had occured, or the presence of hydrosilicates of lime, should the pozzolanic reaction have taken place. Since the moisture content of these clays varied depending upon the treatments performed, there occured some changes in the listed values for interplanar spacings of the clay mineral. This change in the interplanar spacing, due to the expansion of the lattice with access of water, was found to be pronounced in Bentonite. Anyhow, they concluded that the changes in the interplanar spacings with moisture content are not indicative of changes in crystal structure due to addition of calcium hydroxide. The clay with 4 percent of calcium hydroxide content does not compare exactly with that of 8 percent, nor with the clay without added calcium hydroxide. They concluded that there is no reasonable explanation for these differences, and there is no evidence of the formation of hydrosilicates of lime in appreciable quantity in any of the materials.

For differential thermal analysis, the three nichrome-wire furnaces were used. The rate of temperature change of the samples averaged about 8° C per minute to 80° C, but subsequently remained constant for the remainder of the test at 12° C per minute. This investigation also did not reveal any specific change in structure due to the treatment by calcium hydroxide.

Goldberg and Klein (2), on treating a Wyoming bentonite with amounts of calcium hydroxide up to 8 percent reported no change in X-ray spectrum except that the calcium hydroxide reflections disappeared. Messrs. Ralph E. Grim and James L. Eades (3) of the University of Illinois, conducted an extension to the above experiment by using a much larger percentage of lime and heat cured samples at 140° F for 60 days. If the reaction could be recorded for the above conditions, by comparing with the specimens cured for shorter periods of time and with smaller percentages of lime, Grim and Eades hoped to find the nature of the reaction between clay and hydrated lime. The former paper had reported that when clays treated with calcium hydroxide are exposed to the atmosphere, calcium carbonate is formed. Hence, Grim and Eades, in their experiments, allowed the material to dry in absence of carbon dioxide, and they found new interplanar spacings in the X-ray patterns showing that there had been considerable reaction between clay and the lime.

The Georgia Kaolin which is well crystallized gives a diffraction pattern of Kaolinite with sharp basal and prism reflections in the untreated stage. As the Kaolin is treated with small percentages of lime the prism reflections lose their sharpness and intensity. This seems to indicate that this mineral, usually considered quite stable, was attacked at the edges and within the two layer silicate sheets, thereby causing a weakening of the prism reflections. That is, the initial reaction is not merely one of spreading apart the silicate layers, but it is an attack on the basic structure. As the lime content and curing period were increased there also appeared a reduction of the basal reflection and an increase in the percentage of the new minerals as indicated by nonkaolinite diffraction lines. It is significant that new crystalline phases appear almost immediately with the treatment of Kaolinite with lime.

Grim and Eades (3) continued their investigation with several samples of clay such as halloysite, illite, montmorillionite etc. It is impossible to be certain of the identity of the new crystalline reaction products, but the data give every indication that the new minerals are hydrous calcium silicates. The new reaction products for Kaolinite give essentially the same X-ray diagram characteristics as those given by Bernal (4) for the low temperature calcium silicate hydrate and dicalcium silicate hydrates which are formed during the hydration of cement. Since there are a number of intermediate products in the calcium silicate hydrate system, it is believed that several different compounds may exist at one time until the equilibrium between the silica, which is removed from the structure of the clays and the excess lime, is reached. There is a possibility that, although the X-ray diagrams do not contain reflections for new minerals, calcium silicate hydrate gels are formed which are not crystalline. These gels could just as easily interlock the particles together and give the added strength without having a crystalline structure.

They continued the investigation by differential thermal analysis also. Two nichrome wire furnaces with a maximum range of 1000° C are used for differential thermal analysis. It was felt that the thermal analysis would reveal the presence of new calcium compounds and would serve as a guide for their identification. From a series of experiments, it was concluded that formation of a new crystalline phase of calcium silicate is true in clay lime stabilization, which can tentatively be identified as calcium silicate hydrates. Finally they suggested that the development of a strength in lime stabilization is accompanied by distinct structural changes in clay minerals, and hence their strength is permanent.

III. CLAY CRYSTAL

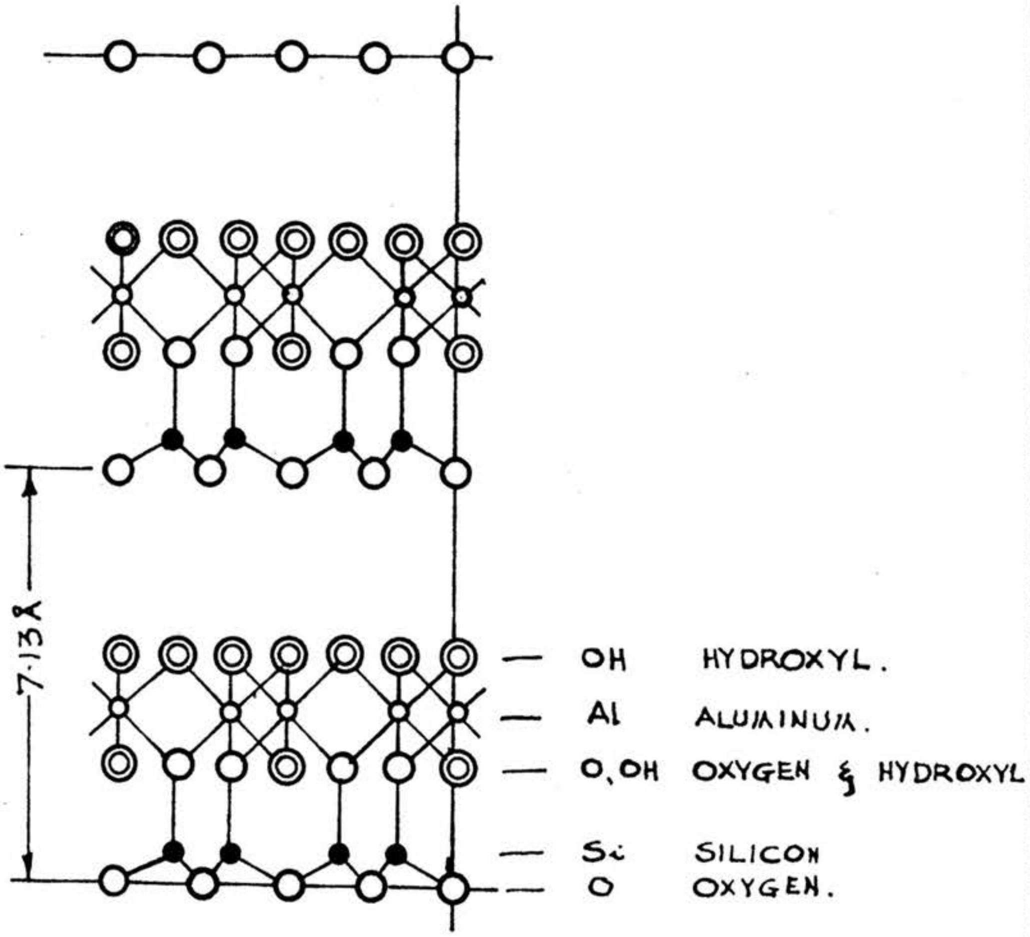
1. FORMATION

Geologically, clays are composed of various minerals of primary and secondary origin, all of which are of a comparatively fine or small grain size. Some minerals are often present in grains which are larger than those of the other minerals, but because of the nature of their formation, true clays only infrequently contain fragments visible to the unaided eye. Clays in their natural form may consist of many different minerals, none of which predominates. There are certain minerals or classes of minerals which occur in all clays and have been termed "clay minerals."

Due to agencies of heat, pressure, and other chemical phenomena, several changes occur under the surface of the earth. Under conditions of high temperature and pressure, the feldspar component was largely altered to the clay mineral, Kaolinite. The hydrolysis reaction may be expressed simply in the following terms.

$$\underset{\text{Orthoclase feldspar}}{K_2O.Al_2O_3.6\ SiO_2} + H_2O + \text{acid vapours} \longrightarrow \underset{\text{Kaolinite}}{(OH)_4Al_2Si_2O_5} + \underset{\text{Silica}}{4\ SiO_2} + \underset{\text{Potash}}{2\ KOH}$$

Kaolinite is the name given to the specific mineral which is found in certain localities, and it has certain properties which enable it to be distinguished from others. China clay is largely composed of Kaolinite which has been freed from impurities of micaceous, feldspathic types.



CRYSTAL STRUCTURE OF
KAOLINITE.

FIGURE 1.

2. MOLECULAR STRUCTURE

The molecular formula of Kaolinite is often written as $(OH)_4Al_2Si_2O_5$ and it is composed of three layers of anions and two layers of cations, as shown in the figure (1). The first anion layer in the crystal is hydroxyl, the middle anion layer is hydroxyl and oxygen, while the third anion layer is oxygen. The two layers of cations are aluminum and silicon.

The first two anion layers are bonded together by the aluminum atom in octahedral coordination and the second and the third are joined by silicon in tetrahedral coordination in the three dimensional crystal lattice. It is difficult to present a three dimensional picture by a two dimensional drawing unless the model of the structure is made three dimensionally for better understanding of the crystal lattice.

IV. PREPARATION OF THE CLAY SAMPLE

The sample of clay used in this experiment was Georgia Kaolin, obtained from the Ceramic Engineering Department, Missouri School of Mines and Metallurgy. To enable a series of electron micrographs of the clay particles to be prepared it was necessary to separate the clay into a sample whose particles would range in size from one to five microns. In order to accomplish this separation, about two pounds of the Georgia Kaolin was mixed with distilled water in a five gallon jar. The sample was well stirred mechanically and further dispersed by air diffusion. Sodium carbonate was added to the clay water system to aid in dispersing the clay particles. The mixing and air diffusion were continued until it was certain that the clay was well dispersed.

To separate the particles of less than the five micron size, the detention time necessary for the above size clay particles to stay in suspension was calculated by using Stoke's Law.

Stoke's Law states that

Velocity of a particle falling through a resistant medium may be considered equal to $\frac{d}{t} = \frac{\gamma_s - \gamma_\omega}{18\mu} D^2$

where γ_s = density of solid

γ_ω = density of water

μ = viscosity of the liquid

D = diameter of the particle

d = distance through which the particle will fall in time t seconds.

The height of the clay-water suspension in the jar = 30 cms

Density of clay = 2.65 gm/cc

Density of water at 27° C lab. temperature = 0.999 gm/cc

Viscosity of water at 27° C lab. temperature = 0.01009 poise

Velocity of the falling particle

$$= \frac{\gamma_s - \gamma_\omega}{18\mu} D^2$$

$$= \frac{2.65 - .999}{18 \times \frac{.01009}{980.7}} (.0005)^2 \text{ cm/sec}$$

$$= 22.3 \times 10^{-4} \text{ cm/sec}$$

Detention time required for the particles of size less than five microns to remain in suspension

$$= \frac{30}{22.3 \times 10^{-4}} \text{ sec}$$

$$= 13,450 \text{ sec}$$

$$= 4.35 \text{ hrs.}$$

After exactly 4.35 hours of suspension, the top layer of the solution containing particles of size less than five microns was taken out in another jar of the same size. Now, particles of size less than one micron had to be separated from the above clay suspension. Using the same formula as above,

Velocity of a particle of size one micron

$$= \frac{\gamma_s - \gamma_\omega}{18\mu} D^2$$

$$= \frac{2.65 - .999}{18 \times \frac{.01009}{980.7}} (.0001)^2 \text{ cm/sec}$$

$$= 8.925 \times 10^{-5} \text{ cm/sec}$$

Time required for the above particle to travel 30 cms

$$= \frac{30}{8.925 \times 10^{-5}} \text{ sec}$$

$$= 3.36 \times 10^{5} \text{ sec}$$

$$= 3 \text{ days } 21.3 \text{ hrs.}$$

Thus allowing the particle to settle for 3 days, 20 hours, the solution containing the colloidal particles was taken out. The remaining solution had particles ranging from one micron to five microns in size.

Because of the use of sodium carbonate as the deflocculating agent, the clay crystal had Na + ions in its diffuse layer. To replace the Na + ions, about 5 cc of hydrochloric acid was added to the clay solution, the volume of which had been increased to 5 gallons with distilled water. H + ions in the hydrochloric acid now replaced the Na + ions in the diffuse layer, and therefore the clay started to flocculate, and settled on the bottom of the jar within a short interval of time. To remove the traces of the sodium chloride formed, the clay was washed several times with distilled water. After removing the surface water from the clay water solution, the sample was allowed to dry in free air, at room temperature, and finally in the oven at 100° F.

V. X-RAY DIFFRACTION TEST

X-ray diffraction

Among the many methods of studying clay minerals, the X-ray method is probably now the most widely used for identification purposes and is of paramount importance for studying their crystalline characteristics.

A crystal lattice may be conceived as sets of atomic or ionic groups arranged with a certain symmetry so that planes of atoms occur throughout the lattice at equal spacings along the crystallographic directions. Crystals behave as three dimensional grating which can diffract suitable radiation just as light is diffracted or scattered by a grating of closely spaced objects or lines. Because these planes are very small separation, radiation of comparable wave length is required. Consequently, X-rays which have a wave length about ten thousand times as short as visible light are used.

An X-ray beam on passing through a set of lattice points will be diffracted and reinforcement will occur in accordance with W.L. Bragg's equation $n\lambda = 2d \sin\theta$

Where n is a whole number.

λ is the wave length of the diffracted X-ray beam.

d is the spacing of the planes.

θ is the angle through which the beam is reflected.

A series of reflections occurs from atoms in particular planes at different angles where n is 1, 2, 3, ...etc.

The characteristic X-ray pattern produced by any crystal thus enables the arrangement of the atoms in the crystal to be fully ascertained.

IV. EQUIPMENT USED

1. GEIGER COUNTER X-RAY SPECTROMETER

The Geiger counter X-ray spectrometer of the Ceramic Engineering Department, Missouri School of Mines and Metallurgy, is used for the study of X-ray diffraction patterns of the various samples. The above machine consists mainly of a spectrometer which contains the following major components.

1) A stabilized X-ray source.
2) A goniometer comprising a scanning arm bearing a Geiger counter tube provided with suitable beam receiving slits and traversing a graduated quadrant, together with a specimen mount geared to rotate at half the angular speed of the scanning arm.
3) An automatic recorder for the preparation of charts.
4) Damping and amplitude controls.
5) X-ray tube or tubes.

2. ELECTRON MICROSCOPE

The electron microscope used for studying the clay crystals was "Philips Electron Microscope", of the Bureau of Mines, Rolla, Missouri. The microscope operates at 100 KV, and has an automatic focusing device, an objective pole piece of unusually large bore, and other features that give improved performance compared to most other microscopes. It has a special lens, called intermediate lens, and change in magnification is easily obtained by varying current through this intermediate lens. This permits a continuous change in magnification between 6000 to 80,000 times. The instrument also contains arrangements for taking photographs at the required magnification.

The majority of the photographs taken for this research were at a magnification ratio of 7,500 to 1, and others were taken at magnification ratios as high as 20,000 and 30,000 to 1. At the border of each picture is a scale marker consisting of two black straight marks having a distance of exactly 1 micron between them (1 micron = 0.0001 cm = 0.00004 in.). By adding a special solution, Polystyrene Latex, which contains spherical particles 0.557 micron in diameter, to the dispersed clay particles, a visual comparison of the particle sizes was possible. The spherical particles in the standard solution had approximately the same diameter, the standard deviation of diameter being 0.0108 micron. These particles can be seen in the pictures as dark circular spots.

VII. STUDY OF THE REACTION OF KAOLIN WITH HYDRATED LIME

Even though the percentage of lime added to clay in clay stabilization is of the order of 2-10 percent, for studying the reaction in the laboratory, 50 percent of pure hydrated lime was added to 50 percent of Kaolin clay from the prepared sample. High percentages of lime were added to study the reaction of the clay lime system with high concentration of lime. 5 gms of carefully weighed clay were added to 5 gms of hydrated lime and the two materials were mixed thoroughly. Enough distilled water was added to the clay-lime mixture to make it into a stiff paste. This stiff suspension was placed in a test tube and kept in a moist room at 80° for the duration of the specified reaction time.

Several such mixtures were made and allowed to react with hydrated lime for varying time periods, Viz., 0, 1, 3, 6, 12, 20, 40, and 60 days. At the end of each period, the mixture was dried in air and later in the oven at 100° F, and powdered in a ball mill. Each powdered specimen is thus ready for the identification of clay, lime and the formation of silicates or other minerals, if any.

1. X-RAY DIFFRACTION TESTS

For the identification of clay minerals, powder specimens are most convenient and give better results. The mixture which had been allowed to react only during mixing was designated as the zero day mixture, and was studied first in the X-ray diffraction machine. The X-ray diffraction pattern shown in figure 2 shows the peaks which indicate the crystals of Kaolin and calcium hydroxide.

Details of adjustments of the X-ray spectrometer:

X-ray	copper radiation
X-ray tube slit	medium
Geiger slit	medium
X-ray wedge	0
Geiger wedge	4
Amplitude	10 maximum
Damping	10 maximum

The experiment was repeated for all other specimens obtained after 1, 3, 6, 12, 20, 40, and 60 days of reaction time, and X-ray diffraction patterns as shown in figures 2, 3, 4, and 5 were obtained.

2. TESTING BY MEANS OF ELECTRON MICROGRAPHS

The reaction of clay with hydrated lime can also be studied by comparing the clay crystals through electron micrographs before and after treatment with calcium hydroxide to determine if there are changes in edge sharpness or corner erosion which would indicate the accumulation of new chemical phases at the edge. The above method required the removal of calcium hydroxide from the clay lime mixture, and the testing of the residue in the electron microscope. Also, the residue can be checked for quality, nature of reaction, and possibility of the formation of new compounds by means of X-ray diffraction tests. The removal of calcium hydroxide can be effected by means of A) density separation and B) dissolving calcium hydroxide in ammonium chloride.

A. DENSITY SEPARATION

The density separation requires the preparation of an insoluble suspension for the clay-lime combination. The mixed solution of carbon tetrachloride ($C\,Cl_4$) and tetrabromoethane ($CHBr_2$-$CHBr_2$) was chosen because neither clay nor lime is soluble in it. Since the density of clay is 2.65 gms/cc, and the density of lime is 2.3 gms/cc, the prepared solution of carbon tetrachloride and tetrabromoethane should have a density midway between the densities of clay and lime: approximately 2.45 gms/cc.

Density of carbon tetrachloride $d_1 = 1.59$ gms/cc at 25°C

Density of tetrabromoethane $d_2 = 2.946$ gms/cc at 25°C

Required density of the mixture $d = 2.45$ gms/cc

Density $d = \frac{\text{Mass}}{\text{Volume}} = \frac{M}{V}$

Weight of carbon tetrachloride $M_1 = V_1 d_1 = 1.59\ V_1$ gms

Weight of tetrabromoethane $M_2 = V_2 d_2 = 2.946\ V_2$ gms

Total volume of mixture $= V_1 + V_2$

$$\frac{1.59\ V_1 + 2.946\ V_2}{V_1 + V_2} = 2.45$$

Solving $V_2 = 1.735\ V_1$

Volume of carbon tetrachloride taken $= 100$ cc

Volume of tetrabromoethane required $= 173.5$ cc

1) Checking the Density of the Mixed Solution:

The checking of the density of the mixed solution was done by using a specific gravity bottle.

Weight of the specific gravity bottle empty = 31.550 gms

Weight of the specific gravity bottle + solution = 97.450 gms

Weight of the specific gravity bottle + water = 58.467 gms

Weight of the solution = 65.900 gms

Weight of an equal quantity of water = 26.917 gms

Density of the mixed solution = $\frac{65.900}{26.917}$ gms/cc

= 2.45 gms/cc

2) Separation by Using the Centrifuge:

A test tube of about one inch in diameter was cut to a length of 2 1/4 inches and fitted into cups of the Universal Centrifuge Machine by means of a rubber cork. The clay lime mixture was oven dried and powdered in the ball mill. The prepared solution was poured into the test tube to a height of 1 1/2 inches and about 1/2 gm of the clay lime mixture was added to it and mixed thoroughly. Four such cups were filled with the same solution for better balancing of the centrifuge. The centrifuge was operated for 6 minutes at 600 r.p.m.

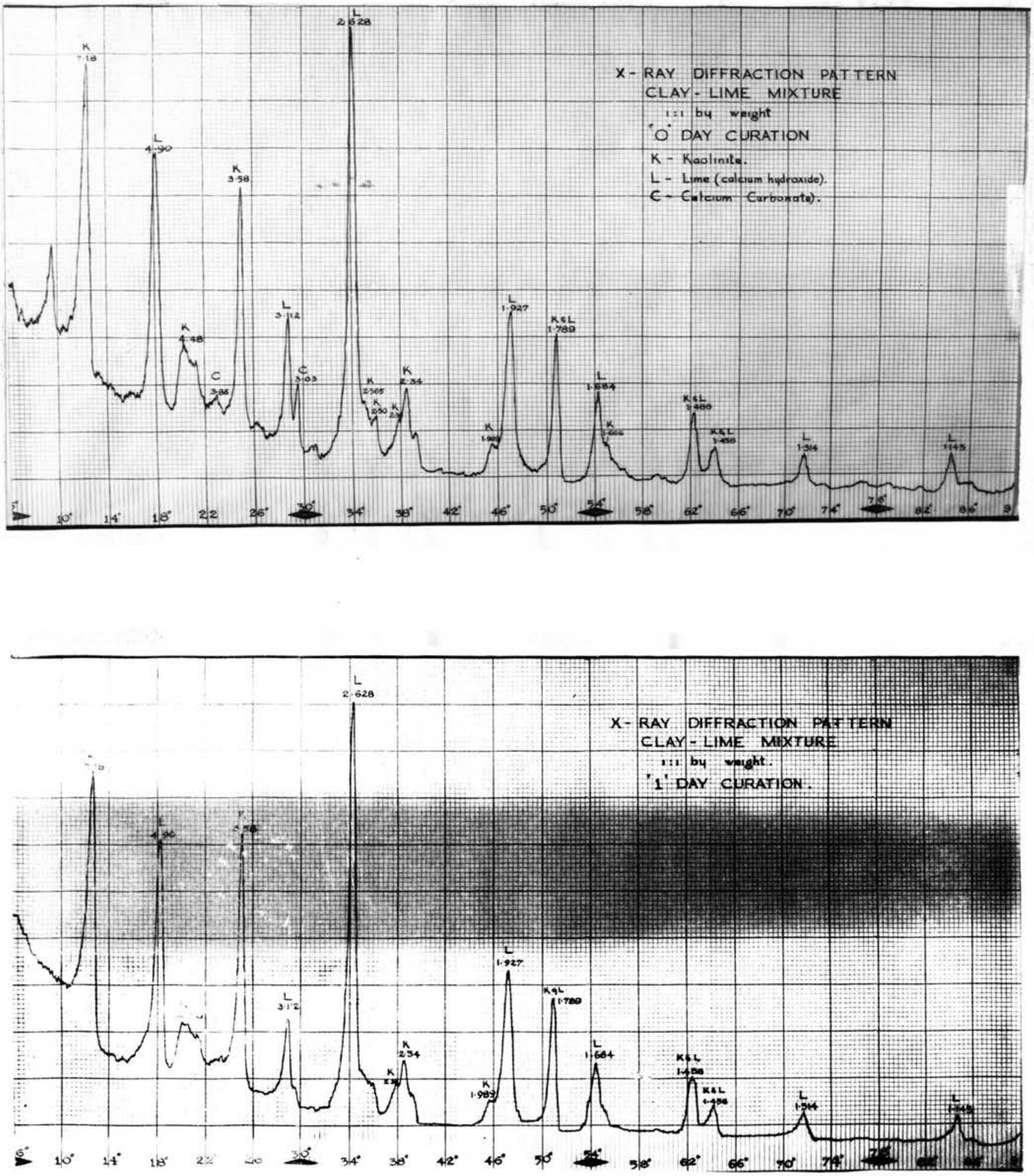
The centrifuge was used for easy separation of denser particles such as clay, which will accumulate in the bottom of the test tube due to centrifugal force. Lime, being lighter than the prepared solution, will float in the system and accumulate in the upper level of the solution.

The attempt to separate the calcium hydroxide from the clay-lime mixture by using the above method failed because of the formation of a yellow gelatinous suspension on the top of the mixed solution which prevented separation. The same type of yellow gelatinous formation was experienced for clay-lime mixture of 20 days and 40 days curation.

B. SEPARATION BY DISSOLVING CALCIUM HYDROXIDE IN AMMONIUM CHLORIDE

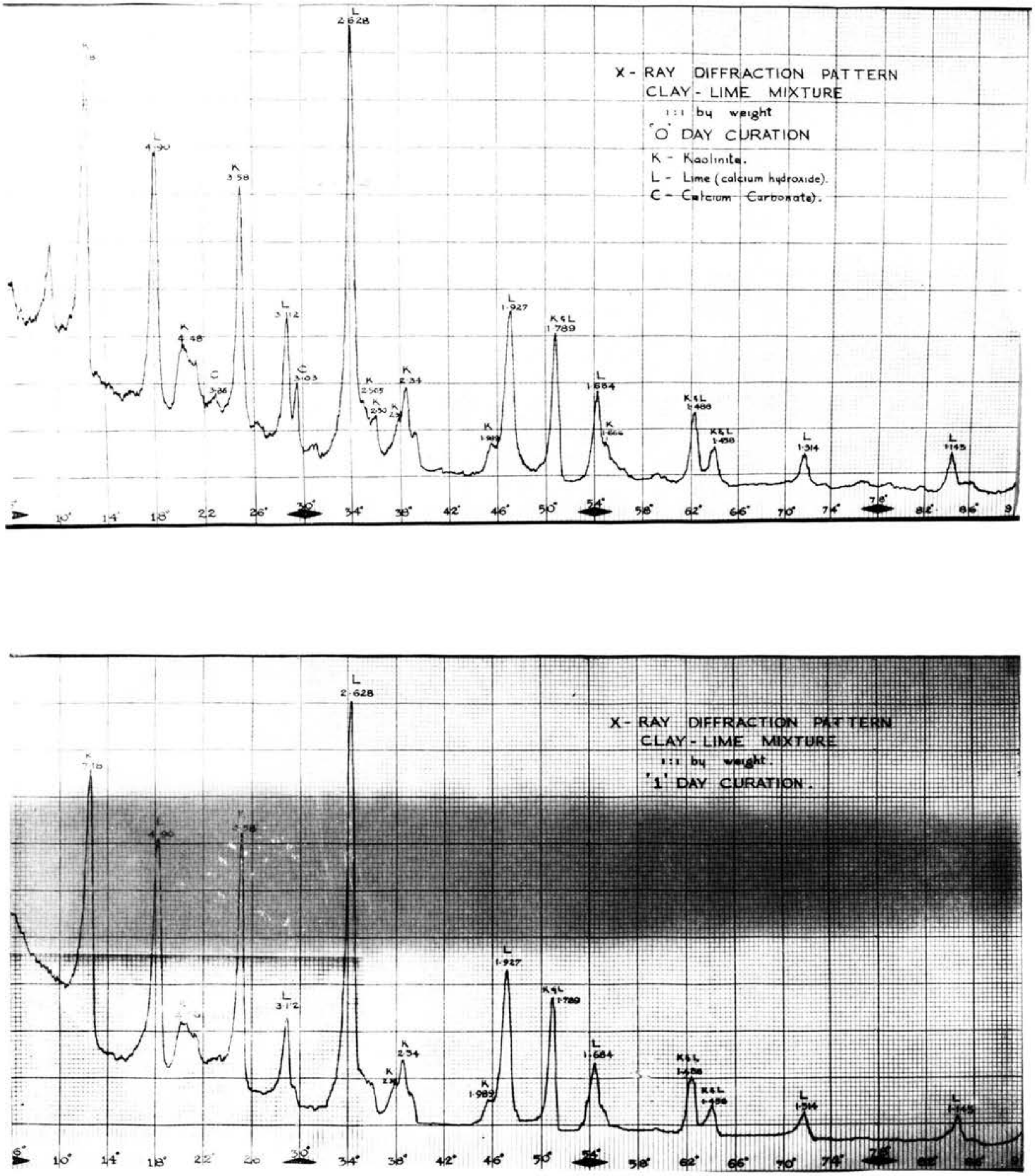
The sample of clay lime which had cured 40 days was oven dried and powdered in the ball mill. 2 gms of the above sample were mixed thoroughly in a concentrated solution of ammonium chloride. The calcium hydroxide was dissolved in the ammonium chloride solution for about 24 hours which was a sufficient period for all traces of the calcium hydroxide to dissolve. The above solution was then washed thoroughly with distilled water and the undissolved suspension was filtered and dried in the oven at 100° F.

The filtrate was again placed in the X-ray diffraction machine for identification of clay, calcium hydroxide, and any silicates that might be present.



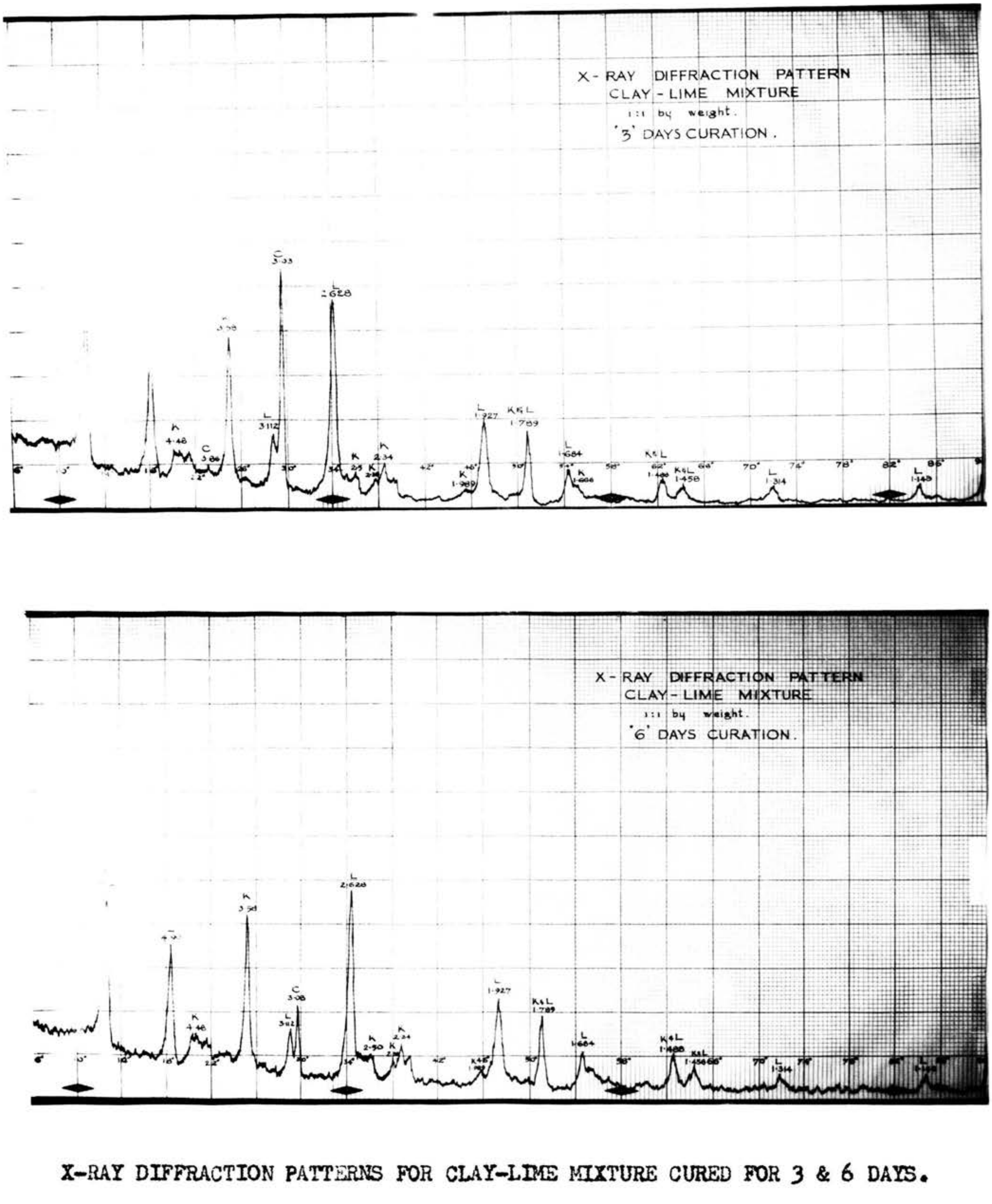
X-RAY DIFFRACTION PATTERNS FOR CLAY-LIME MIXTURE CURED FOR 0 & 1 DAY.

FIGURE 2.



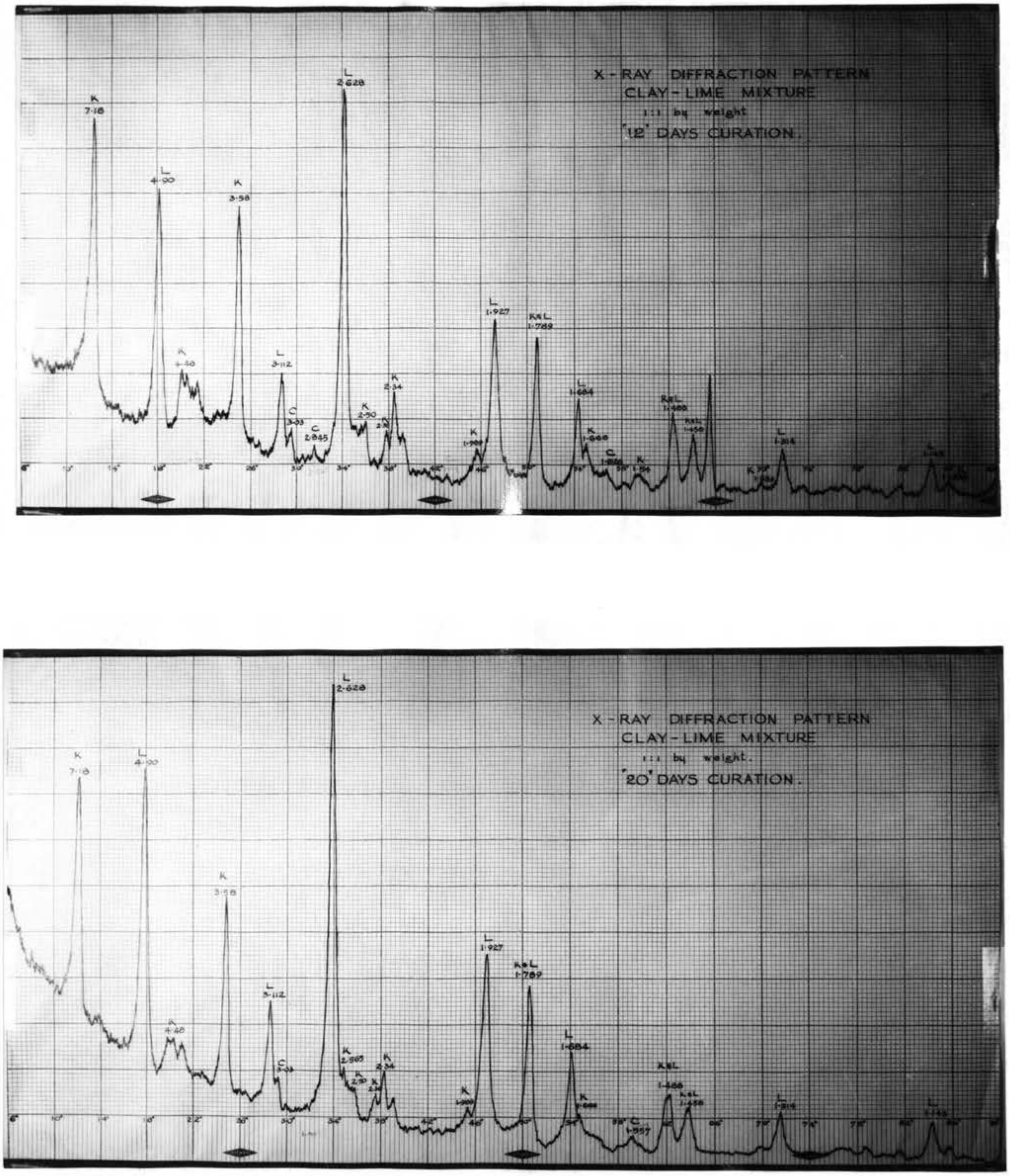
X-RAY DIFFRACTION PATTERNS FOR CLAY-LIME MIXTURE CURED FOR 0 & 1 DAY.

FIGURE 2.



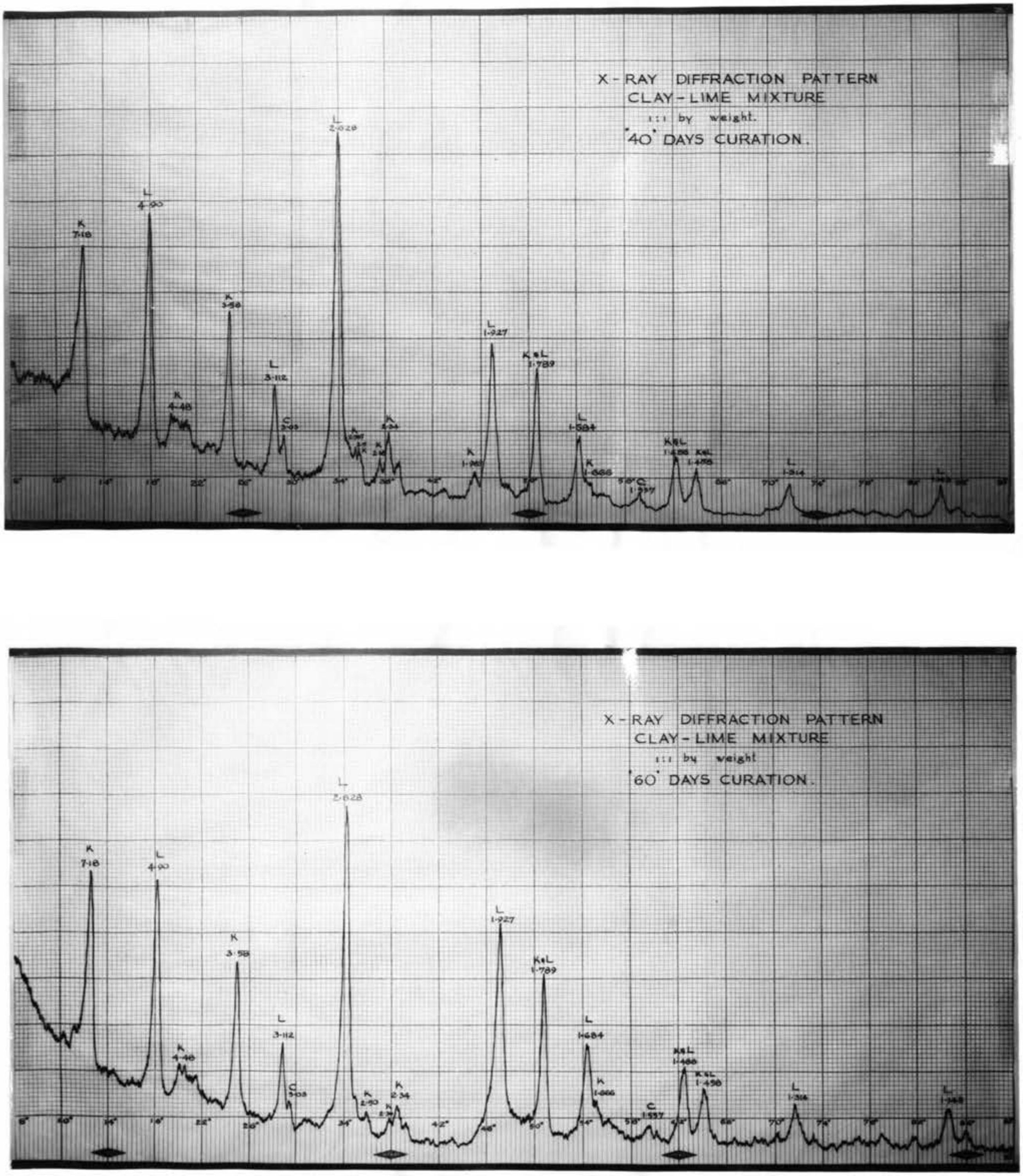
X-RAY DIFFRACTION PATTERNS FOR CLAY-LIME MIXTURE CURED FOR 3 & 6 DAYS.

FIGURE 3.



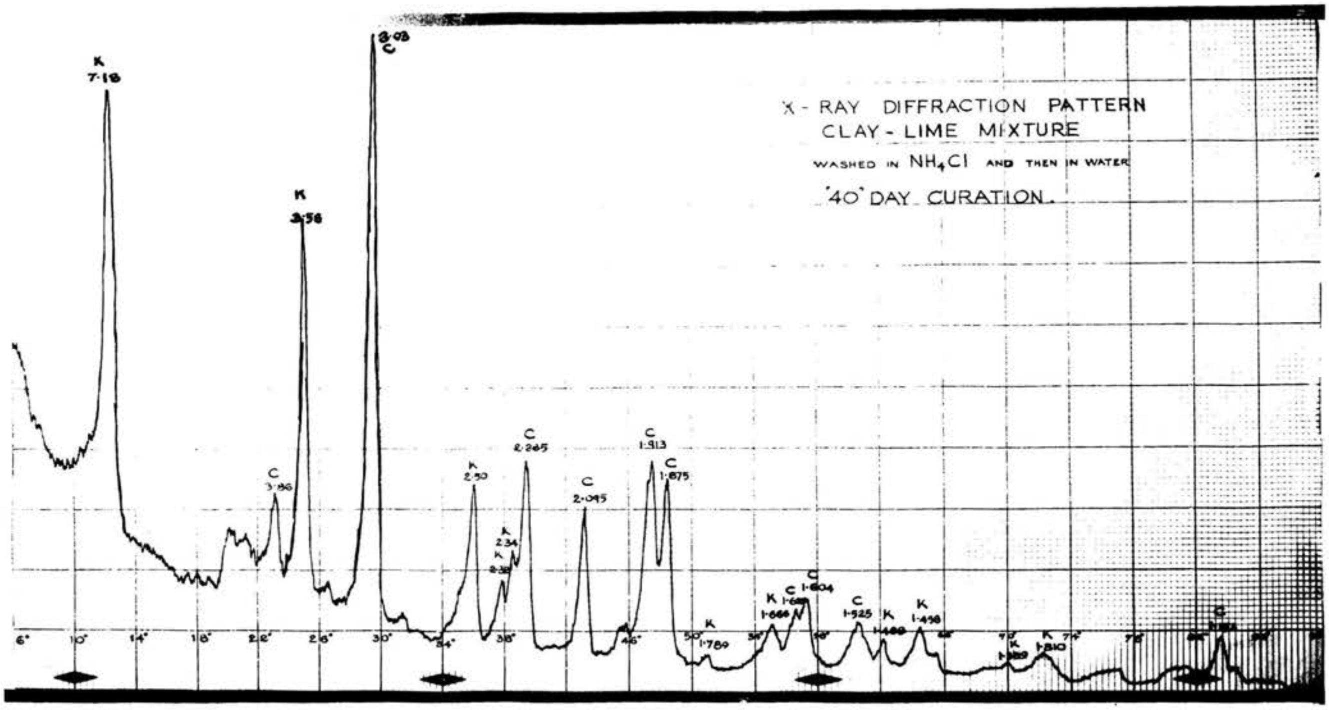
X-RAY DIFFRACTION PATTERNS FOR CLAY-LIME MIXTURE CURED FOR 12 & 20 DAYS.

FIGURE 4.



X-RAY DIFFRACTION PATTERNS FOR CLAY-LIME MIXTURE CURED FOR 40 & 60 DAYS.

FIGURE 5.



X-RAY DIFFRACTION PATTERN FOR CLAY-LIME MIXTURE CURED FOR 40 DAYS,

WASHED IN AMMONIUM CHLORIDE AND IN WATER.

FIGURE 6.

d A d-values in Angstroms	I/I_1 Relative Intensity	hkl
7.18	100	001
4.48	80_B	02-
3.58	100/	$\underline{0}02$
2.565	80	$20\underline{1}$,130
2.502	80	131,200
2.386	80	$\underline{0}03$
2.341	90_B	$20\underline{2}$,131
2.206	10_B	$13\underline{2}$,201
1.989	40_B	203,132
1.789	40	$\underline{0}04$
1.666	50_B	$20\underline{4}$,133
1.541	10_B	134,$20\underline{3}$
1.488	100	$06\underline{0}$,$33\overline{1}$
1.458	30_B	332,061 330
1.432	20	$\underline{0}05$
1.375	10_B	$33\overline{3}$,062 331
1.339	10	$13\overline{5}$
1.310	10_B	$\underline{2}04$
1.287	30	$26\underline{1}$,$40\overline{1}$
1.265	10	334,063 $33\underline{2}$
1.249	5	$26\underline{2}$,400
1.236	30_B	403,261
1.194	10	006

Table I

X-RAY DIFFRACTION DATA

FOR THE MINERAL KAOLINITE ($(OH)_4Al_2Si_2O_5$)

(TAKEN FROM A.S.T.M. CARDS)

d A d-values in Angstroms	I/I_1 Relative Intensity	hkl
4.90	74	001
3.112	23	100
2.628	100	101
2.447	3	002
1.927	42	102
1.796	36	110
1.687	21	111
1.634	1	003
1.557	3	200
1.484	13	201
1.449	13	112 103
1.314	8	202
1.228	1	004
1.211	1	113
1.1762	3	210
1.1432	11	211 104
1.1275	2	203
1.0599	12	212
1.0366	5	300
1.0143	7	301 114
0.9551	4	302 213
.9369	1	105
.8979	1	220

Table II

X-RAY DIFFRACTION DATA

FOR THE MINERAL CALCIUM HYDROXIDE ($Ca(OH)_2$)

(TAKEN FROM A.S.T.M. CARDS)

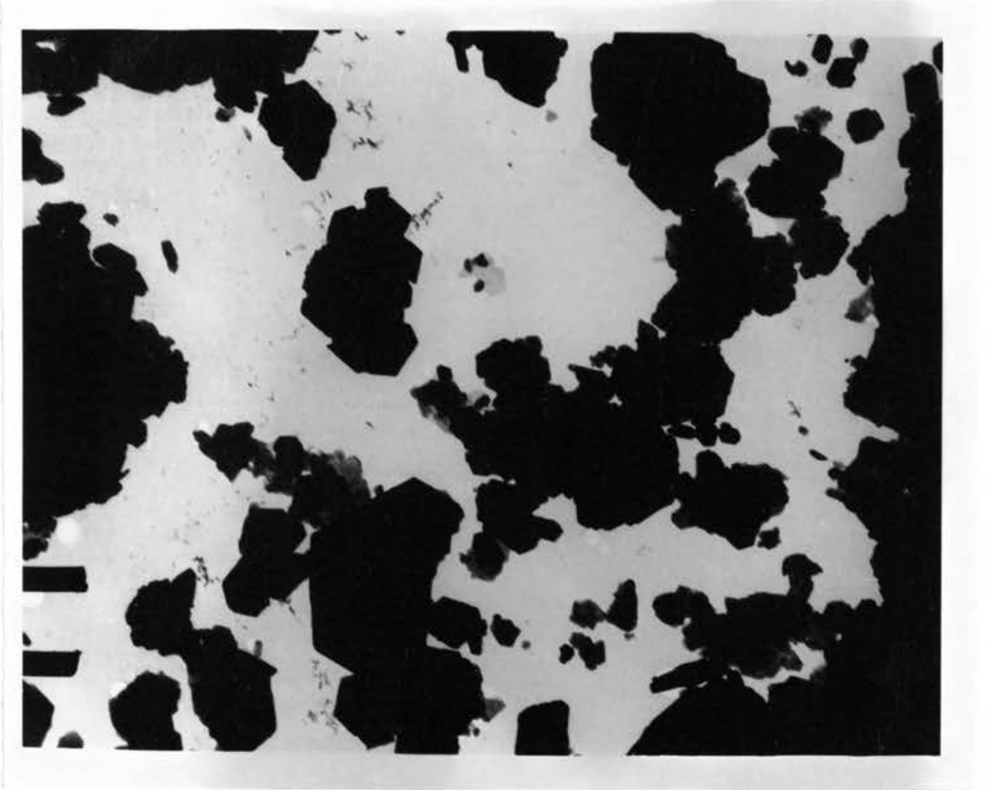
d A d-values in Angstroms	I/I_1 Relative Intensity	hkl
3.86	12	102
3.035	100	104
2.845	3	006
2.495	14	110
2.285	18	113
2.095	18	202
1.927	5	204
1.913	17	108
1.875	17	116
1.626	4	211
1.604	8	212
1.587	2	1.0.10
1.525	5	214
1.518	4	208
1.510	3	119
1.473	2	215
1.440	5	300
1.422	3	0.0.12
1.356	1	217
1.339	2	2.0.10
1.297	2	218
1.284	1	306
1.247	1	220
1.235	2	1.1.12
1.1795	3	2.1.10
1.1538	3	314
1.1425	1	226

Table III

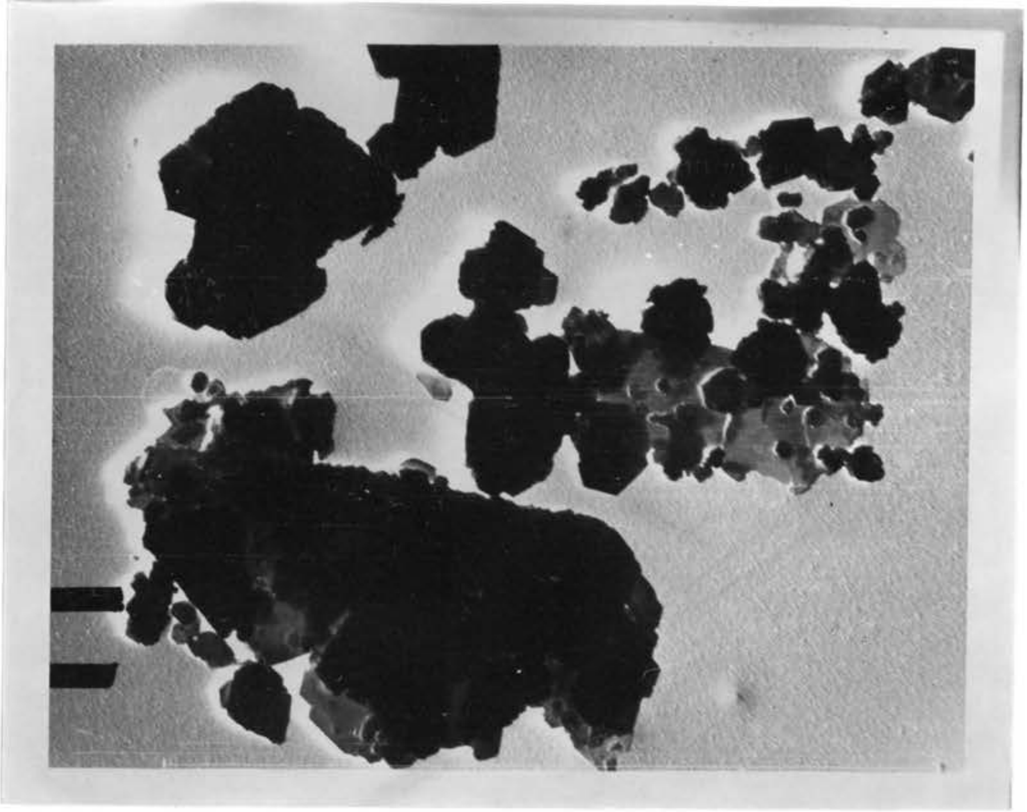
X-RAY DIFFRACTION DATA

FOR THE MINERAL CALCIUM CARBONATE ($CaCO_3$)

(TAKEN FROM A.S.T.M. CARDS)

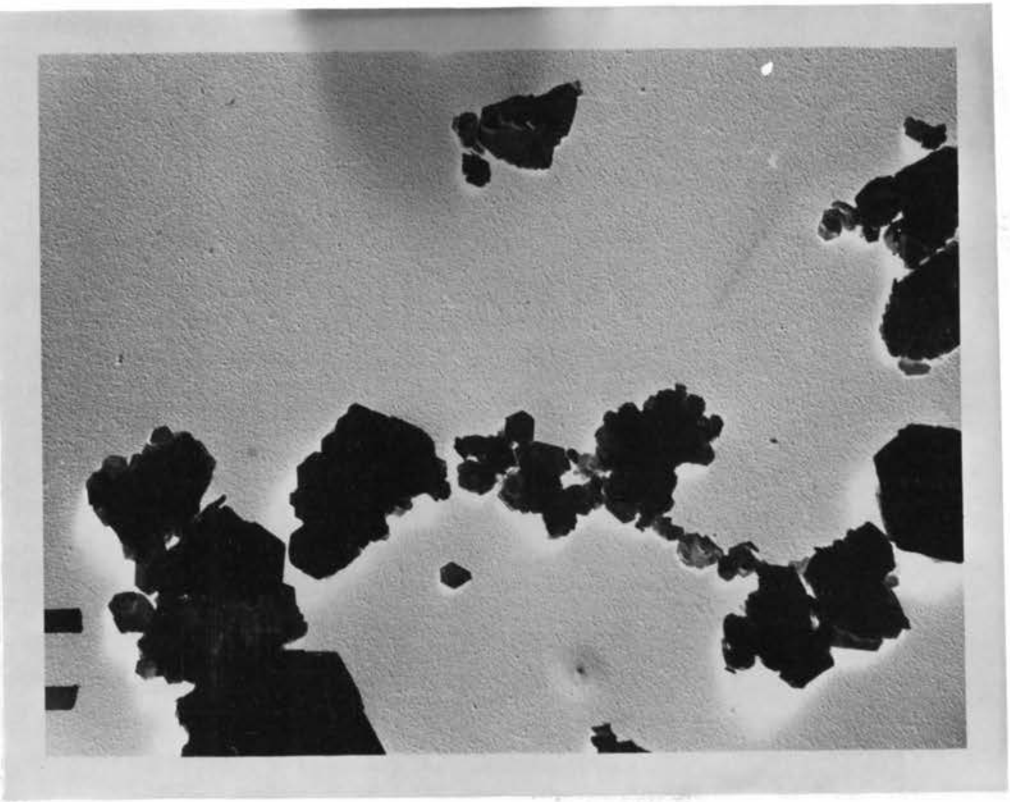


KAOLINITE BEFORE TREATMENT

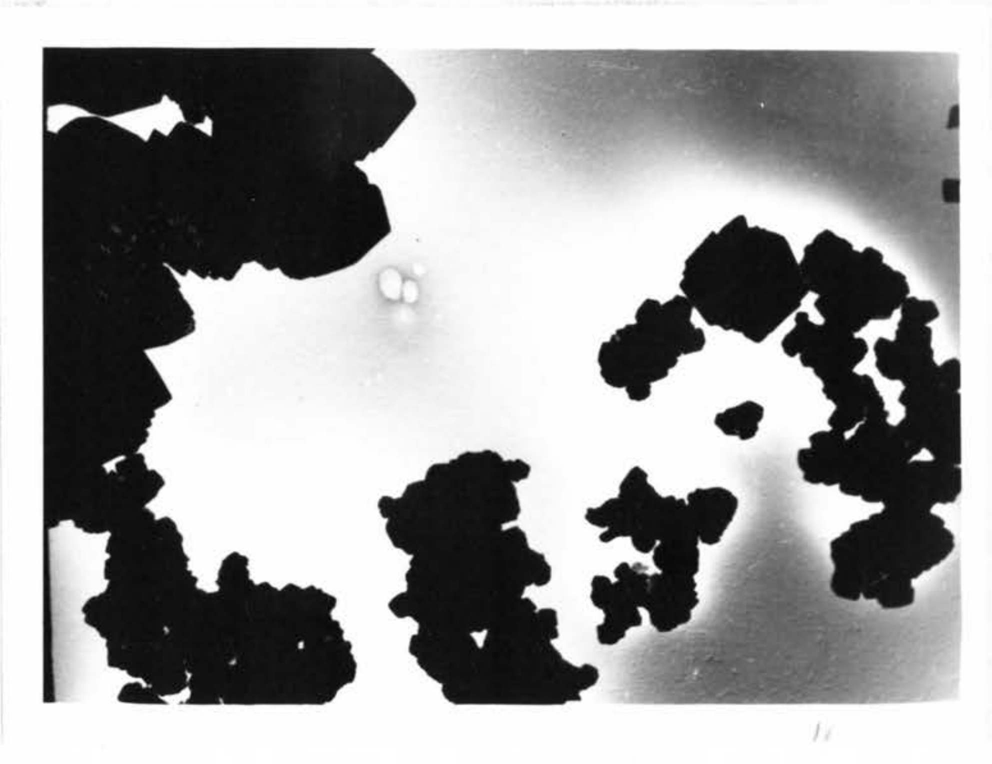


KAOLINITE AFTER TREATMENT WITH LIME FOR 20 DAYS.

ELECTRON MICROGRAPHS - FIGURE 7.

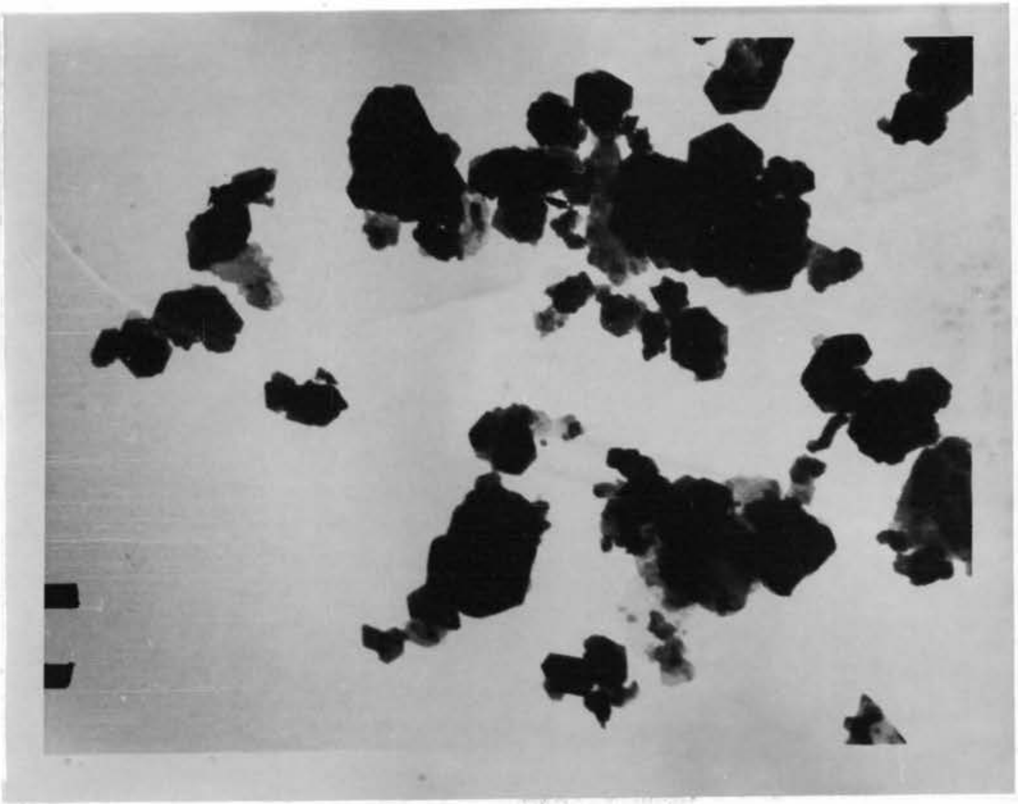


KAOLINITE BEFORE TREATMENT

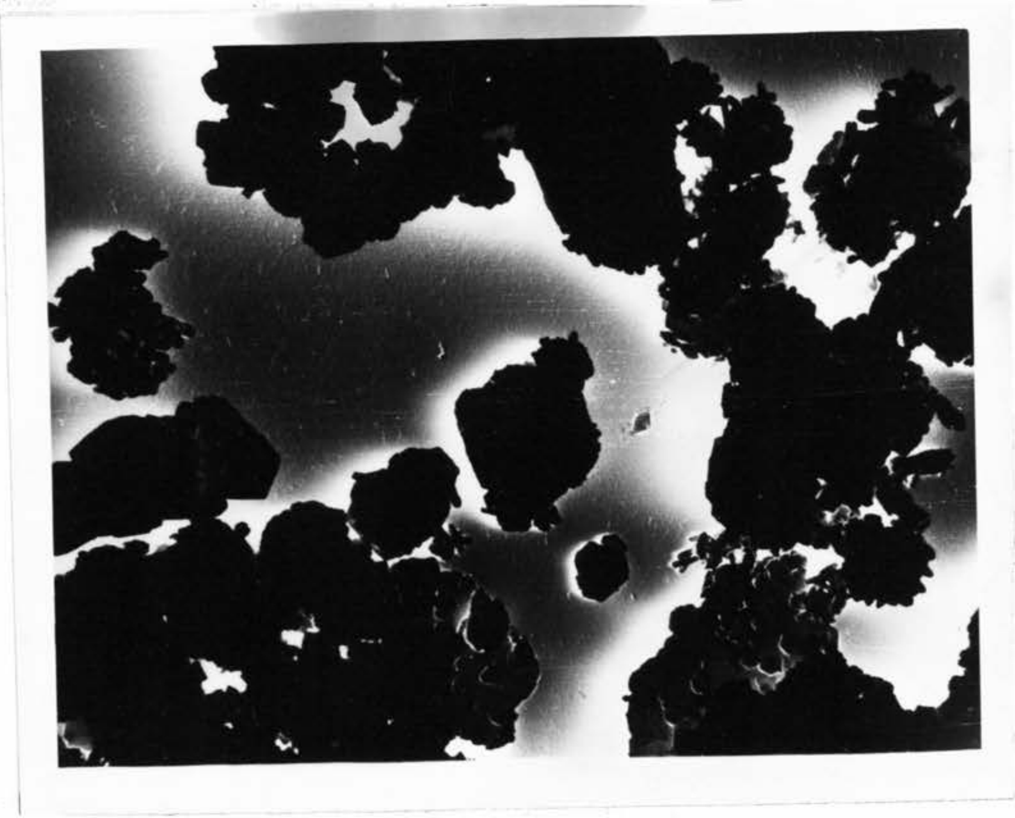


KAOLINITE AFTER TREATMENT WITH LIME FOR 20 DAYS.

ELECTRON MICROGRAPHS - FIGURE 8.

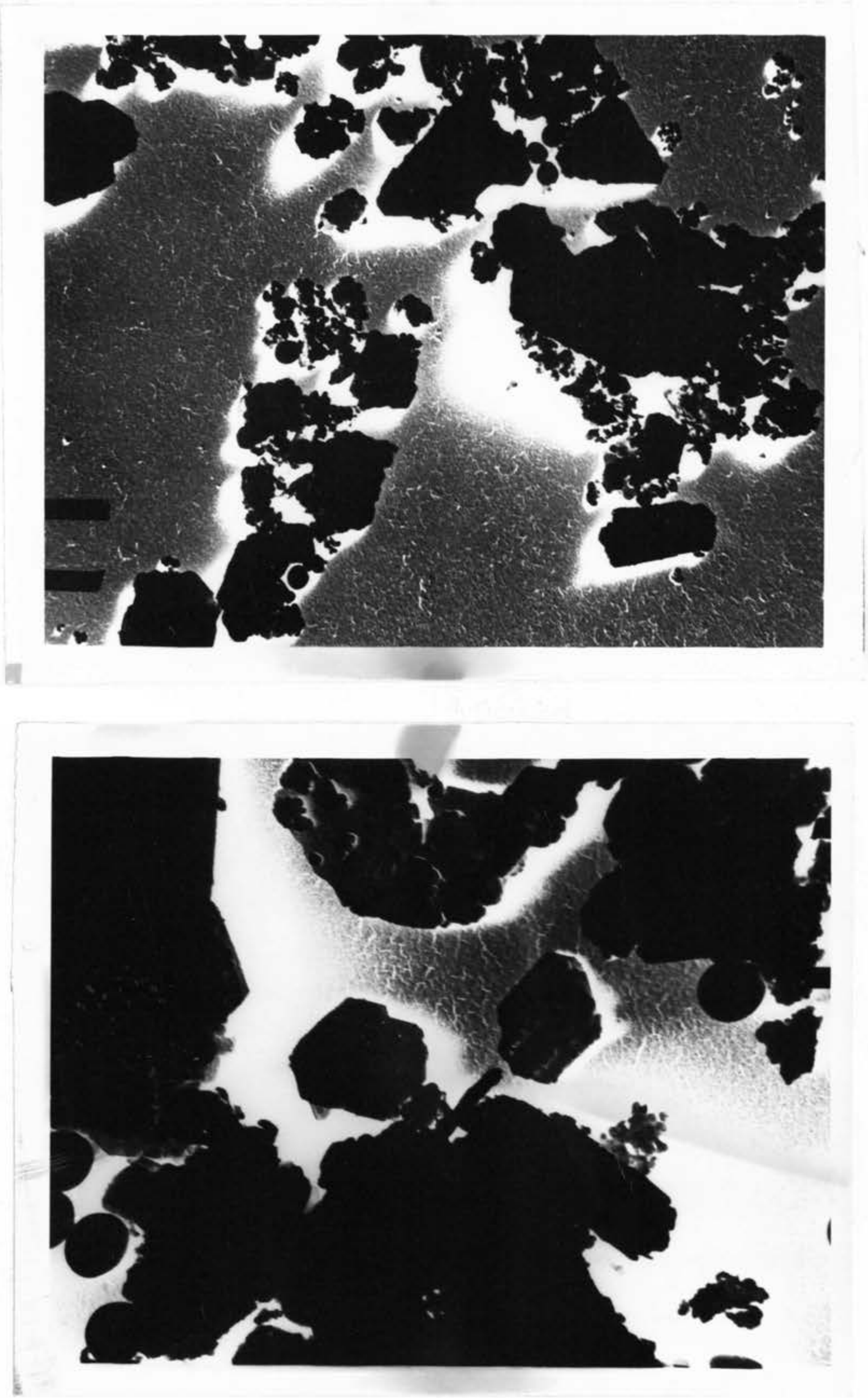


KAOLINITE BEFORE TREATMENT



KAOLINITE AFTER TREATMENT WITH LIME FOR 20 DAYS.

ELECTRON MICROGRAPHS - FIGURE 9.



KAOLINITE AFTER TREATMENT WITH LIME FOR 20 DAYS. WASHED IN NH_4Cl.

ELECTRON MICROGRAPHS - FIGURE 10.

VIII. DISCUSSION OF THE RESULTS AND CONCLUSION

The X-ray diffraction pattern obtained for the clay lime mixture for zero days curation showed peaks representing the Kaolin crystal and calcium hydroxide crystal. There was a small peak indicating the presence of calcium carbonate, which may be present in the calcium hydroxide used for the experiment. Calcium carbonate may have formed due to the absorption of carbon dioxide from the atmosphere by the calcium hydroxide when exposed to air.

Comparing the X-ray diffraction pattern obtained for one day curation with the diagram for zero days, it was found that the pattern of one day curation was very similar to the pattern obtained for zero days curation even though a small difference was observed in the peak values. The primary difference observed was a reduction in certain peak values, as can be verified from Figure 2. The X-ray pattern obtained for the 3 days curation was a similar curve, but the reduction in peak values was considerable compared with the pattern obtained for one day curation. A similar pattern was obtained for the sample cured for 6 days. As the X-ray pattern might show some difference of intensity in peak values (depending upon the difference in particle size of the sample used, difference in supply voltage response of the Geiger counter tube etc.) it was impossible to infer that there was a chemical reaction between clay and lime resulting in the formation of any silicates or any other material. Grim and Eades (3) explained that the difference of intensities in peak values is due to the formation of calcium silicates. Since no definite sign was observed, it should be concluded that the reduction of intensity in the peak values was due to the use of crystals of different sizes varying from one micron to five microns, or due to the varying supply voltage, or due to the error inherent in the machine.

The above conclusion was subsequently found to agree favorably with the following X-ray diffraction patterns of the samples cured for 12, 20, 40, and 60 days (see Figures 3 and 4). Even though all these patterns showed some slight differences in the peak values, it was observed that the X-ray pattern of the sample cured for 60 days was similar to the original pattern obtained for zero days curation. The above diagram definitely shows that there is no chemical reaction between clay and lime and no new formation of silicates or other material. It should be concluded that there may not be any crystalline silicate formation due to the reaction of Kaolinite with calcium hydroxide even under high concentration of lime, up to 50 percent by weight, and prolonged reaction for 60 days.

Hence, the reaction of clay (Kaolin) with lime must be a surface phenomenon only, i.e. an aggradation of the dispersed clays, or an ion exchange, the calcium ions being exchanged for the hydrogen ions in the diffuse layer of the clay crystal. Because of this surface reaction on the clay particles, a yellow gelatinous precipitate was formed in the mixed solution of carbon tetrachloride and tetrabromoethane. This yellow precipitate prevented the mechanical separation of the clay from the lime by the centrifuge machine rotating at 600-700 r.p.m. for about 6 minutes.

The nature of the X-ray diffraction pattern obtained for the sample cured for 40 days, washed in a concentrated solution of ammonium chloride and finally in water and oven dried, also strongly supported the above conclusion. The diagram shows peaks representing Kaolin clay and calcium carbonate only. Except for the predominance of the calcium carbonate crystals and the disappearance of the calcium hydroxide crystals, there was no sign of any new crystalline phase. The formation of calcium carbonate might be due to the absorption of carbon dioxide from the atmosphere while the clay lime mixture was exposed to the air. The calcium carbonate crystals did not dissolve in the ammonium chloride solution. Consequently the diagram indicates the presence of calcium carbonate.

Electron micrographs of the Kaolin clay sample ranging in size from one micron to five microns, taken before treatment with lime, show a few perfect crystalline hexagonal phases as shown in Figures 7, 8, and 9, in the midst of certain irregular crystals. The clay lime mixture after 20 days of curation and oven dried at 100° F, was also photographed in the electron microscope, and the photographs as shown in Figures 7, 8, and 9 were obtained. These photographs also show some perfect crystalline phases almost identical to the pictures taken before the addition of lime. There is no sign of any corner erosion or accumulation of any material on the surface or edges of the clay crystals. A comparison of these two photographs again supports the conclusion that the clay lime reaction is only a surface phenomenon, and there is no observed chemical reaction between Kaolin clay and lime.

Photographs of the sample of clay lime mixture cured for 40 days, washed in concentrated solution of ammonium chloride and in water, were also taken in the electron microscope. It was observed that the pictures of these samples were almost identical with the former pictures of the pure Kaolin crystals. Hexagonal crystalline edges were also seen in those pictures, thus supporting the above conclusion.

There is very good scope for further research concerning the reaction of clay minerals, such as montmorillionite and illite, etc. with hydrated lime. The above investigation is restricted to the reaction of Kaolinite clay with lime. Considerable work in this field of research will be essential for obtaining valuable information for further development of stabilization of clayey soil with hydrated lime.

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In August 1959, he was selected by the Government of India for higher studies in the United States of America under the International Cooperation Administration Program. He came to the Missouri School of Mines and Metallurgy, Rolla, in September 1959, and pursued a course of study leading to the Master of Science degree in Civil Engineering.