Proc. of JSCE
No. 192, Aug., 1971

INFLUENCE OF EXCHANGEABLE CATIONS (Na^+, Mg^{++}, Ca^{++}) HELD ON BENTONITE ON THE BENTONITE-CEMENT INTERACTION

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I. INTRODUCTION

As previously revealed by the authors[1], in clay-cement mixture (especially, montmorillonitic clay-cement mixtures), ion exchange proceeds between montmorillonite and cement hydration products until the montmorillonite is finally saturated with Ca ions as far as sufficient Ca ions are supplied. Therefore, cations held on the original bentonite sample should have a certain effect on the physicochemical process in the clay mineral hydrating cement interaction. Especially, it may be presumed that the cation held on an original clay mineral has an important effect on the formation of CSH (gel), further on the strength development of the compacted clay-cement mixtures.

Various cations are held on the soils to be stabilized with cement. Thus, it may be one of the significant problem to be revealed what cations held on soils are favorable to the strength development of soil-cement mixtures. In this paper, the effect of such exchangeable cations on the bentonite-cement interactions is discussed by the use of the experiments such as X-ray diffraction, differential thermal analysis, pH test and unconfined compression test. An alteration in the fabric of the bentonite-cement mixture with curing time is also estimated from the change in the basal spacing of montmorillonite included in the Na-bentonite-cement mixture.

II. MATERIALS AND OUTLINE OF EXPERIMENTS

1. Experiments

(a) X-ray diffraction, (b) Differential thermal analysis, (c) pH test, (d) Unconfined compression test.

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2. Materials and Preparation of Samples

(1) Cement

Cement used is the normal portland cement. Chemical compositions of the cement are given in Table 1.

(2) Clay Mineral Samples

Mg-bentonite (MB) and Ca-bentonite (CB) are supplied by the Kanto Bentonite Co. and Kunimine-kokakogyo Co., respectively. Na-bentonite (NB) is obtained by exchanging Mg ions in Mg-bentonite (MB) for Na ions through the process described later. Kaolinite from Hiraki, Hyogo Prefecture is made under 105 μ by grinding the rock.

The predominant clay and non-clay minerals contained in samples and their physical properties are presented in Table 2. The chemical compositions and cation exchange capacity of these clay samples are also shown in Table 3. The method employed for determination of cation exchange capacity is Yoshida et al's method which is based on Schollenberger's method[2]. That is to say, a clay sample is allowed to be saturated with ammonium. The ammonium is replaced by sodium cations using 10

Table 1 Chemical Compositions of Cement

Cement		Normal Portland Cement
SiO_2	(%)	22.2
Al_2O_3	(%)	5.4
Fe_2O_3	(%)	3.2
CaO	(%)	64.7
MgO	(%)	1.2
SO_3	(%)	1.6
Ig. Loss	(%)	0.5
Insol.	(%)	0.1
Total	(%)	99.0
C_3S	(%)	49
C_2S	(%)	27
C_3A	(%)	9
C_4AF	(%)	10

Table 2 Physical Properties

Properties	Mg-bentonite	Ca-bentonite	Na-bentonite
Size Ranges :			
>74 μ (%)	0	0	0
74-5 μ (%)	17	21	22
<5 μ (%)	83	79	78
L.L. (%)	328	420	443
P.L. (%)	41	34	48
P.I.	277	386	395
Maximum Dry Density (g/cm³)	1.015	1.345	—
Optimum Moisture Content(%)	50.0	35.0	—
Predominant Clay and Non-clay Minerals	montmorillonite cristobalite	montmorillonite quartz	montmorillonite cristobalite

Table 3 Chemical Compositions and Cation Exchange Capacity

	Mg-bentonite	Ca-bentonite	Na-bentonite
SiO_2 (%)	70.98	70.93	71.48
Al_2O_3 (%)	16.41	13.01	15.02
Fe_2O_3 (%)	1.92	2.07	1.60
CaO (%)	0.56	1.90	0.28
MgO (%)	2.17	0.34	0.06
Na_2O (%)	0.15	0.15	4.90
K_2O (%)	0.23	0.24	0.71
Cation Exchange Capacity (meq./100 g)	73	68	—

percent sodium chloride solution and the amount of ammonium replaced is determined by the colorimeter.

The Na-bentonite (NB) sample used is obtained through the following process, which is based on the method of the determination of cation exchange capacity described above.

2 *l* of a 1 N ammonium acetate solution (pH 7) are added to 200 g of Mg-bentonite (MB) sample and filtered using a funnel for about 10 hours. The excess ammonium acetate remaining in the clay sample, after the filtration, is removed using 1 *l* of 80 percent methyl alcohol (the first grade reagent). Ammonium ions are leached out by filtrating 2 *l* of 10 percent sodium chloride solution through the ammonium-saturated clay for about 10 hours, producing the Na-bentonite sample. Finally, extra salts

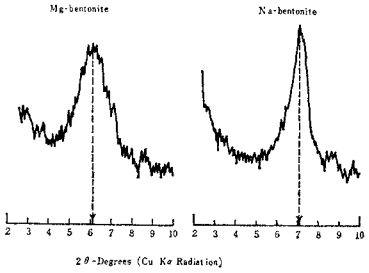


Fig. 1 (001) peak of montmorillonite in Mg- and Na-bentonite

are leached out using 2 *l* of 80 percent methyl alcohol. The Na-bentonite sample obtained is dried in a constant temperature oven held at 30°C and ground in a ball mill to pass the 74 μ sieve. The (001) peak in X-ray diagram of montmorillonite in the bentonite after the treatment stated above is found at 12.6 Å, while that in Mg-bentonite at 15 Å (Fig. 1). This fact proves that the predominant component in the bentonite is Na-montmorillonite. The change of Mg-bentonite to Na-bentonite is proved by the chemical composition as well, as given in Table 3.

Water used is distilled water.

(3) The Amount of Cement and the Curing Time of Specimens

The cement contents selected are 10, 20 and 30 percent by weight of dry clay mineral samples. Each experiment is carried out for specimens cured for 3, 7, 14, 28, 91, 182 and 364 days.

(4) Procedure

(a) Unconfined compression test

Air-dried minerals and cement are first mixed and followed by the addition of the distilled water and the subsequent mixing by hand until an uniform specimen is obtained. Cylindrical specimens, which are 5 cm in diameter and 10 cm high, are compacted statically by an oil jack so as to equal the optimum moisture content and maximum dry density of each clay-cement combination. However, those for Na-bentonite-cement mixtures are made under the same moisture content and maximum dry density as Mg-bentonite-cement mixtures. Specimens sealed by paraffin wax are cured at 20°C under a 85 percent relative humidity. The loading speed at the compression test is 0.2 kg/cm²/sec. Each type of specimens are made in triplicate; the compressive strength is their average.

(b) pH test

The pH value for each sample is the abration pH, which is measured by a glass electrode pH meter (manufactured by Toadempakogyo Co.) for filtrate prepared by the following procedure: Ten grams of the ground specimens to pass the 74 μ sieve are mixed with 50 cc distilled water with an electric stirrer for 10 minutes. The suspension is filtered immediately.

(c) X-ray diffraction

The samples ground in a mortar are examined by an X-ray diffractometer, "Geigerflex" of Rigakudenki Co., under the following measuring conditions.

Target : Cu, Filter : Ni, Voltage : 30 kV, Current : 15 mA, Scale factor : 2, Time constant : 8, Multiplier : 0.8, Scanning speed : 2°/min, Divergency slit : 1°, Scattering slit : 1°, Receiving slit : 0.15 mm, Chart

speed : 1 cm/min.

(d) Differential thermal analysis

The same ground sample as those for X-ray diffraction are used for differential thermal analysis. A "Derivatograph", manufactured in Hungary, equipped with a single-unit platinum blok with platimun-rhodium thermocouples is used at the heating rate, 10°C/min., with 1 000 mg sample. Calcined aluminum oxide is used as the reference material.

III. RESULTS AND DISCUSSIONS

(1) X-ray Diffraction

The basal spacing of montmorillonite in the Na-bentonite-cement mixture changes with curing time, as shown in Fig. 2. The X-ray diffraction experiments were made for the samples with the moisture content equilibrated at room conditions. Such samples were prepared as follows :

The original samples with optimum moisture content (about 40 percent) were dried in a vaccum desiccator at room temperature of about 15°C for about 8 hours and left in a room atmosphere.

As to the relationship between the degree of the calcium saturation of montmorillonite and its basal spacing, Lagulos and Handy state as follows[3] : "The basal d-spacing of montmorillonite reflects the amount of interlayer water. Previous investigators have reported the tendency for a sodium montmorillonite to retain one layer of water between the mineral sheets when dried under room conditions, and the tendency for calcium montmorillonite to retain two layers. This is essentially true for sample 1 (the percent calcium saturation : 19.4%) and 5 (the

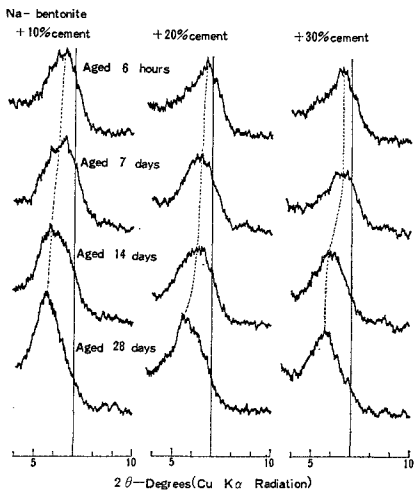


Fig. 2 (001) peaks for Na-bentonite+30, 20 and 10 % cement samples cured for 6 hours, 7, 14 and 28 days

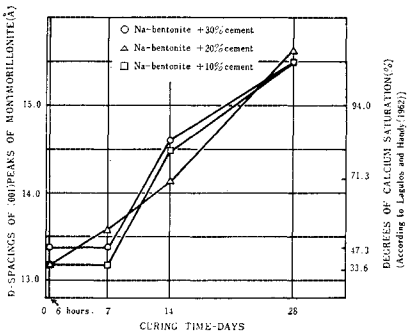


Fig. 3 Changes in d-spacings of (001) peaks of montmorillonite in Na-bentonite+30%, 20 % and 10% cement samples with curing time

percent calcium saturation : 94.0%) equilibrated at 50 percent relative humidity, the basal d-spacings being 12.6 Å and 14.9 Å, respectively. Of particular interest is that the intermediate sample show intermediate spacings according to $d=0.031\,Ca+12.0$ in which Ca is the percent calcium saturation".

The Na-bentonite sample produced by exchanging Mg^{++} in the Mg-montmorillonite for Na^+ shows its basal reflection at 12.6 Å (Fig. 1). Considerably broad (001) peaks at 7 and 14 days ages, as shown in Fig. 2, appear that various peaks ranging that at 12.6 Å to 15 Å overlap one another. This may indicate that montmorillonite in the specimens at 7 and 14 days ages are varied in the degree of the calcium saturation. That is to say, the clay-cement mixtures compacted under a very limited moisture content such as optimum moisture content have an non-homogeneous structure in the respect of the degree of the calcium saturation, when the diffusion of Ca ions progresses only to an insufficient extent. However, the X-ray diagram of the 28 days age sample has the sharp (001) peak at 15.5 Å, indicating that the complete transformation of the original Na-montmorillonite to the calcium one extends over the interior of the specimens at the end of 28 days curing. Plots of the d-spacing of the (001) peak against curing time are given in Fig. 3. The scale of the percent calcium saturation in Fig. 3 is noted according to Lagulos and Handy's formula described above.

(2) Unconfined Compression Test

The strength vs. curing time curves for three types of bentonite-cement mixtures are plotted in Fig. 4, Fig. 5 and Fig. 6. The characteristic of the strength gain of bentonite-cement is found to vary with cations held on the original bentonite samples used.

It may be impossible to compare the strength development characteristic of the Ca-bentonite-cement mixtures with other two types of Na- and

Mg-bentonite-cement mixtures, because the physical properties and mineral compositions of the Ca-bentonite sample are somewhat different from those of Na- and Mg-bentonite.

The lower compressive strength of Ca-bentonite-cement mixtures may be due to the poorer reactivity in the $Ca(OH)_2$-bentonite interaction and/or to the slower progress in cement hydration in the mixture, as expected from the pH tests results to acertain extent.

The effect of exchangeable magnesium and sodium ions held on the bentonite on the strength development may obviously be characterized by the relationship between the cement content and strength at 91 days age; the compressive strength of the Mg-bentonite-30% cement mixtures at 91 days age is

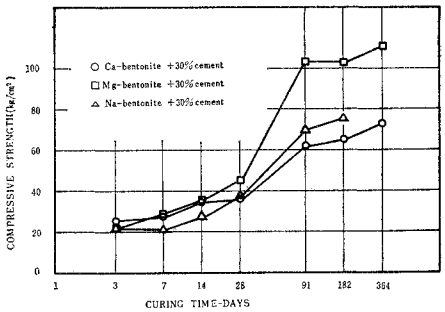


Fig. 4 Variation of compressive strength with curing time in Na-, Mg- and Ca-bentonite +30% cement mixture

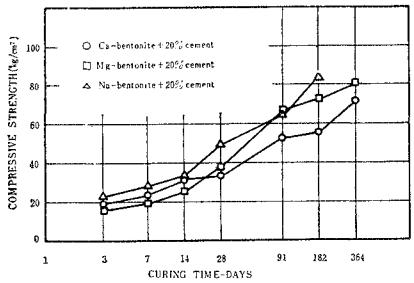


Fig. 5 Variation of compressive strength with curing time in Na- Mg- and Ca-bentonite+20% cement mixture

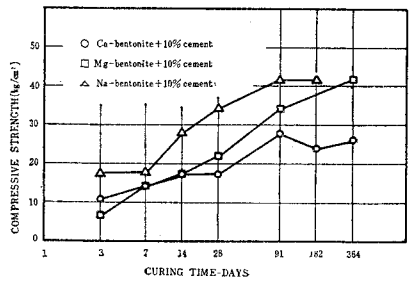


Fig. 6 Variation of compressive strength with curing time in Na-, Mg- and Ca-bentonite+10% cement mixture

markedly greater than that of the Na-bentonite-30% cement mixture; on adding 20 percent cement, there is a little difference between them; contrary to 30% cement content specimens, the addition of 10 percent cement gives the Na-bentonite-cement greater strength than the magnesium one (Fig. 4, Fig. 5 and Fig. 6). Such greater strength of the Na-bentonite-cement mixtures at the low cement content may be due to the effect of the coarsened clay grains produced as a result of the cation exchange treatment. Since such "new" grains may be capable of withstanding mechanical dispersion to a certain extent, they should behave themselves like silt particles. As cement hydration proceeds, sodium and magnesium ions originally retained on the bentonite must be exchanged by calcium ions. Especially, it is evidenced by the X-ray diffraction test that the Na-montmorillonite in the Na-bentonite-cement is almost completely changed to the Ca-montmorillonite during the 28 days curing (Fig. 2). Thus, the amount of $Ca(OH)_2$ consumed by the cation exchange and the behavior of sodium or magnesium ions substituted by calcium ions should greatly affect the strength development of the bentonite-cement mixtures. As to the former, more $Ca(OH)_2$ certainly seem to be consumed in sodium-bentonite-cement than in magnesium-bentonite-cement, because the replacing power of the common ions is $Li < Na < NH_4 < K < Mg < Rb < Ca < Co < Al$[4]. Concerning the latter, the possibility of the substitution of silicon by magnesium in the tobermorite lattice could be expected. Such an effect of Mg ions would favor the strength of the bentonite-cement. In this respect, it is much interesting to note the following statement for the reaction in the $Ca(OH)_2$-MgO-bentonite system:[5] "A possibility in that large amounts of magnesium ions have entered the tobermorite structure and thus made more calcium ions available for further pozzolanic reactions". A great difference in the strength between the Na-and Mg-bentonite-cement mixtures at 91 days age could be explained by two effects described above.

All Na-bentonite-cement specimens gain strength even before 28 days curing. This strength development appears to contradict with the concept of retention point, since, before 28 days curing, montmorillonite in the Na-bentonite-cement mixtures is considered not to attain a retention point beyond which further $Ca(OH)_2$ liberated is consumed by the pozzolanic reaction contributing to strength gain. However, as stated in the X-ray diffraction results, the degree of the calcium saturation of montmorillonite in the Na-bentonite-cement specimens at 3, 7 and 14 days ages is non-homogeneous through over the interior of the specimens. Therefore, even at the

ages until 28 days, a part of the montmorillonite in the Na-bentonite-cement may participate in the pozzolanic reaction with $Ca(OH)_2$ through the calcium saturation and subsequent attainment of a retention point. Naturally, calcium silicate hydrate resuteing from cement hydration also serves the strength development.

(3) pH Tests

Fig. 7 shows pH changes of Ca-, Mg- and Na-bentonite-cement mixture with curing time. The pH values of the Ca-bentonite-cement mixtures for every cement contents are greater than the comparable ones of the Mg- and Na-bentonite-cement mixtures, more slowly decreasing with curing time. Such higher pH values in the Ca-bentonite-cement mixtures are due to the poorer reactivity in the $Ca(OH)_2$-bentonite interaction and/or to the slower progress in the cement hydration in the mixture. Such differences between the Ca-bentonite-cement and other two mixtures would be responsible for the effect of the crystallinity of montmorillonite and non-clay minerals included in the bentonite samples ratner than for the effect of the exchangeable cations held.

(4) Differetial Thermal Analysis

Fig. 8 and Fig. 9 show the D.T.A. curves of the Ca- and Na-bentonite-cement mixtures at various ages, respectively.

The changes of the peak at about 900°C with curing time in the Ca- and Na-bentonite-cement mixtures are different from those of the Mg-bentonite-cement mixtures (Fig. 10 and Fig. 11). That is to say, the former has a large exothermic peak at about 900°C in the D.T.A. curves at all ages. On the other hand, the D.T.A. curves of the latter mixtures at 91 and 182 days curing exhibit no such a large peak found in those at 3 and 28 days ages.

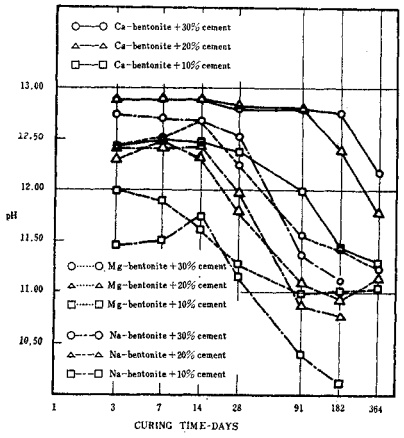


Fig. 7 pH changes of Ca-, Mg- and Na-bentonite-cement mixture with curing time

Concerning the calcium silicate hydrate synthesized in the laboratory, Kalousek and Prebus stated as follows[6]: "The 1.5 c/s sample showed a rounded exothermic peak between 880 and 910°C in the differential thermal analysis, but the 1.75 c/s product exhibited no such thermal change". Thus, the calcium silicate hydrate produced in the bentonite-cement mixtures at the initial stage of curing (until 28 days) is of the low lime-silica ratio. However, the calcium silicate hydrate with low lime content produced at the initial ages in the Mg-bentonite-cement changes to the high lime one during the long-term curing; that in the Ca- and Na-bentonite-cement mixtures remains the low lime content one even at the end of the long-term curing. Since, in the Na-bentonite-cement, a comparatively large amount of lime is consumed by the cation exchange reaction in the

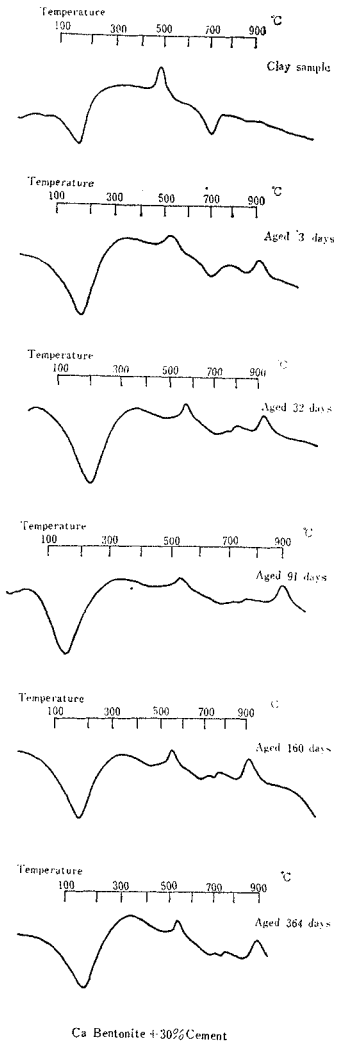
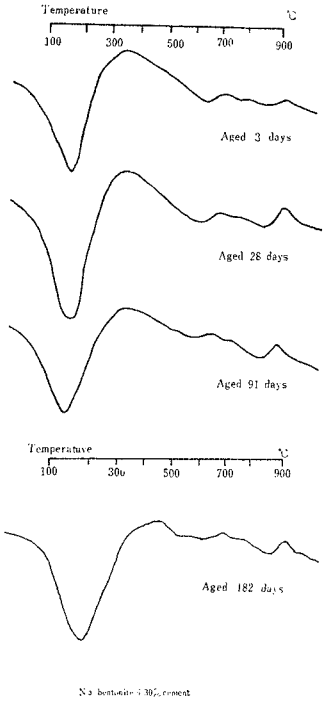
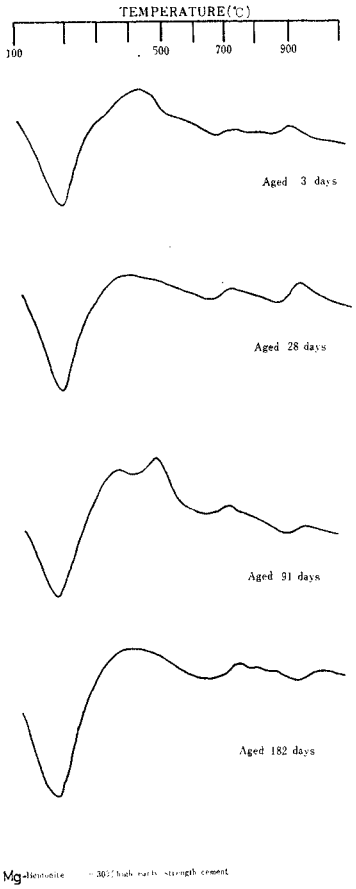


Fig. 8 D.T.A. curves for Ca bentonite+30% samples curd for 3, 32, 91, 160 and 364 days



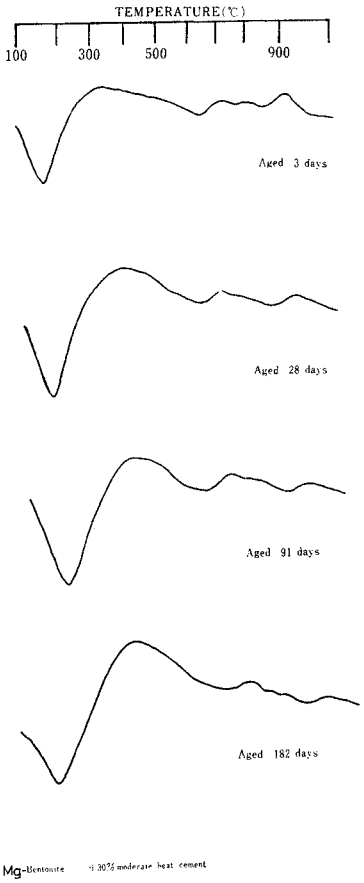
Na-bentonite+30% cement

Fig. 9 D.T.A. curves for Na-bentonite+30% cement sample cured for 3, 28 and 91 days



Mg-bentonite +30% high early strength cement

Fig. 10 D.T.A. curves for bentonie+30 % high early-strength cment samples cured for 3, 28, 91 and 182 days



Mg-Bentonite +30% moderate heat cement

Fig. 11 D.T.A. curves for bentonite +30% moderate-heat cement samples cured for 3, 28, 91 and 182 days

initial stage of curing, the amount of lime available for pozzolanic reactions occuring during the long-term curing may not be enough to convert the low lime-CSH(gel) to the high lime one.

The formation of the low lime product in the Ca-bentonite-cement mixture can not be interpreted by the effect of the exchangeable cation (Ca^{++}). This mixture may be lacking in free lime compared with the Mg-bentonite, because of the suppression of the cement hydration.

It should bear in mind that the substitution of silicon by magnesium in the tobermorite lattice takes part in the formation of the high lime-CSH(gel) by the pozzolanic reaction occuring over the long-term. Furthermore, special attention should be paid to the fact that the long-term strength of the Mg-bentonite-cement mixtures with the high lime-silica ratio-CSH (gel) is far greater than that of the Na- and Ca-bentonite-cement with the low lime-silica ratio one.

IV. SUMMARY AND CONCLUSIONS

The physicochemical reaction processes in the Mg-bentonite-cement interaction are remarkably different from those in the Na-bentonite-cement interaction. Especially, the compressive strength of the Mg-bentonite-30% cement mixtures at 91 and 182 days ages is markedly greater than that of the Na-bentonite-30% cement mixtures. Such differences may be attributed to the lime-silica ratio of CSH(gel) formed in the mixtures. The exchangeable cations (Na^{+}, Mg^{++}) held on the original bentonite greatly affect the physicochemical processes in the cement hydration and subsequent pozzolanic reactions, CSH (gel) having different lime-silica ratios being formed according to the exchangeable cations.

The results obtained are summarized as follows:

1) Clay-cement mixtures compacted under a very limited moisture content such as optimum moisture content have an non-homogeneous structure in the

respect of the degree of the calcium saturation, when the diffusion of Ca ions progresses only to an insufficient extent. The X-ray diagram of the 28 days age sample has the sharp (001) peak at 15.5 Å, indicating that the complete transformation of the original Na-montmorillonite to the calcium one extends over the interior of the specimens at the end of 28 days of curing.

2) The behavior of sodium or magnesium ions substituted by calcium ions should greatly affect the strength development of the bentonite-cement mixtures. In this respect, the possibility of the substitution of silicon by magnesium in the tobermorite lattice could be expected. Such an effect of Mg ions may favor the strength of the bentonite-cement.

3) The Ca- and Na-bentonite-cement mixtures has a large exothermic peak at about 900°C in their D.T.A. curve at all ages On the other hand, the D.T.A. curves of the Mg-bentonite-cement mixtures at 91 and 182 days ages exhibit no such a large peak found in those at 3 and 28 days ages. The calcium silicate hydrate produced in the bentonite-cement mixtures at the initial stage of curing is found to be of the low lime-silica ratio. However, such a calcium silicate hydrate changes to the high lime one during the long-term curing in the Mg-bentonite-cement; that in the Ca- and Na-bentonite-cement mixtures remains the low lime content one even at the end of the long-term curing.

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(Received Dec. 14, 1970)