

Studies on Soil Cements:
***1 - Role of Hydrated Lime and Dolomitic
Monohydrate in Montmorillonite Stabilization***

by

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ABSTRACT

Montmorillonite clay was stabilized by either hydrated lime or the dolomitic monohydrate ($\text{Ca}(\text{OH})_2 \cdot \text{MgO}$) during suspension hydration at 25 and 60°C for 45 days. The distinct phases produced from the hydration of each stabilized clay suspension were identified by means of X-ray diffraction analysis. The role of either $\text{Ca}(\text{OH})_2$ and/or MgO in soil stabilization could be clearly understood in order to extend the use of portland cement for the stabilization of montmorillonite to produce soil cements.

Introduction

The two chemicals commonly combined with soil for stabilization are cement and lime. Addition of hydrated lime to clay causes two kinds of beneficial reactions; (a) rapid flocculation due to increased calcium absorption at high pH⁽¹⁾, the amount of lime required for flocculation being dubbed the "lime retention point"; and (b) availability of lime added in excess of the lime retention point for a slow setting reaction commonly believed to be pozzolanic in nature⁽²⁾.

The pozzolanic reaction between lime and clay was not substantiated by X-ray data until 1960,^(3,4) when unidentified calcium silicate hydrates and calcium aluminate hydrate were found in various cured clay lime mixtures. Several specific compounds including 10 A tobermorite, $C_4 AH_{13}$ and monocarboaluminate were reported in 1962^(5,6); and other studies characterized the pozzolanic reaction products from lime and clay minerals.^(7,8)

In this paper, hydrated lime and dolomitic monohydrate ($Ca(OH)_2 - MgO$) were used for the stabilization of montmorillonite clay. The distinct phases produced during the suspension hydration of the stabilized clay were identified in order to clarify the role of either $Ca(OH)_2$ and / or MgO in soil stabilization. The results of physicochemical properties of the hardened soil cement pastes made from montmorillonite, by using portland cement as a stabilizer, will be presented in the next paper of this series.

Experimental

The soil used is the cured clay mineral montmorillonite; its major constituents, as determined by X-ray diffraction, are; montmorillonite, 35.59 % Kaolinite, 33.90 % and quartz, 30.50 %, respectively. The oxide composition of montmorillonite; as obtained from chemical analysis, is found to be : SiO_2 , 48.60 %; Al_2O_3 , 24.40 %; Fe_2O_3 , 5.40 %; CaO , 4.06 %; MgO , 2.60 %; TiO_2 , 0.20 %; SO_3 , 0.61 %; Na_2O 1.22 %; K_2O , 0.63 %; and ign. loss, 12.36 %, respectively.

The clay was first ground and passed through a 170 mesh B. S. sieve. Very fine $Ca(OH)_2$ and MgO (analytical grade) were used for montmorillonite stabilization.

Three series of stabilized soil suspensions were prepared as follows:—

1. $Ca(OH)_2$ - clay suspensions prepared by using various proportions of the clay and $Ca(OH)_2$ corresponding to the CaO/SiO_2 molar ratios (C/S) of

0.22, 0.45, 0.90, 1.30 and 1.80. The mixtures, thus obtained, were suspended in water for 45 days by using an initial water: solid ratio of 5 : 1. These mixtures were hydrated at 25 and 60°C and the hydrated samples obtained are designated as I.1, I.2, I.3, I.4, and I.5 corresponding to the molar C/S ratios of 0.22, 0.45, 0.90, 1.30 and 1.80, respectively. Two series of samples were thus, obtained; series "a" prepared at 25°C and series "b" prepared at 60°C. At the end of the curing period (45 days), the samples were filtered off, washed with acetone and then D - dried for 24 hours.

2. $\text{Ca}(\text{OH})_2 - \text{MgO} - \text{clay}$ suspensions prepared at a constant (C+M) / S molar ratio of 0.90 and various C / M molar ratios of ∞ , 4, 2, 1, 0.5, 0.25 and 0, respectively. The samples obtained from the suspension hydration for 45 days - after filtration, washing and D - drying - are designated as II.1, II.2, II.3, II.4, II.5, II.6 and II.7 according to the above mentioned C/M molar ratios. The sample designations include the symbols "a" and "b" for the hydration temperatures of 25 and 60°C, respectively.
3. $\text{Ca}(\text{OH})_2 - \text{MgO} - \text{clay}$ suspensions prepared by using a constant molar C/S ratios of 1.0 and various (C+M) / S molar ratios of 0.22, 0.45, 0.90, 1.30 and 1.80, respectively. The samples obtained after suspension hydration for 45 days are designated as III.1, III.2, III.3, III.4 and III.5 corresponding to the prescribed (C+M) / S ratios. The sample designations also include the symbols "a" and "b" for the hydration temperatures of 25 and 60°C, respectively.

In each D-dried clay - stabilized sample, produced from suspension hydration, the distinct phases were identified by means of X-ray diffraction analysis using the D-dried samples.

Results and Discussion

1. Clay-hydrated lime suspensions:

The results of X-ray investigations of $\text{Ca}(\text{OH})_2$ -montmorillonite mixtures, suspended in water (water/solid ratio of 5 : 1 by weight) at 25°C for 45 days, indicated the existence of calcium silicate hydrate, CSH-gel; tetracalcium aluminate hydrate, C_4AH_{13} ; hydrogarnet, $\text{C}_3\text{AS}_2\text{H}_2$ as the main hydration products in addition to the lines of $\text{Ca}(\text{OH})_2$ and silica reported in the ASTM cards (cf. Fig. 1).

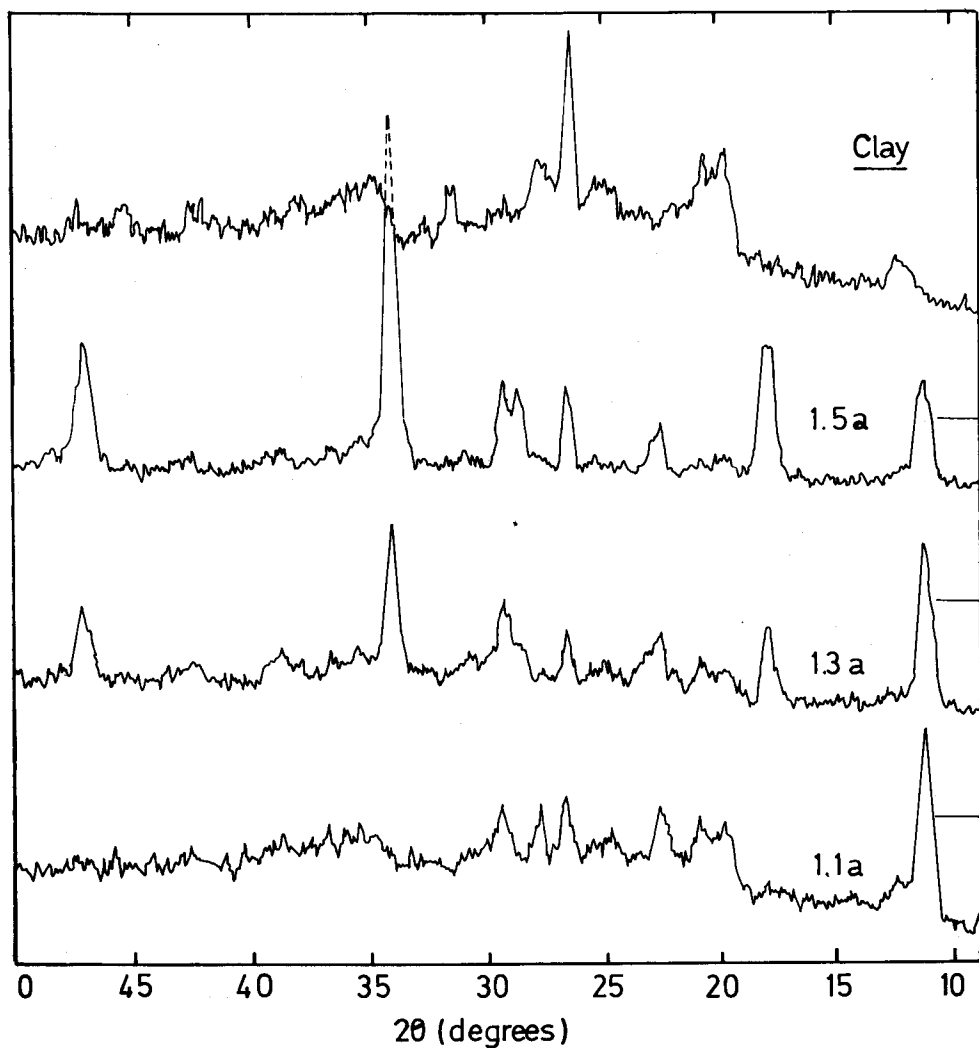


Fig. 1: X-ray diffraction patterns of $\text{Ca}(\text{OH})_2$ - montmorillonite suspensions cured at 25°C .

The X-ray diffraction pattern of calcium silicate hydrate tobermorite, is characterized by the triple peaks located at 3.07 , 2.96 and 2.80 \AA ⁽⁹⁾. In the present study the tobermorite formed through the reaction between montmorillonite and $\text{Ca}(\text{OH})_2$ is assumed to be the Al-and/or Fe-substituted phases because of the presence of large amounts of Al_2O_3 and Fe_2O_3 in the montmorillonite. The predominance of these tobermorite phases was confirmed by the weak intensity of the 2.80 \AA peak ^(6,10).

The relative amount of each phase depends mainly on the Ca(OH)_2 -content in the hydrated lime-montmorillonite mixture. The CSH-, C_4AH_{13} -, and $\text{C}_3\text{AS}_2\text{H}_2$ -contents increase with the increase in the hydrated lime-content in the original mixture. Their stabilizations become more favourable in presence of excess Ca(OH)_2 .

In addition to the hydration products mentioned above the d-lines of Ca(OH)_2 and quartz, as free constituents, were noticed in the diffraction patterns of clay and these hydrated clay- Ca(OH)_2 samples (cf. Fig. 1).

The results of X-ray investigations of stabilized hydrated lime-clay mixtures, suspended in water at 60°C for 45 days, showed the existence of the following phases at the various Ca(OH)_2 contents: tetracalcium aluminate hydrate, C_4AH_{13} ; hydrogarnet (plazolite) phase, $\text{C}_3\text{AS}_2\text{H}_2$; tobermorite-like calcium silicate hydrate, CSH; as well as free Ca(OH)_2 and free quartz.

The hydrogarnet (plazolite) phase cannot be detected using lower Ca(OH)_2 content in the stabilization of montmorillonite; and the tetracalcium aluminate hydrate phase appears only as a semicrystalline material at low Ca(OH)_2 content (cf. Fig. 2).

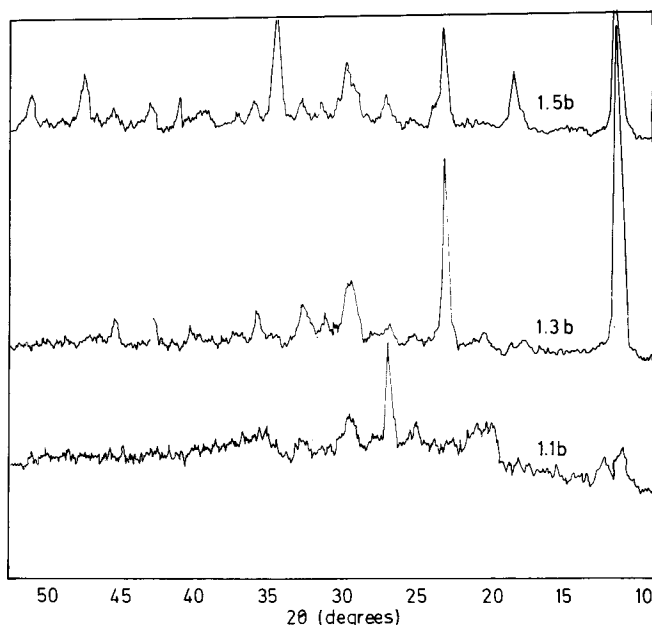


Fig. 2: X-ray diffraction patterns of Ca(OH)_2 -montmorillonite suspensions cured at 60°C .

At higher Ca(OH)_2 contents in the hydrated lime-clay mixtures, the intensities of all of the d-lines characteristic for free Ca(OH)_2 were reduced when the hydration was carried out at 60°C (samples I.1b-I.5b) as compared with the same samples when hydrated at 25°C (samples I.1a - I.5a). This indicates a higher reactivity for the reaction between Ca(OH)_2 and montmorillonite at the higher temperature (60°C). Therefore, almost all of the Ca(OH)_2 in samples (I.1b-I.3b) was consumed (cf. Fig. 2).

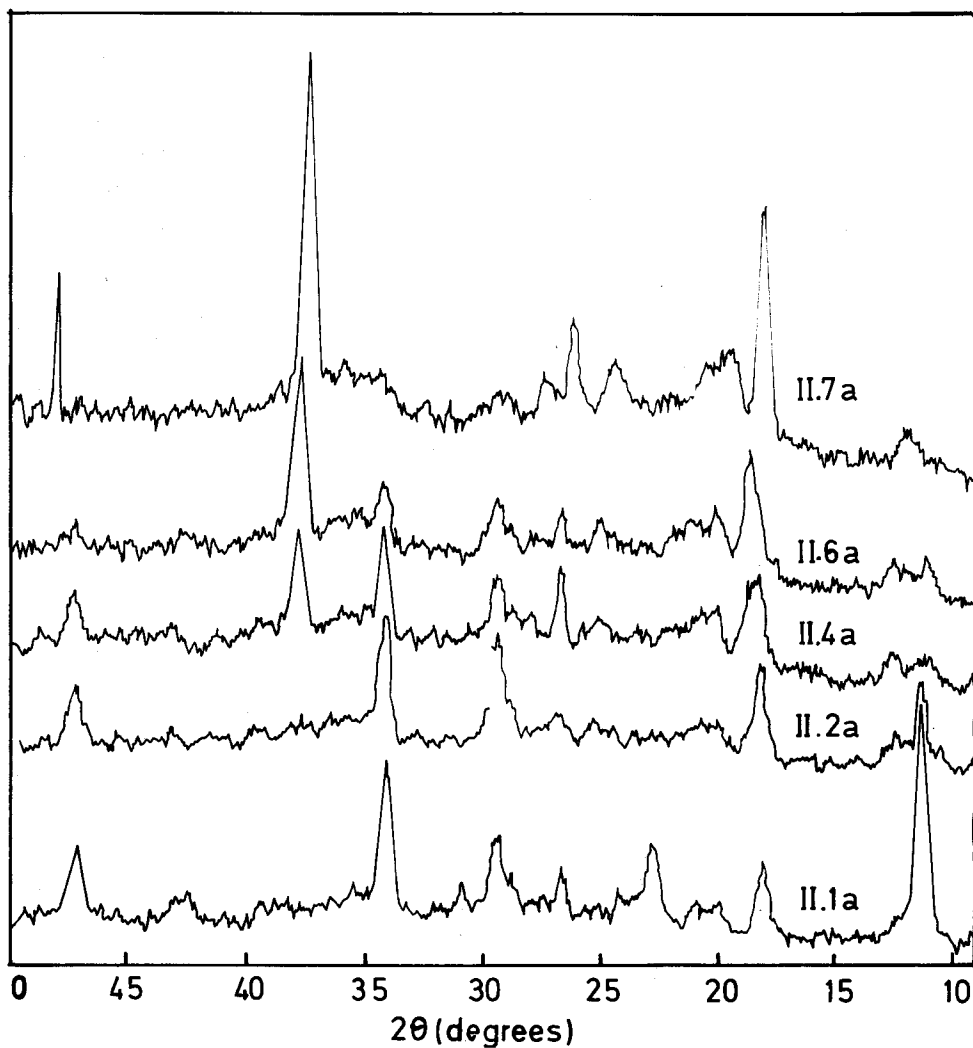


Fig. 3: X-ray diffraction patterns of Ca(OH)_2 -MgO-montmorillonite suspensions $(\text{C}+\text{M})/\text{S} = 0.90$ cured at 25°C .

2. $\text{Ca}(\text{OH})_2$ -MgO-clay suspensions at a constant molar (C+M)/S ratio:

By using a constant (C+M)/S molar ratio of 0.90 and various C/M ratios in the stabilized $\text{Ca}(\text{OH})_2$ -MgO- montmorillonite mixtures, the results of X-ray investigations indicated the formation of the same phases similar to those detected in the hydration of the $\text{Ca}(\text{OH})_2$ -montmorillonite mixtures with some interesting variations, as a result of the contribution of MgO, in the crystal structure of the hydrated phases.

For the $\text{Ca}(\text{OH})_2$ -MgO-clay mixtures hydrated at 25°C (II.1a - II.5a), the results of X-ray diffraction patterns indicated the formation of tetracalcium aluminate hydrate (C_4AH_{13}) and tobermorite like calcium silicate hydrate (CSH) as the main hydration products at higher $\text{Ca}(\text{OH})_2$ contents (samples II.1a and II.2a); all of the d-lines of free $\text{Ca}(\text{OH})_2$ and free quartz appeared also in the diffraction patterns (cf. Fig. 3). Higher MgO contents (lower C/M ratios) in the initial $\text{Ca}(\text{OH})_2$ -MgO-clay mixtures, hinder the formation of the tetracalcium aluminate hydrate phase (C_4AH_{13}) because of the decrease in $\text{Ca}(\text{OH})_2$ contents. Therefore only CSH phase was detected at higher MgO contents in the initial mixtures; the hydrogarnet-like plazolite phase ($\text{C}_3\text{AS}_2\text{H}_2$) makes its appearance in the hydration of MgO-rich mixtures in addition to the d-spacings of $\text{Mg}(\text{OH})_2$ as a free constituent during the hydration of MgO-rich suspensions (samples II.6a and II.7a).

When the same $\text{Ca}(\text{OH})_2$ -MgO-montmorillonite suspensions were cured at a higher temperature of 60°C, the formation of hydrated aluminates and hydrogarnet phases become more favourable. Therefore by using higher C/M ratios, the phases identified were tobermorite (CSH), tetracalcium aluminate hydrate (C_4AH_{13}) and hydrogarnet ($\text{C}_3\text{AS}_2\text{H}_2$) (samples II.1b-II.4b). a complete consumption of all of the $\text{Ca}(\text{OH})_2$ contents was observed in the X-ray diffraction patterns of these samples (cf. Fig. 4). The hibschite (plazolite)-like hydrogarnet phase ($\text{C}_3\text{AS}_2\text{H}_2$) becomes more dominant in addition to the tetracalcium aluminate hydrate phase (C_4AH_{13}) in samples II.1b and II.2b, rich in $\text{Ca}(\text{OH})_2$ in the starting mixtures, and disappears in samples (II.4b - II.7b) where only the CSH and the C_4AH_{13} phases were detected. Moreover the formation of the tetracalcium aluminate hydrate phase becomes more hindered in MgO-rich samples and appeared only as a semicrystalline phase in samples II.6b and II.7 b. In samples II.7b, in which only MgO is used in the stabilization of montmorillonite clay, only poorly crystalline CSH and C_4AH_{13} phases were detected (cf. Fig. 4). The d-lines of free $\text{Mg}(\text{OH})_2$ appeared only in MgO-rich samples.

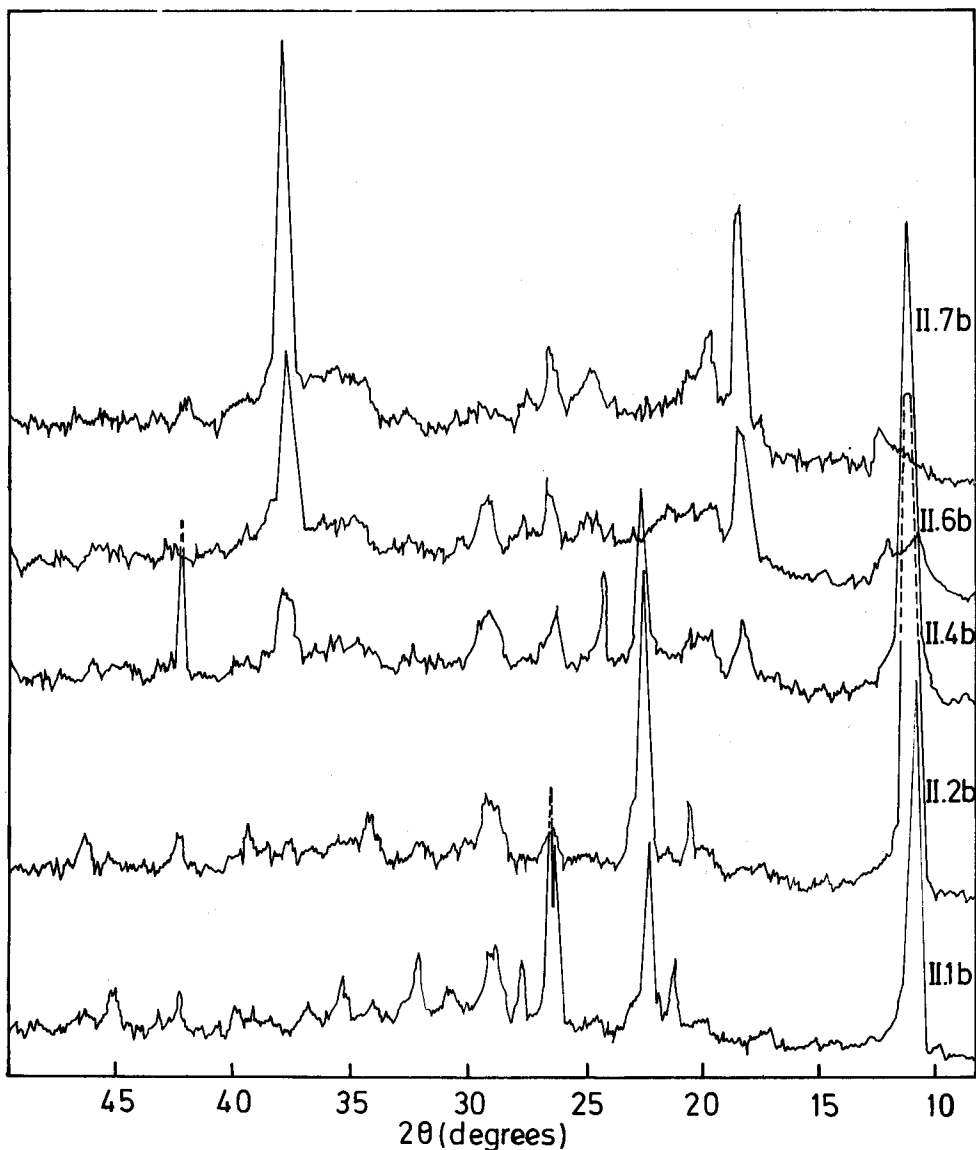


Fig. 4: X-ray diffraction patterns of $\text{Ca}(\text{OH})_2$ -MgO- montmorillonite suspensions $(\text{C}+\text{M})/\text{S} = 0.90$ cured at 60°C .

During the hydration of these $\text{Ca}(\text{OH})_2$ -MgO- montmorillonite suspensions, at 25°C and at 60°C , there is no new formation of magnesium silicate hydrated compounds. The formation of calcium silicate hydrate and calcium aluminate hydrate appears to have first priority as a result of the relative chemical activity of the $\text{Ca}(\text{OH})_2$ and MgO used in the stabilization of the montmorillonite clay.

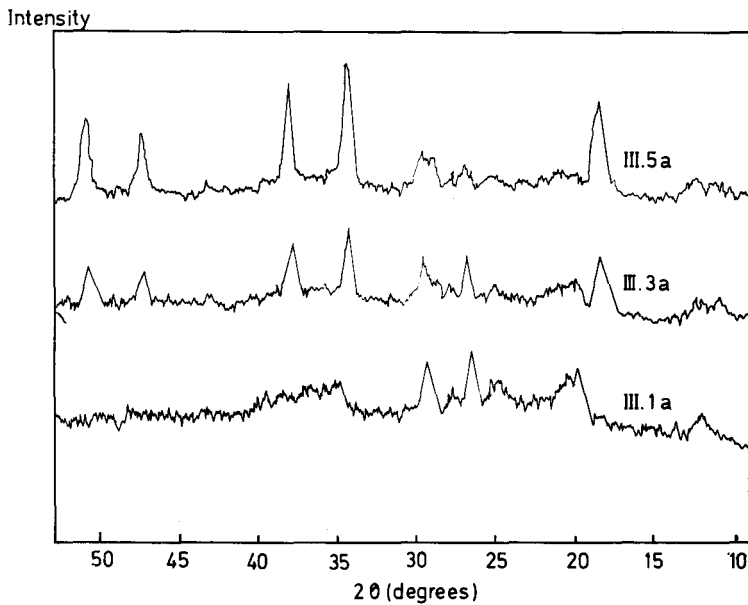


Fig. 5: X-ray diffraction patterns of $\text{Ca}(\text{OH})_2\text{-MgO}$ - montmorillonite suspensions ($C/M=1$) cured at 25°C .

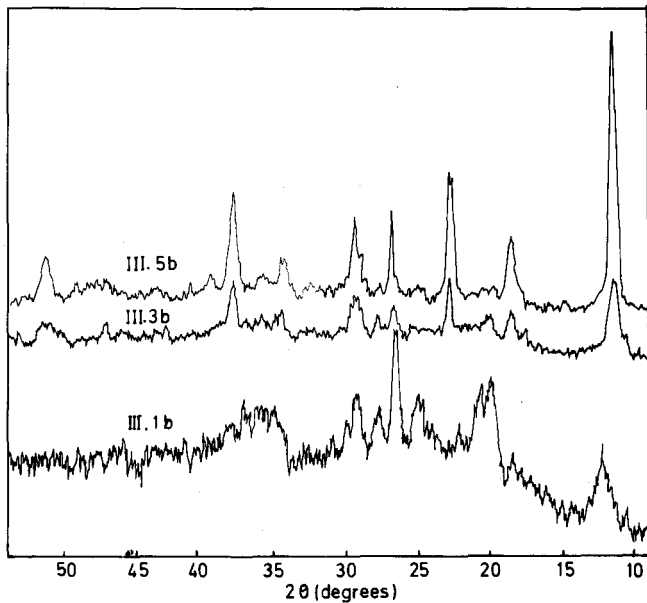


Fig. 6: X-ray diffraction patterns of $\text{Ca}(\text{OH})_2\text{-MgO}$ - montmorillonite suspensions ($C/M=1$) cured at 60°C .

3. Ca(OH)₂-MgO-clay Suspensions at a constant molar C/M ratio:

This series of Ca(OH)₂-MgO-montmorillonite mixtures was prepared by using a constant C/M molar ratio of 1.0 and various (C+M)/S molar ratios in these stabilized clay suspensions. The (C+M)/S ratio is varied from 0.22 to 1.8.

At 25°C hydration, the tobermorite-like calcium silicate hydrate was the predominant phase identified as well as the nearly-amorphous (ill-crystallized) tetracalcium aluminate hydrates (C₄AH₁₃). The d-lines of Ca(OH)₂ and Mg(OH)₂, as free phases during the hydration, appeared only at higher (C+M)/S ratios in samples. III.3a, III.4a and III.5a (cf. Fig. 5). No hibschite (plazolite) type of hydrogarnet was detected in these samples (III.1a - III.5a).

When these mixtures were hydrated at 60°C, the same CSH and C₄AH₁₃ phases were identified in the X-ray diffraction patterns with one main basic difference, namely, the crystal state (degree of crystallinity) of these hydration products becomes more obvious (cf. Fig. 6). The well crystallization of tobermorite and tetracalcium aluminate hydrate phases, in these Ca(OH)₂ - MgO - montmorillonite suspensions is mainly due to the fact that substantial amounts of magnesium ions can substitute in the structure of tobermorite and calcium aluminate hydrate phases and make more calcium available for the pozzolanic reactions. Free Ca(OH)₂ and Mg(OH)₂ appeared in the X-ray diffraction patterns of the samples richer in the (C+M) content, e.g. samples (III.3b - III.5b).

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« دراسات على أسمنت التربة »

١ - دور الجير المتأدرت والدولوميت أحادى التأدرت في استقرار طفلة المونتموريللونيت

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ملخص

أجريت دراسة استقرار طفلة المونتموريللونيت أما بإضافة الجير المتأدرت (هيدروكسيد الكالسيوم) أو بإضافة الدولوميت أحادى التأدرت (أكسيد المغنسيوم مع هيدروكسيد الكالسيوم) وذلك بإجراء تفاعل الأماهة في صورة عالق لمدة ٤٥ يوما عند درجات الحرارة ٢٥ ، ٦٠ م . ولقد أمكن التعرف على نواتج الأماهة التي تم الحصول عليها بواسطة تحليل حيود الأشعة السينية . ولقد تم تفهم دور هيدروكسيد الكالسيوم - في وجود وغياب أكسيد المغنسيوم - في استقرار التربة وذلك تمهيدا لاستخدام الأسمنت البورتلاندي في استقرار طفلة المونتموريللونيت لإنتاج أسمنت التربة .