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WANG, Jerry Wen-Hann, 1936-
ROLE OF MAGNESIUM OXIDE IN SOIL-LIME
STABILIZATION.

Iowa State University of Science and Technology
Ph.D., 1964
Engineering, civil

University Microfilms, Inc., Ann Arbor, Michigan

ROLE OF MAGNESIUM OXIDE IN SOIL-LIME STABILIZATION

by

Jerry Wen-Hann Wang

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Soil Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1964

TABLE OF CONTENTS

Page

INTRODUCTION 1

REVIEW OF LITERATURE 3

Chemistry of Lime Manufacture 3

Thermal decomposition of limestone 3
Commercial lime manufacture 5

Major Constituents in Hydrated Limes 8

Calcium hydroxide, $Ca(OH)_2$ 8
Magnesium oxide (magnesia), MgO 9
Magnesium hydroxide, $Mg(OH)_2$ 10

Reactions Between Soil and Lime 11

Modification of soils by lime 11
Cementation of soil by lime 12

Calcium Silicate Hydrates 17

Tobermorite 18
Substituted tobermorite 19
Calcium silicate hydrate (I) 20
Calcium silicate hydrate (II) 22
Calcium silicate hydrate (gel) 24

Calcium Aluminate Hydrates 26

The cubic phase, C_3AH_6 27
The hexagonal phases 27

C_4AH_{13} 27
C_2AH_8 29
CAH_{10} 29

The needle-habit phase, C_6AH_{33} 31

Magnesium Silicate and Magnesium Aluminate Hydrates 31

Page

Magnesium silicate hydrates 32
Magnesium aluminate hydrates 34

ANALYTIC STUDIES 35

Objectives 35

Methods of Studies 35

Reaction products studies 35

Reactions at 165°C 35
Reactions at 110°C 36
Reactions at 40°C and at 23°C 36

X-ray diffraction 37
Differential thermal analysis 37
Electron microscopy 38
Hydraulic properties 38
X-ray measurement of crystallite size 39

Materials and Procedures 41

Reaction product studies 41
Hydraulic properties 43

Results 45

Reaction products studies 45

Reaction products of bentonite-$Ca(OH)_2$ pastes 45
Reaction products of bentonite-$Ca(OH)_2$-MgO pastes 55
Reaction products of bentonite-$Ca(OH)_2$-$Mg(OH)_2$ pastes 79

Hydraulic properties of the chief components in hydrated limes 83

Hydraulic properties of MgO 84
Reactivity of MgO 91

Discussion 102

Pozzolanic reactions 102
Hydraulic properties of magnesium oxide 105
Carbonation 108

STRENGTH STUDIES 111

Page

Objectives 111

Material and Procedures 112

Results and Discussion 114

CONCLUSIONS 118

REFERENCES 121

ACKNOWLEDGMENTS 129

INTRODUCTION

Soil stabilization is any process designed to maintain or improve the performance of a soil for use as a construction material. Such a process frequently involves, along with other treatments, the use of one or more admixtures to achieve the desired performance. Lime shows promise of being the best stabilizer for high clay content "problem" soils by reducing the plasticity and increasing the bearing value. Among all types of limes, hydrated limes are commonly used in soil-lime works because they are more easily handled in powder form.

Hydrated lime is commercially available in three types: high-calcium hydrated, $Ca(OH)_2$, dolomitic monohydrate, $Ca(OH)_2$ + MgO, and dolomitic dihydrate, $Ca(OH)_2$ + $Mg(OH)_2$. Dolomitic monohydrate limes are, in general, the best for producing strength of compacted soil-lime mixtures at room temperature, with high-calcium hydrated next and dolomitic dihydrate last (53, 56, 67, 81, 83).

Why dolomitic monohydrate lime should be best for producing soil-lime strength has not been explained. The key to the explanation lies in finding the role of magnesium oxide in soil stabilization. The goal of the present investigation was to try and evaluate the role by studying the reaction products between soil and limes, at ordianry and at elevated temperatures, and the hydraulic properties of the chief components found in hydrated limes.

REVIEW OF LITERATURE

Chemistry of Lime Manufacture

Thermal decomposition of limestone

Chemically speaking, lime refers only to calcium oxide (CaO); however, in common usage the term includes the calcination products of calcitic and dolomitic limestones. Calcitic (high-calcium) limes are produced by calcination of calcareous materials (e.g., calcitic limestone, calcite, oyster shells, and chalk) containing from 95 to 99 percent calcium carbonate ($CaCO_3$). Dolomitic limes are produced from dolomitic limestone or dolomite which contains from 30 to 40 percent magnesium carbonate ($MgCO_3$), the rest being calcium carbonate.

At atmospheric pressure, calcite in limestone decomposes at approximately 900°C to form CaO and CO_2. The decomposition of dolomite, $CaMg\ (CO_3)_2$, is a two-stage process. At temperatures between 650°C to 750°C dolomite decomposes to form MgO, CO_2 and $CaCO_3$. It is necessary to raise the temperature to 900°C to decompose the $CaCO_3$ (15, 35). This phenomenon is extremely important, as is shown later.

Various investigators have studied the effects of stone size, temperature, and time of calcination of commercial limestones (2, 20, 34). The maximum temperature to which the limestone is subjected during the calcination process greatly affects the properties of the oxides formed. The retention time (i.e., the duration of calcination) is also important. However, many investigators have found that the retention time has much less effect than the temperature on the properties of lime produced (2, 21). "Hard-burning" and "soft-burning" are descriptive terms frequently used to indicate the intensity of the heat obtained during calcination. Hard-burned limes consequently are more dense and less reactive than soft-burned limes because of sintering of the oxide (2, 20, 27).

The complex mechanisms involved in sintering usually result in increased bulk density, decreased porosity, and growth of particles as well as crystallites of the oxides. These changes reduce the reactivity of the sintered material. Impurities or other oxides increase the sinterability of the pure compound, decreasing reactivity. In general, the higher the temperature, the greater the amount of sintering (20, 27, 64, 66).

Under normal manufacturing conditions limestone does not commence to evolve CO_2 freely until a kiln temperature of 900°C is reached. The actual temperature achieved in lime-burning practice is at least 1100°C, and may reach as high as 1500°C to shorten the time for complete calcination. These temperatures are much higher than that for the formation of MgO, and at these elevated temperatures the MgO previously formed undergoes severe sintering. Therefore, high temperature calcination has a negative effect on the reactivity of dolomitic limes, and specifically on the MgO component.

A part of this decrease in the reactivity of MgO has also been attributed to an increase in crystallite size with increasing calcination temperature and retention time (27, 70, 71). The term crystallite is defined as the microscopic or submicroscopic units or blocks that compose a crystal (74). These mosaic fragments are believed to be the basic reacting units of materials. Their size correlates closely with chemical reactivity. It has been shown that hydration rate of MgO decreased with an increase in crystallite size (26, 28, 71).

Commercial lime manufacture

In commercial calcination of limestone two types of kilns are employed--the shaft kiln and the rotary kiln.

A shaft kiln is essentially a vertical metal cylinder lined with refractory brick and with a hopper for stone storage at the top. Many shaft kilns are fired from dutch ovens which open into the shaft near its base. The kiln may be designed to use coal, producer gas, natural gas, or oil as fuel. Generally, limestone chunks ranging in diameter from 5 to 12 in. are charged into the top of the kiln. At periodic intervals of about 8 hours the calcined product is drawn off at the bottom, and fresh stone moves down into the hot zone of the kiln.

The rotary kiln is also a metal cylinder lined with refractory brick, but it is nearly horizontal. Rotary kilns are many times the length of shaft kilns, and are set up to slope down from the entry end at 1/2 to 3/8 in. per ft. The same fuels employed in shaft kilns can also be used in rotary kilns. In rotary kiln practice the limestone is crushed to a maximum size of 2 in. and then screened into several size groups, each of which is fed separately into the kiln at a prescribed rate which depends on size. The proper range in each size group for uniform calcination is such that the diameter of the largest piece is about twice that of the smallest. Due to the rotary motion and inclination of the kiln, the stone moves continuously down through a counter flow of heat toward the lower hot discharge end.

After calcination in either type of kiln the calcined product is cooled and may then be further processed.

The calcined product comes from rotary kilns in pebble form; from shaft kilns, in lumps. Before being slaked, both types are ground to a fairly uniform size, usually finer than 1/2 in., and sieved.

Dry hydrated lime is produced when quicklime is reacted with just enough water to satisfy its chemical affinity for moisture under conditions of hydration. The hydrated product is essentially dry. High calcium lime reacts readily with water to produce calcitic hydrated lime, in which all the CaO is converted to $Ca(OH)_2$. However, dolomitic lime, specifically the less reactive MgO component, does not hydrate readily in ordinary processing equipment. Dolomitic limes, hydrated in equipment operated at atmospheric pressures and low retention times, are known as dolomitic normal hydrated limes (Type N), or dolomitic monohydrate limes. These are essentially $Ca(OH)_2$ and MgO. The MgO portion of dolomitic lime can be hydrated in special equipment using longer retention periods or elevated temperatures and pressure. These pressure-hydrated limes are commercially known as dolomitic dihydrate, or special hydrated limes (Type S), and contain $Ca(OH)_2$ and $Mg(OH)_2$.

Because slaking is accompanied by evolution of heat and an increase in volume, lumps of lime change to powder during the process. Any unhydrated lime can be removed from the finished product by screening through a No. 30 sieve or by an air separation system. After being slaked, the product is usually stored in bins for 48 hr or so to allow cooling and evaporation of excess moisture.

Because a larger stone size and longer retention time are used in the shaft kiln, the quality of the calcined product is less uniform than that of the rotary kiln. In other words, lime has a greater tendency toward overburning in the shaft kiln. Rotary kilns have the advantage of better control of temperature and feed rate, which in turn results in a better quality of the calcined product.

Major Constituents in Hydrated Limes

The chemical and physical properties of $Ca(OH)_2$, MgO, and $Mg(OH)_2$ can be found in most inorganic chemistry textbooks and various handbooks. Briefly, some properties pertinent to the present studies are reported in the following:

Calcium hydroxide, $Ca(OH)_2$

The product of the water hydration of lime, or calcium oxide, is calcium hydroxide, molecular weight 70.10, sp.gr. 2.434. It may exist in nature, though rarely, under the mineral name portlandite. It is usually obtained in the slaking of lime as a white, amorphous powder. If crystallized slowly it forms large, well-developed hexagonal plate crystals.

Calcium hydroxide reacts with carbon dioxide to form calcium carbonate, and this reaction is the cause of the hardening of high-calcium lime mortars. Carbonation takes place only in the presence of moisture.

Magnesium oxide (magnesia), MgO

Magnesium oxide, with a molecular weight of 40.32, is the ultimate product in the thermal decomposition of numerous magnesium compounds and minerals. It occurs infrequently in nature as the mineral periclase, MgO(sp.gr. 3.6), usually embedded in crystalline limestone deposits. The physical properties of commercial magnesium oxides vary so much with the nature of the initial material, time and temperature of decomposition, and trace impurities present that it is difficult to ascribe definite properties to the variety of products corresponding to the chemical composition MgO. Most commercial oxides show surprisingly stable pseudostructures derived from the starting materials, although the crystal structure of all primary particles is face-centered cubic (32).

The increase in density and crystallite size resulting from increasing calcination temperatures is paralleled by a decrease in reactivity. Oxides prepared in the temperature range between 400 and 900°C (from magnesium hydroxide or basic magnesium carbonate) are readily soluble in dilute acids and hydrate rapidly even in cold water. The fused oxides unless very finely pulverized are virtually insoluble in saturated acids and are indifferent to water.

Magnesium hydroxide, $Mg(OH)_2$

The hydration of all grades of magnesium oxide leads to the formation of magnesium hydroxide, molecular weight 58.34, sp.gr. 2.43. It is found in nature as brucite, usually together with periclase as a hydration product of the latter, or as inclusions in deposits of serpentine, magnesite, and dolomite.

Magnesium hydroxide crystallizes in the form of hexagonal platelets. Even the apparently gelatinous magnesium hydroxides obtained by precipitation from magnesium salt solutions with alkalies show the same x-ray diffraction pattern as the coarse-crystalline varieties. The crystal size of the hydroxides is affected by the calcining rate of the magnesium oxide (32). The hydration rate of various magnesium oxides is determined by the active surface area, and may vary from a few hours in the case of reactive oxides obtained at low temperature from the hydroxide or basic carbonate, to months or years for the dead-burned grades.

Both magnesium hydroxide and magnesium oxide absorb moisture and carbon dioxide from the air. If exposed to the air long enough, reactive grades of magnesium oxide and hydroxide gradually convert into the basic carbonate, $5MgO.4CO_2.xH_2O$.

Reactions Between Soil and Lime

The use of lime in road construction is not new. The Romans used it extensively in building roads, including the famous Appian Way built about 2200 years ago. The lime was usually used in a mortar of sand and gravel; today it is used with soils either to modify their properties and/or to cause hardening or cementation.

Modification of soils by lime

Hydrated lime, usually calcium hydroxide, mixed with wet clay soils quickly reduces their plasticity, i.e., it brings about a change from sticky to crumbly texture. Such lime modification is useful for "drying up" mud holes for support of construction equipment, or for pre-treatment of clays to aid later pulverization for stabilized roads. The effect is mainly one of increasing the plastic limits, thus lowering the plasticity indices (38).

The mechanism of lime modification has been studied by Ho and Handy (40, 41), who suggest that the reaction involves at first a conversion of clays from saturation with ions such as sodium, to saturation with calcium, through cation exchange. Simultaneously hydroxyl ions from the hydrated lime cause dissociation of the clay OH groups and increase the negative charges on the clay surface. The more negative clay attracts more calcium ions which results a stronger floc formation of clay particles. Both a high pH and the presence of polyvalent cations are required for this type of flocculation. The amount of calcium hydroxide needed for a maximum flocculation, termed the lime retention point, may range from less than 1 up to 8 percent by weight depending on the type and amount of clay present.

In hydrated limes calcium hydroxide is the main component needed for modifying soil plasticity. Magnesium oxide shows a moderate effect, but magnesium hydroxide show practically no effect (82). Nevertheless, there is practically no difference between different types or between the same types of commercial hydrated limes for reducing soil plasticity, though those limes may show significant difference in pozzolanic strength production characteristics (81, 82). This may be because of that the amount of calcium hydroxide present in any type of lime has already met the Ca++ saturation needs for maximum flocculation of clay particles, while the stregth characteristics depend more upon the reactivity of the MgO present, as will be reviewed later.

Cementation of soil by lime

The addition of lime to siliceous materials has been used to make a construction material for centuries. The ancient Romans used this method frequently, many of their buildings being constructed with mortar consisting of quicklime and burnt clay. Clays are siliceous and aluminous materials of definite crystalline structures. Upon heating the clay to high temperature, silica can be brought to a reactive state simply by breaking up the clay structure. The Romans also used natural materials, predominantly of volcanic origin and containing non-crystalline, reactive silica and alumina. The best known of these materials was found at Pozzuoli, near Naples. It is in this way that the term pozzolan was coined to denote all materials which, owing to their reactive silica content, are capable of hardening by reacting with hydrated lime. The reaction is called a pozzolanic reaction (17).

It is only the recent 20 years that the mechanism of pozzolanic hardening has been gradually understood. Several investigators have studied the strength characteristics of calcium silicate hydrates and characterize all the products as cementitious (44, 55, 63, 73, 80). Furthermore, the formation of calcium aluminate and calcium silicate hydrates during the hydration of portland cement is believed to be responsible for the strength and cementing ability of portland cement concrete (4, 17, 54), although the former play a less significant role (4). The CSH(gel), a poorly crystalline colloidal substance, has been called the "heart of concrete" (8).

When the level of lime treatment exceeds the amount needed for modification of clay, additional strength is gained (38). The finding of pozzolanic reaction products in soil-lime mixtures is definitely the reason for the strength-gains. The strong alkaline property of $Ca(OH)_2$ (pH=12.3), that causes the dissociation of clay, makes silica and alumina available for reactions with lime (40, 41).

In investigations of pozzolanic reaction products between $Ca(OH)_2$ and clays, Hilt and Davidson (39) reported new X-ray diffraction lines at 8.1, 7.59 and 3.04Å for $Ca(OH)_2$-montmorillonite reacted for 30 days at room temperature. Various moisture contents were used in the studies. The 7.59Å compound was isolated and studied by single-crystal X-ray diffraction procedures. The compound was tentatively identified as a hexagonal calcium aluminate hydrate, probably C_4AH_{11}.[1] The 8.1 peak was found stronger in mixes of higher moisture content and may represent the phase of α-C_4AH_{13}, which is isostructural with C_4AH_{11} but of higher hydrated state (42, 68, 78). The small broad 3.04Å line probably represents the formation of some poorly crystalline CSH(gel) rather than

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[1] It is customary in cement chemistry to denote the following compounds by short symbols: CaO=C; SiO_2=S; Al_2O_3=A; Fe_2O_3=F; MgO=M; H_2O=H. Thus, the compound $4CaO.Al_2O_3.11H_2O$ is referred to as C_4AH_{11}.

calcium carbonate as interpretated by the authors, because calcium carbonate peaks are usually sharp and intense, which occur at 3.03Å.

Glenn and Handy (30, 31) studied the reaction products from clay minerals and different types of hydrated limes reacted under room temperature conditions. Among the reaction products are some polymorphs of tetra-calcium aluminate hydrates and probably a poorly crystallized calcium silicate hydrate. A 7.6Å peak was ascribed to a carbo-aluminate. No new magnesium compounds were found, except a conversion of MgO to $Mg(OH)_2$ in mixes containing dolomitic monohydrate lime.

Further studies confirmed the formation of calcium aluminate hydrates and the lower crystalline forms of the calcium silicate hydrates, namely, CSH(gel), CSH(I), and probably CSH(II), during two and one-half years curing at room temperature on the mixes of different types of hydrated limes, bentonite, and water (29). Again no new magnesium compounds were found, except the formation of $Mg(OH)_2$ from MgO.

It is to be noted that all these studies were made on mixes of high lime contents and at room temperature. Many investigators have studied the reaction between limes and clays at elevated temperatures and hydrothermal conditions for the purpose of accelerating the reaction (18, 19, 25, 29, 57). Calcium aluminate hydrates and calcium silicate hydrates, ranging from poorly crystalline CSH(gel) to well-crystallized tobermorite, were always found.

Nevertheless, the problem of the superior strength-gaining property of dolomitic monohydrate lime still remains unsolved. One study found a distinct difference in strength production property even among dolomitic monohydrate limes, depending upon the reactivity of MgO in lime (81). The more intense the calcination during manufacturing and the larger the MgO crystallite size of the lime, the lower is the soil-lime strength. This coincides with the statement in the preceding section on "Chemistry of Lime Manufacture" that dead-burning reduces the reactivity of dolomitic monhydrate limes.

An early study on Wisconsin magnesian lime mortars revealed that the magnesian limes produced by the different Wisconsin plants were not all alike, and that all magnesian lime mortars were stronger than those of high calcium limes (3). The hardening of magnesian lime putties upon aging was attributed to the gradual hydration of magnesium oxide content of the putty.

Carbonation of lime, generally calcium hydroxide, contributes to the hardening of lime mortar in plaster and to the hardening of concrete to some extent. Carbonation may be considered as a minor source of cementation in soil-lime stabilization, provided that the access to CO_2, such as that present in the air, is allowed. Nevertheless, the effect is usually considered detrimental because the availability of lime for pozzolanic reaction may thus be reduced. No data, however, are available to support this assumption.

Calcium Silicate Hydrates

The compounds of greatest significance in the chemistry of hydration of portland cement are tobermorite and tobermorite-like calcium silicate hydrates. Tobermorite is the well-crystallized member of a family of several closely related compounds that includes also phases now generally known as calcium silicate hydrate (I), calcium silicate hydrate (II), and calcium silicate hydrate (gel), also called tobermorite (gel). These are abbreviated as CSH(I), CSH(II), and CSH(gel), respectively.

The structure of tobermorite is similar to that of some clay minerals, particularly vermiculite (60, 79). Calcium silicate hydrates of the tobermorite-like family, however, do not have precisely the same structure. In addition to the structural similarities, these calcium silicate hydrates also have the small particle size, large surface area, and a number of other properties analogous to clay minerals (18,78).

Tobermorite

Tobermorite is a platy calcium silicate hydrate with a composition approximating $5CaO.6SiO_2.5H_2O$. It is a rare mineral, but it may be synthesized readily by hydrothermal means by using finely-divided quartz or silica gel with CaO at various temperatures between 100°C and 200°C (22, 36, 45, 77). McCaleb (57) and Glenn (29) have also succeeded recently in synthesizing this mineral through hydrothermal reaction of lime with montmorillonite.

There are several known discontinous hydration states of tobermorite, each marked by a characteristic c-axis spacing. The mineral exists normally with a c-axis spacing of 11.2Å, which may be collapsed to 9.5Å on heating. A 14Å variety, presumably having an extra layer of water between the structural units, has been observed to occur naturally and been prepared synthetically (50, 58). A typical X-ray diffraction pattern of the 11Å tobermorite (45) is shown in Table 1.

A number of investigators (25, 43, 45, 46, 58) have studied the differential thermal analysis (DTA) behavior of hydrothermally synthesized tobermorite with 11Å spacings. Fair agreement has been obtained. Samples of both 0.8 and 1.0 c/s composition behaved similarily and yielded only a small dehydration endotherm at about 260°C and a very weak and indefinite high-temperature exotherm at about 810°C to 830°C.

Substituted tobermorite

Isomorphous substitutions in tobermorite have been studied by Kalousek (46) and Diamond (18). It was found that a considerable amount of aluminum, magnesium, or iron ions can be incorporated into the lattice of synthetic tobermorite without any significant change in the x-ray diffraction pattern of the material. Presumptions were made that these ions substituted for silicon in the tetrahedral coordination, rather than for calcium in the structure. Except for aluminum, there was, however, no definite proof that magnesium and iron actually substitute in the silica chains.

The X-ray diffraction pattern of Al-substituted tobermorite showed a shift of basal spacing from 11.2Å to 11.5Å in the sample having 15 percent replacement of SiO_2 by Al_2O_3. Also, Kalousek first reported the appearance of a hydrogarnet phase (C_3ASH_4) in his compositions prepared with more than 11 percent nominal Al-substitution. The strongest line for the hydrogarnet is at 2.76Å. He used this line, in addition to a line at 5.07Å, as the criteria to reveal the presence of this phase.

Diamond observed that the substitution of magnesium and iron (both of which have ionic radii substantially larger than aluminum) resulted in some disorder in the c-axis direction, because the basal intensities of the (002) and the (222) peak are approximately halved, while the strong peaks due to reflecting planes entirely within the unit layer, viz. the (220) and the (400), are essentially unchanged in intensity.

Diamond also observed that certain new peaks (2.7Å, 4.2Å) appeared with all the substituents, including aluminum, while others (1.95Å, 7.0Å) appeared only with the substitution of the larger ions, such as iron and magnesium.

The DTA pattern of Al-substituted tobermorite is characterized by a strong, sharp exotherm at about 810°C to 860°C. In contrast to this behavior, Fe- and Mg-substituted tobermorite do not show any difference from the unstubstituted materials in DTA pattern.

The morphology of Al-substituted tobermorite is similar to that of unsubstituted, except that the thin plates do not show particular tendency toward elongation. No reference is available for the morphology of Mg-substituted tobermorite.

<u>Calcium silicate hydrate (I)</u>

This phase has been called "CSH(B)", the "fibrous phase", or "C/S 0.80-1.33 hydrate", etc. by different investigators. The designation "CSH(I)" is now most generally used. This phase is not known to occur naturally, but may be produced in a variety of ways, either hydrothermally or by reaction at room temperature, through the reaction of silica or silica sol with calcium hydroxide solution or reaction of sodium silicate solution with calcium salts (45, 76, 78). Recent studies by Diamond (18) and Glenn (29) have shown that CSH (I) can be readily formed by reaction between $Ca(OH)_2$ and clay minerals at both room temperature and at elevated temperatures.

The product is a poorly crystallized gelatinous precipitate which is structurally related to tobermorite, but the exact structure is not known. Its composition may vary. The C/S ratio exists probably between 0.8 and 1.33 (49); the lower limit is well established but the upper one is less definite, and higher values, up to 1.5 or even farther, have been suggested (76). Furthermore, this product is metastable and eventually transforms to tobermorite and other phases depending on the composition (45).

Irrespective of C/S ratio, the x-ray powder pattern resembles that of tobermorite, except that only a few of the strongest reflection can be seen. These are mainly ones with (hko) indices. "Typical" data obtained by Taylor (78) are given in Table 1; similar results have been obtained by other investigators (18, 33, 45, 62). A basal spacing is sometimes present in the region 10-13Å; some investigators report this line as "very strong", while some list it as "very weak, broad", and in few cases absent entirely. The fact is that this basal spacing is often not observable on diffractometer equipment, but can be observed on film camera diffraction technique, which permits long-time exposure and hence more certain recognition of peaks of overall weak intensity. Diamond (18) recently reported a CSH(I) X-ray pattern which exhibits only 3.25(w), 3.02(w), 2.78(w), 1.81(w), and 1.66(vw) peaks.

The differential thermal analysis pattern of CSH(I) differs from that of tobermorite by the presence of a sharp and intense exothermic peak in the 835°C to 900°C region (43, 45). In addition to this strong exothermic peak, Diamond (18) reported two weak endothermic peaks at 660°C and 790°C. These features closely resemble those displayed by the aluminum-substituted hydrothermal tobermorites.

The morphology revealed by electron microscopy is usually described as one consisting of crumbled or crinkled foils, sometimes partially rolling into tubes or fibers (16, 18, 24, 33, 45, 49).

It has been reported recently that potassium can partially substitute for calcium in a room-temperature synthetic phase that is probably CSH(I) (75).

Calcium silicate hydrate (II)

The common abbreviation for this phase is CSH(II), but "C_2SH_2", "hydrate II", "1.8 C/S hydrate", "$C_7S_4H_n$", etc. have also been used as designations. It denotes a lime-rich phase, having C/S ratio at least 1.5 and probably up to 2.0 (24, 49, 78), and a low degree of crystallinity, comparable with that of CSH(I). It is formed as an intermediate product by hydrothermal reactions, usually below 200°C, between lime and silica (45, 49). This appears to be true even when the overall C/S ratio of the mixture is low; in this case, CSH(II) is formed initially and later reacts with more silica to give products of lower C/S ratio. At room temperature, the synthesis is carried out by reaction of tricalcium silicate with water (76). Evidences of the formation of CSH(II) by reactions of limes with clay minerals have also been reported recently (29).

The X-ray powder pattern resembles that of CSH(I), except that the basal spacing of this compound appears to be comparatively strong and fairly consistent between 9.8 and 10.5Å, and the (620) line at 1.67Å, present in CSH(I), is not found in CSH(II), while a new 1.56Å line characterizes the existence of CSH(II) (24, 49, 62, 76). A representative pattern given by Heller and Taylor (37) is given in Table 1.

The characteristic DTA of CSH(II) is "variable" (49). Kalousek (43) noted a small exothermic bulge in the temperature range 350°-450°C, often a very small endotherm in the region around 800°C, and finally a small, but definite, exotherm at around 850°C.

The morphology is typically fibrous, and sometimes involves characteristic cigar-shaped bundles of fibers (16, 24, 33, 49).

No data have been reported on lattice substitution of CSH(II).

Calcium silicate hydrate (gel)

CSH(gel) has sometimes been called "tobermorite (G)" (G for gel) to imply its structural resemblance to the natural or synthetic tobermorite, although the crystal structure of this considerably distorted phase is unknown. It is produced on hydration of the portland cement constituent C_3S in paste form or by bottle technique, or by hydration of β-C_2S by paste or ballmill technique (8, 16, 78). It is a relatively high-lime phase having C/S ratio usually at 1.5 or higher (8, 78).

The CSH(gel) is very poorly crystallized. Its x-ray diffraction pattern, as reported by Brunauer (8), normally consists of three lines: a very strong and very broad reflection, with a maximum at 3.05Å, and two much weaker broad lines at 2.79 and 1.82Å (Table 1). These three lines correspond to three of the strongest (hk0) lines of tobermorites. Nevertheless, Diamond recently observed only two lines at 3.03 and 1.82Å in his CSH(gel) samples prepared by paste and bottle hydration of α-C_2S, C_3S and alite (18). Furthermore, a CSH (gel) synthesized by Kantro, Brunauer, and Weise from the hydration of C_3S in a small steel ball-mill exhibited only a single broad diffraction band with the maximum in the vicinity

Table 1. X-ray data for tobermorite and tobermorite-like calcium silicate hydrates

Synthetic tobermorite (45)		CSH(I) (78)		CSH(II) (37)		CSH(gel) (8)	
d,Å[a]	I[b]	d,Å[a]	I[b]	d,Å[a]	I[c]	d,Å[a]	I[b]
11.2	vs	12.5	vs	9.8	9	3.05	s,vb
5.4	m	5.3	vvw	4.9	2	2.79	wb
3.49	w	3.04	vs	3.07	10	1.82	wb
3.30	w	2.80	s	2.85	5		
3.07	vs	2.4	w,d	2.80	9		
2.96	s	2.1	w,d	2.40	4		
2.80	s	1.82	s	2.20	1		
2.51	w	1.67	mw	2.10	1		
2.41	w	1.52	vw	2.00	6		
2.24	w	1.40	w	1.83	9		
2.13	w			1.72	1		
2.06	w			1.62	1		
1.99	w			1.56	5		
1.838	s			1.40	4		
1.671	ms						
1.620	w						
1.531	m						
1.431	vw						

[a] The spacings given in Ångstrom units.

[b] Relative intensity: S, strong; m, medium; w, weak; v, very; b, broad, d, diffuse.

[c] Relative intensities on an arbitrary numerical scale; 10 being the strongest and 1 the weakest.

of 3Å. This was termed the lowest limit in the degree of crystallinity in the tobermorite family (51).

The DTA pattern of CSH(gel) consists of a fairly definite but relatively weak exothermic peak at about 860°C, as reported by Diamond (18). No other published DTA data of this phase has been found in the literature.

The morphology of CSH(gel) is reported as straight fibers, the fibers themselves being apparently composed of rolled-up sheets of a few tens of Å thick (8, 16, 18).

Calcium Aluminate Hydrates

Calcium aluminate hydrates are relatively well-crystallized as compared with the calcium silicate hydrates. They are of frequent occurrence as products of portland cement hydration, and of the reactions between $Ca(OH)_2$ and aluminum-bearing clay minerals. There are three groups of calcium aluminate hydrates that may be distinguished: (a) cubic tricalcium aluminate hexahydrate, (b) several hydrates having hexagonal or pseudohexagonal plate crystal form, (c) another group of hexagonal or lower symmetry crystallizing as needles (42, 68, 78). Except for the cubic phase, the exact structures of the hydrated calcium aluminates are unknown.

The cubic phase, C_3AH_6

C_3AH_6 is usually formed at slightly elevated temperatures above 50°C and is thermodynamically stable at room temperature (78, 84). The structure of C_3AH_6 is related to that of garnet, $Ca_3Al_2(SiO_4)_3$, by replacement of each SiO_4^{-4} by $4OH^-$, giving $Ca_3Al_2(OH)_{12}$ (78). The common habit is rectangular or octahedral plates (59). A DTA curve up to 600°C is given by Majumder and Roy (59) which shows a strong endotherm at about 325°C followed by a weaker endotherm at about 480°C. Few selected x-ray diffraction lines for the C_3AH_6 are shown in Table 2 (62).

The hexagonal phases

The hydrates of this group are readily formed under appropriate conditions at room temperature and do not change quickly to give the stable products. A thorough study by Roberts (68) clearly reflects the metastable equilibria of some of these hydrates.

$\underline{C_4AH_{13}}$ Roberts found that this phase when existing in contact with aqueous solutions was actually in the form of C_4AH_{19}. The C_4AH_{19} hydrate, characterized in the x-ray patterns by a longest basal spacing of 10.6Å, is dehydrated relatively easily on washing with acetone or alcohol, or on moderate drying at room temperature to give a mixture of α- and β-forms of a $13H_2O$ hydrates, characterized by longest basal spacings of 8.2Å and 7.9Å, respectively. There is little difference in stability between the two forms and it appears to be a matter of chance as to the relative amount of each which may be formed. Drying over $CaCl_2$ results in further loss of water to form a phase of composition C_4AH_{11}, with a basal spacing of 7.4Å. Still more intensive drying over P_2O_5 or by heating at 120°C reduced the water content to about $7H_2O$, while the longest basal spacing of 7.4Å remains unchanged.

The DTA pattern shows a strong endotherm at around 150°C with a broad dip continuing to approximately 350°C, while two other small endotherms appear at 500°C and 850°C, respectively (47).

There are several phases iso-structural with the C_4AH_{13} in which some of the hydroxyls are replaced by a different anion. Replacement is nearly isomorphous, in that the dimensions of the structural element and the essential features of the structure are unaffected. A wide range of anions can be incorporated, the ones most important to cement chemistry being CO_3^{-2} and SO_4^{-2} (78). Two such phases in which the anion is carbonate have been known; they are hydrocalumite, a natural mineral with only a small carbonate content, and calcium monocarboaluminate, $C_3A.CaCO_3 11H_2O$. The latter compound is formed very readily from aqueous suspensions or supersaturated solutions at or below room temperature when small amounts of CO_2, such as normally exist in the atmosphere, are present (78), and is now believed to be unavoidable in reaction studies. Its X-ray pattern resembles to that of C_4AH_{13}, except the basal spacing is at 7.57Å rather than 7.9Å, the value for α-C_4AH_{13} (13).

A summary of these compounds and related phases is given in Table 2.

<u>C_2AH_8</u> The structure of this phase is related to C_4AH_{13} with certain $Al(OH)_3$ substitution for H_2O in the latter (42). There are two polymorphs with longest basal spacings of 10.7Å (α) and 10.4Å (β) (68). The α-C_2AH_8 appeared to be more stable than the β-form. On washing with acetone or alcohol or drying very moderately at high humidity, the basal spacings remain unchanged. On drying over anhydrous $CaCl_2$ or P_2O_5 or heating at 102°C, C_2AH_5 is formed with a basal spacing of 8.7Å. Further heating at 120°C, a 7.4Å-C_2AH_4 is revealed.

<u>CAH_{10}</u> The structure of this phase and its relationship between the other calcium silicate hydrates is not clear (42). It occurs primarily at temperatures below room temperature with a basal spacing at 14.3Å (62). Table 2 shows some relevant feature to this compound.

Table 2. Selected calcium aluminate and magnesium aluminate hydrates

Composition	Morphology	d-spacing, Å				Reference to X-ray data
		Longest	Strongest three			
C_3AH_6	cubic	5.14	2.30(10)[a]	5.14(9)	2.04(9)	(62)
C_4AH_{19}	hexagonal plates with excellent (0001) cleavage	10.6		-[b]		(68)
α-C_4AH_{13}		8.2	8.2(vs)[c]	4.1(m)	2.9(m)	(68, 84)
β-C_4AH_{13}		7.92	7.92(vvs)	3.99(vs)	2.87(s)	(9, 68)
C_4AH_{11}		7.4		-[b]		(68)
C_4AH_7		7.4		-[b]		(68)
α-C_2AH_8		10.7	10.7(10)	5.36(8)	2.86(7)	(62, 68, 84)
β-C_2AH_8		10.4		-[b]		(68)
$C_3AH_{11}\cdot CaCO_3$	hexagonal	7.57	7.57(10)	3.784(4)	2.858(3)	(13)
CAH_{10}	hexagonal prisms	14.3	14.3(10)	7.16(10)	3.56(7)	(62)
M_4AH_{13}	-[b]	7.68	7.68(s)	2.56(ms)	3.78(m)	(14)
M_2AH_{10}	-[b]	10.63	10.63(s)	5.43(m)	3.63(m)	(14)

[a] Relative intensities on an arbitrary numerical scale: 10 being the strongest and 1 the weakest.

[b] Data not obtained.

[c] Relative intensities: v, very; s, strong; m, medium.

The needle-habit phase, C_6AH_{33}

This compound has only been made in the presence of sugar which was added to permit an abnormally high-lime concentration to be used in the system $CaO-Al_2O_3-H_2O$ (78). Isomorphous replacement of hydroxyl by large SO_4^{-2} anions is possible; the formation being a compound analagous to the natural mineral ettringite, $C_3A.3CaSO_4.32H_2O$. The latter is usually formed in the hydration of portland cement containing gypsum retarder.

Magnesium Silicate and Magnesium Aluminate Hydrates

Little work has been done on the reaction between magnesium oxide or hydroxide and clay minerals. One study (57) reported $Mg(OH)_2$-montmorillonite and $Ca(OH)_2$-$Mg(OH)_2$-montmorillonite reactions: at room temperature after 2 years ageing, the $Mg(OH)_2$ - $Ca(OH)_2$- treated montmorillonite showed no change, while the $Mg(OH)_2$-treated mixture revealed new formations of Mg-montmorillonite and small amounts of a vermiculite-chlorite-like mineral, in addition to some $Mg(OH)_2$ that originally existed. After hydrothermal treatment at 176°C for 168 hours, an 11.7Å tobermorite, a 14.7Å vermiculite, and a 12.9Å montmorillonite were observed in the $Ca(OH)_2$-$Mg(OH)_2$-montmorillonite mixture, while $Mg(OH)_2$-treated montmorillonite showed the existence of montmorillonite, Mg-vermiculite, and probably some saponite. Results are inconsistant and confusing, and neither X-ray tracings nor any other evidences are given in that report to witness these formations.

The addition of dolomitic lime to soil may lead to the reaction between the magnesium compound in the lime and some minerals in the soil. Hence a brief review of some hydrated magnesium silicates and aluminates that may be relevant to the present study is in order.

Magnesium silicate hydrates

The system $MgO-SiO_2-H_2O$ is one of the systematically and quantitatively investigated silicate systems which is of significance for metamorphic petrology. Bowen and Tuttle (5) have established the equilibrium and stability relationships among minerals in this system in the temperature-pressure range $300^{\circ}C$, 2000 psi to $1000^{\circ}C$ and 40,000 psi. The serpentine group, which is completely unstable above $500^{\circ}C$, is one of them. It is believed of prime importance to the present study, since serpentine minerals have close structural affinities to the clay mineral group kaolin and they are of frequent occurrence associated with many clay minerals, especially chlorite.

Serpentine may be thought of as the magnesium analogue of kaolin, $Al_2Si_2O_5(OH)_4$, which is made up with the layer structure of a silicon tetrahedral and an aluminum octahedral sheet. Serpentine minerals tend towards a constant ideal composition of $Mg_3Si_2O_5(OH)_4$ with 3Mg playing the role of 2Al in the octahedral sheet in the kaolin composition. They are composed of hydrated magnesium silicate layers with various ordered and disordered stacking arrangements.

The classification and nomenclature of the serpentine minerals have been discussed in detail by Brindley (6). Included are the fibrous and the platy minerals. A fibrous morphology is caused by the strain resulting from the misfit between the tetrahedral and octahedral sheets. The introduction of Al into both sheets of the serpentine structure, according to the substitution of one Mg and one Si by 2Al, tends to form a platy crystal because the Al is larger than Si but smaller than Mg, which will modify both the tetrahedral and the octahedral layers in the direction of a better fit. Very careful X-ray studies, aided by electron microscope techniques are essential for the identification of these minerals.

Little work has been done on the synthesis of magnesium silicate hydrates at relatively low temperatures and pressures, because of the extremely slow rate at which equilibrium is reached at low temperatures and the poor characterization of the compounds formed under such conditions.

Kalousek and Mui (48) and Yang (86) have described attempts to prepare various low-temperature (70°C to 350°C) intermediate reaction products and to determine their relation. The data are inconclusive due to the reasons stated above. Nevertheless, indications obtained from X-ray, DTA, and electron microscope were sufficient to show that talc- or chrysotile-like solids, depending primarily upon the initial M/S reaction in the mixture, had been formed. It is also interesting to note that both reports have found that MgO possesses higher reactivity than $Mg(OH)_2$ as a starting material.

Magnesium aluminate hydrates

The occurrence of hydrated magnesium aluminates in nature is rare. Cole and Hueber (14) reported their formation by the action of sea water on concrete. Compounds M_4AH_{13} and M_2AH_{10} can be readily synthesized in laboratory by reacting sodium aluminate with MgO or $MgSO_4$ over a water bath at 65-70°C. It was found that the structure of the compounds M_4AH_{13} and M_2AH_{10} resemble those of C_4AH_{13} and C_2AH_8, respectively. Selected X-ray diffraction lines of the two compounds are given in Table 2. Partially substitution of MgO by SiO_2 in M_4AH_{13} appeared to be possible without significantly changing the X-ray diffraction pattern.

ANALYTIC STUDIES

Objectives

It is believed that the formation of pozzolanic reaction products, e.g., calcium silicate and/or calcium aluminate hydrates, has been the primary cause of hardening of the compacted soil-lime mixtures. The purpose of this phase of studies was to examine, detect or define the role of magnesium oxide in the reactions between calcium hydroxide and clay, i.e., whether the presence of MgO in lime will favor or disfavor the formation of calcium silicate and/or calcium aluminate hydrates, or will cause formation of magnesium silicate and/or magnesium aluminate hydrates.

In addition, the hydraulic properties of the chief components in hydrated limes, namely, $Ca(OH)_2$, MgO, and $Mg(OH)_2$ were studied to see whether any of these compounds would harden in the presence of water, with and without the supply of CO_2.

Methods of Studies

Reaction products studies

Reactions at 165°C   Lime-bentonite mixtures were reacted hydrothermally in a Pressure Reaction Apparatus, manufactured by Parr Instrument Company, Moline, Illinois, with a maximum range of 1000 psi. Samples were placed in polypropylene containers which were put in the pressure chamber and sealed. The chamber contained sufficient water to provide steam at its saturated vapor pressure for indicated temperatures. Heating was controlled by rheostat, and temperatures were measured in a well provided inside the reaction chamber. After reaction, the chamber was cooled in a water bath and samples were taken for necessary analyses.

Reactions at 110°C An autoclave made by the American Sterilizer Company, Erie, Pennsylvania was used to effect the chemical reactions between lime and bentonite under pressure of steam. The pressure of the steam is an indication of temperature. In the case of 110°C, the absolute pressure is 20.78 psi. Mixtures were prepared in paste form, sealed in polypropylene bottles with excess water, and cured in the pressure chamber for predetermined periods. At the end of each curing period, part of the mixture was taken from the bottle for further examinations.

Reactions at 40°C and at 23°C Separate lime-bentonite pastes were sealed in polypropylene bottles with excess water. An electric oven was used as the chamber for 40°C curing. The 23°C curing was performed in a temperature-controlled humidity room for various periods. The bottles were sealed in order to prevent the entry of carbon dioxide and loss of moisture.

X-ray diffraction

The General Electric XRD-5 diffractometer was used for general investigations of powder samples for the presence of crystalline reaction products. Nickel filtered copper K_α radiation was used. The powder samples were mounted in disc-shaped brass rings with a pressure of 1000 psi in order to obtain a dense packing, avoid effects of preferred orientation, and give good reproducibility (70).

Differential thermal analysis

Samples equilibrated in a $CaCl_2$ desiccator were ground to pass a No. 200 mesh sieve before packing into the DTA apparatus. In this apparatus, an automatic controller provides for a heating rate of 10^oC per min. A vertical furnace arrangement is used. The sample block is 18-8 stainless steel, 3/4 in. high by 1 3/4 in. diameter, supported by a hollow ceramic pedestal. Two vertical 3/8-in. in diameter by 1/2-in. deep sample holes are symmetrically located in each block with centers 1 in. apart. No. 22 Pt-Pt 10 percent Rh differential thermocouples are used; the furnace temperature couple is a separate chromelalumel junction inserted in a 3/8-in. diameter by 1/2-in. deep hole drilled up into the bottom of the block. The inert sample is powdered alumina passing the No. 325 sieve.

Electron microscopy

The instrument used for the electron microscopic investigations of the lime-montmorillonite mixtures was a Siemens Elmiskop I operated at 80 kilovolts under vacuum $>10^{-4}$ in. Hg. The sample preparation procedure employed ultra-sonic vibration to assist in dispersion, following a brief mulling of the sample in a mortar. Nebulizing of a drop of the dispersant onto carbon-filmed grids also was accomplished by ultrasonic means.

Hydraulic property studies

The utilization of 1 in. high by 1/2 in. diameter strength test specimens for hydraulicity studies results in considerable savings of time and materials. The results obtained primarily reflect the cohesive strength of the soil-additive system, and are sufficiently valid especially for comparative studies. The molding apparatus has been described in detail by Roderick (69). The soil-additive mixture is compressed by hand into a cylindrical mold through a lever arrangement. Density and moisture content are used as the controls of the molded specimens.

In the present investigation, the comparisons of the unconfined compressive strengths of various mixtures were always made on the bases of equal dry density and the moisture content which gave greatest strength. The specimens of the mixture were therefore molded at different moisture contents, the highest being the maximum that would allow successful molding without squeezing out excess water, and the lowest value being the minimum that would permit uniform wetting of the mixture. Four moisture contents at an interval of 5% each were usually found sufficient.

Four specimens were used in each testing condition. After the completion of specified curing, unconfined compressive strength was obtained as the average of the four specimens, tested by a proving-ring type of compression apparatus. Graphs of strength vs. moisture content were then drawn, and the maximum value on the curve was the reported strength of the mixture.

X-ray measurement of crystallite size

The average crystallite sizes of the limes were found by a method originally suggested by Scherrer and applied by Rosauer and Handy (70). This method is based on the relation between the breadth of an X-ray diffraction maximum and the size of the diffracting crystallites, more specifically, the mean dimension normal to the diffracting planes of the crystallites.

Individual samples were mounted in disc-shaped sample holders made of brass so that they could be rotated during analysis to avoid effects of preferred orientation and to increase statistical accuracy. A press exerting 1000 psi was used in mounting. A G.E. XRD-5 X-ray diffraction unit with a copper tube was operated at 50 kvp and 16 ma. The radiation was nickel filtered. Proper intensity and resolution of the diffraction peaks were obtained by using an optical system consisting of a 1° beam slit, medium resolution Soller slit, and 0.2° detector slit. A time constant of 8 sec, a slow scanning rate of 0.2° 2θ per min, and a chart speed of 1 in. per min. were used to reduce pen jiggle and give good reproducibility.

The peak breadth, B_o, is the width of the peak (in degrees 2θ) at half maximum intensity and is an inverse measure of crystallite size. The Scherrer equation was used in the calculation of the mean crystallite dimensions from the B_o values. The reflection of fine quartz powder (20-40μ) was recorded in a similar fashion to furnish the instrument and α_1, α_2 radiation broadening. The breadth of the MgO (200) line, and (100) and (001) lines for $Ca(OH)_2$ were measured in five repeat tracings. Because the unit cell of MgO is cubic, the dimension calculated from the (200) reflection represents the total thickness of the diffracting planes. The unit cell of $Ca(OH)_2$ is hexagonal; therefore broadening of the (001) line gives the thickness of the average $Ca(OH)_2$ crystallite prism, and broadening of the (100) line gives the average distance between two opposite faces of the prism.

The unit cell of $Mg(OH)_2$ is also hexagonal and its crystallite size can be determined by measuring the broadenings of the lines (001) and (110). The selection of line (110) instead of (100) is because of the extremely weak intensity of the (100) line of $Mg(OH)_2$, which does not permit accurate measurement of the line broadening. However, the calculated crystallite size from the broadening of line (110) multiplied by a factor Cos 30° is the size obtained from the line (100).

The results of the calculated average crystallite sizes and the 95 percent confidence limits of uncertainty of the averages are listed in Table 8.

Materials and Procedures

Reaction product studies

The clay mineral used was a Ca-saturated montmorillonitic clay commercially produced as the "Panther Creek Southern Bentonite" from White Spring, Mississippi by the American Colloid Company. This bentonite contains approximately 56% SiO_2, 20% Al_2O_3, 8% Fe_2O_3, and 3% MgO as its main constituents[1]. The chemical formula of a similar bentonite from Amoy, Mississippi as listed in AAPG Reference Clay Minerals (52) is

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[1] Information furnished by the American Colloid Company.

$(Al_{1.40}Fe_{0.32}Mg_{0.31})(Al_{0.12}Si_{3.88})O_{10}(OH)_2(Na_{0.02}Ca/2_{0.28})$

Dolomitic monohydrate limes of different mole ratios of calcium oxide to magnesium oxide (C/M) were synthesized from reagent grade $Ca(OH)_2$ and MgO. In some instances, dolomitic dihydrate limes were also synthesized, and the $Mg(OH)_2$ used was also a reagent grade chemical.

Since the formation of calcium silicate hydrates is dependent on the starting calcium oxide to silicon dioxide ratio (C/S), and on the temperature and time of curing (18, 78), three series of lime-bentonite mixtures of varied C/S, (C+M)/S (with C/M=1), and C/M (with C+M/S=0.892) ratios were investigated under different curing temperatures and periods. These mixtures were prepared in paste forms in polypropylene bottles with excess CO_2-free distilled water. The bottles were sealed to prevent the entry of CO_2 and loss of moisture throughout the specified curing conditions.

The curing temperatures used were 23, 40, 110, and 165°C. At the end of each curing period part of the cured mixture was removed from the bottle and allowed to equilibrate under vacuum over $CaCl_2$ for at least 48 hours at room temperature until the sample was visually dried. The dried sample was then ground to a size finer than the No. 200 sieve (74 microns) before undergoing X-ray examination. Differential thermal analyses (DTA) and electron microscopy were often used whenever the identification by X-ray diffraction alone appeared to be insufficient.

Hydraulic property studies

In order to insure that there is no inter-reaction in the presence of water, between the additive and the soil particles, a standard material manufactured from the natural silica sand in Ottawa, Illinois, graded to pass a No. 50 (297 microns) sieve and retained on a No. 200 (74 microns) sieve, was used with different additives in this study. Very well-crystallized sand of this kind is relatively inert to the action of lime at room temperature (29).

Reagent grade $Ca(OH)_2$ and $Mg(OH)_2$ were used to represent the respective compounds in hydrated lime. MgO samples of different degrees of reactivity were prepared by decomposing reagent grade $Mg(OH)_2$ in a silicon resistance furnace for 48 hours under temperature conditions ranging from 600 to 1350°C. Crystallite sizes of all the starting $Ca(OH)_2$, MgO, and $Mg(OH)_2$ used for molding strength test specimens were determined by the X-ray diffraction method. The results are given in Table 8.

1" x 1/2" specimens for strength tests were molded with a weight ratio of sand to additive equal to one, and with different moisture contents. The specimens were cured at room temperature under a relative humidity above 90%. Three different curing atmospheres were used: CO_2-free, ordinary (no control on CO_2), and CO_2-saturated. At the end of 2 days and 7 days, cured specimens were removed from the curing chamber and tested for unconfined compressive strength. Results for the various compacted sand-additive mixtures are shown in Table 9.

After testing, a representative sample from each group of specimens was dried over $CaCl_2$ under vacuum. New formation of carbonates or $Mg(OH)_2$ was then detected by X-ray diffraction, and the results correlated with the strength gains. In the case that $Mg(OH)_2$ was formed, crystallite sizes of this were determined (Table 8).

Results

Reaction products studies

Reaction products of bentonite-$Ca(OH)_2$ pastes   This series of studies was made to find the reaction between clay and $Ca(OH)_2$, without the effect of MgO, under various compositional, temperature, and time conditions. Results identified mainly by means of X-ray diffraction are listed in Table 3, which will be used as the base for comparison with the results under the influence of MgO. In general, CSH(gel), CSH(I) (probably also CSH(II)), tobermorites, hydrogarnet, and tetracalcium aluminate hydrates were formed, depending on the curing conditions as well as the starting compositions of the mixtures.

In the present study, when the mixture is not rich in lime and/or the curing temperature and time are low, CSH(gel) resembling the one synthesized by Kantro et al. (51) that showed only the 3Å line was formed, which is represented by the broken lines in Table 3. Prolonged curing caused a conversion of this phase into the CSH(gel) that possesses the normally 3.05, 2.79, and 1.82Å spacings (represented by the solid lines in Table 3).

Table 3. Reaction products of bentonite-Ca(OH)$_2$ pastes

Curing temperature and period	C/S ratio					
	0.223	0.446	0.892	1.338	1.784	
Starting components	———	———	———	———	———	montmorillonite
	———	———	———	———	———	quartz
	———	———	———	———	———	Ca(OH)$_2$
165°C curing						
4 hours	———	———	———	———		montmorillonite
	———	———	———	———	———	quartz
				———	———	Ca(OH)$_2$
	-----					CSH(gel)
		———	———	———	———	CSH(I)
				———	———	hydrogarnet
16 hours	———	———				montmorillonite
	———	———	———	———	———	quartz
					———	Ca(OH)$_2$
	-----					CSH(gel)
		———			———	CSH(I)
			———	———		tobermorite
			———	———	———	hydrogarnet
36 hours	———	———				montmorillonite
	———	———	———	———	———	quartz
					———	Ca(OH)$_2$
	-----					CSH(gel)
		———			———	CSH(I)
			———	———		tobermorite
			———	———	———	hydrogarnet
81 hours	———	———				montmorillonite
	———	———	———			quartz
					———	Ca(OH)$_2$
	-----					CSH(gel)
					———	CSH(I)
		———	———	———		tobermorite
			———	———	———	hydrogarnet

Table 3 (Continued)

Curing temperature and period	C/S ratio					
	0.223	0.446	0.892	1.338	1.784	
150 hours	—	—				montmorillonite
	—	—	—			quartz
					—	$Ca(OH)_2$
	—					CSH(gel)
					—	CSH(I)
		—	—	—		tobermorite
		—	—	—	—	hydrogarnet
110°C curing 2 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
				—	—	$Ca(OH)_2$
	----					CSH(gel)
		—	—	—	—	CSH(I)
			—	—	—	hydrogarnet
7 days	—	—				montmorillonite
	—	—	—	—	—	quartz
					—	$Ca(OH)_2$
	----					CSH(gel)
		—	—	—	—	CSH(I)
			—	—	—	hydrogarnet
28 days	—	—				montmorillonite
	—	—	—	—	—	quartz
					—	$Ca(OH)_2$
	----					CSH(gel)
		—			—	CSH(I)
			—	—		tobermorite
			—	—	—	hydrogarnet
90 days	—	—				montmorillonite
	—	—	—			quartz
					—	$Ca(OH)_2$
	—					CSH(gel)
		—				CSH(I)
			—	—		tobermorite
			—	—	—	hydrogarnet

Table 3 (Continued)

Curing temperature and period	C/S ratio					
	0.223	0.446	0.892	1.338	1.784	
180 days	ND	ND	—	ND	ND	tobermorite
			—			hydrogarnet
40°C curing 7 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
		—	—	—	—	$Ca(OH)_2$
	- - -	- - -	- - -	- - -	- - -	CSH(gel)
				—	—	C_4AH_{13}
28 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
			—	—	—	$Ca(OH)_2$
	- - -	- - -	- - -	- - -	- - -	CSH(gel)
			—	—	—	hydrogarnet
			—	—	—	C_4AH_{13}
90 days	—	—	—	—		montmorillonite
	—	—	—	—	—	quartz
				—	—	$Ca(OH)_2$
	- - -	—	—	—	—	CSH(gel)
			—	—	—	hydrogarnet
			—	—	—	C_4AH_{13}
180 days	—	—	—	ND	ND	montmorillonite
	—	—	—			quartz
	- - -	—				CSH(gel)
			—			CSH(I)
			—			hydrogarnet
			—			C_4AH_{13}
23°C curing 28 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
		—	—	—	—	$Ca(OH)_2$
	- - -	- - -	- - -	- - -	- - -	CSH(gel)
			—	—	—	C_4AH_{13}

Table 3 (Continued)

Curing temperature and period	C/S ratio 0.223	 0.446	 0.892	 1.338	 1.784	
90 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
			—	—	—	$Ca(OH)_2$
	- -	- -	—			CSH(gel)
			—	—	—	C_4AH_{13}
180 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
			—	—	—	$Ca(OH)_2$
	- -	—	—			CSH(gel)
		—	—	—	—	C_4AH_{13}

The identification of CSH(I) in the present study was difficult due to the frequent formation of the hydrogarnet phase. No basal spacings were observed. The 3.04 and 2.78Å lines of CSH(I) overlap the strong 3.07 and 2.74Å lines of the hydrogarnet. Only from the asymmetry of these two hydrogarnet peaks was the identification of CSH(I) possible. The 3.25, 1.82, and 1.66Å peaks are relatively weak, but the existence of the 1.66Å peak was usually a helpful feature in distinquishing the CSH(I) from CSH(gel). There were few relatively weak peaks in the region of 2.40, 2.01 and 1.545Å often appearing together with the presence of CSH(I). These lines probably indicated the presence of CSH(II) phase since most of the other strong X-ray diffraction lines of CSH(II) were overlapped by that of the CSH(I). Table 3 as well as Tables 5, 6, and 7 to be presented in latter sections made no special effort to distinguish these two phases because they are both intermediate in properties between tobermorite and CSH(gel) and are approximately equivalent in degree of crystallinity.

The X-ray diffraction pattern of tobermorite is characterized by a basal spacing in the vicinity of 11Å, and a set of strong triple peaks at 3.07, 2.96, and 2.80Å. Its identification is relatively easy. In the present study the tobermorite formed through the reaction between bentonite and $Ca(OH)_2$ is believed to be one of the Al- and/or Fe-substituted phase because of the presence of large amounts of Al_2O_3 and Fe_2O_3 in the bentonite. This was confirmed by the evidences that a shift of the basal spacing from 11.2Å of pure synthetic tobermorite to the region of 11.6-11.8Å and a weakening of the 2.80Å peak intensity were observed. Such effects were noted previously by other investigators (18, 46).

Isometric tricalcium aluminate hexahydrate, C_3AH_6, one of the well-established products of hydration of portland cement, forms complete solid solutions with the corresponding ferrite, C_3FH_6, with grossularite garnet, C_3AS_3, and with andradite garnet, C_3FS_3. Hydrogarnets are the hydrous members of this solid solution series and can be synthesized by hydrothermal means (23). In the present study a product having strong d-spacings at 3.07, 2.74, and 1.635Å was identified to be a hydrogarnet phase similar to the natural occurring plazolite, $3CaO.Al_2O_3.2(SiO_2,CO_2).2H_2O$. Table 4 compares the X-ray diffraction pattern of the observed product with that of plazolite. It is seen that this product has slightly higher d-spacings which may be due to substitutions of iron and magnesium into the plazolite structure; both of these ions have ionic radii substantially larger than those of aluminum and silicon. The DTA pattern of this product is characterized by a medium-strong exothermic peak at 910°C.

There was another product showing sharp peaks at 2.67, 1.77, and 5.34Å formed only in lime-rich mixtures (C/S=1.892) under 165°C or 110°C and curing for long periods. It is believed to be another hydrogarnet phase, but precise identification could not be achieved.

The calcium aluminate hydrates found in the present study were the hexagonal tetracalcium aluminate phases, characterized by a 8.2Å spacing for α-C_4AH_{13}, a 7.9Å for β-C_4AH_{13}, and a 7.56Å for the calcium monocarboaluminate, $C_3AH_{11}.CaCO_3$ in X-ray diffraction patterns. The relative amount of each phase which may be formed appeared to be matter of chance. The occurrence can be a mixture of any combination of the three phases. This fact was noted previously by Roberts (68).

Table 4. X-ray diffraction data of hydrogarnet

Plazolite (1)		Observed lines	
d, Å	I[a]	d, Å	I[a]
4.96	40	5.01	15
3.25	40	3.28	20
3.03	80	3.07	65
2.71	100	2.74	100
2.60	20	2.62	Tr.
2.48	60	2.50	35
2.38	60	2.40	35
2.21	80	2.24	40
2.14	20	2.14	Tr.
1.97	80	1.984	45
1.92	20	1.932	Tr.
1.76	50	1.767	10
1.68	80	1.697	35
1.62	100	1.635	55
1.52	50	1.529	10

[a] Relative intensities.

Figure 1 puts into graphical form part of the results in Table 3. Each graph represents one specified curing period, and each enclosed area in the graph indicates a specific formation in reference to curing temperature and starting C/S mole ratio of the reacting mixture. For 165°C curing, the 2- and 7-day results shown in the graphs were obtained from the 36- and 150-hour curing, respectively.

It is seen that the very poor-crystalline CSH(gel) phase can be readily formed either at relatively low curing temperatures at any composition or at high temperatures when the C/S

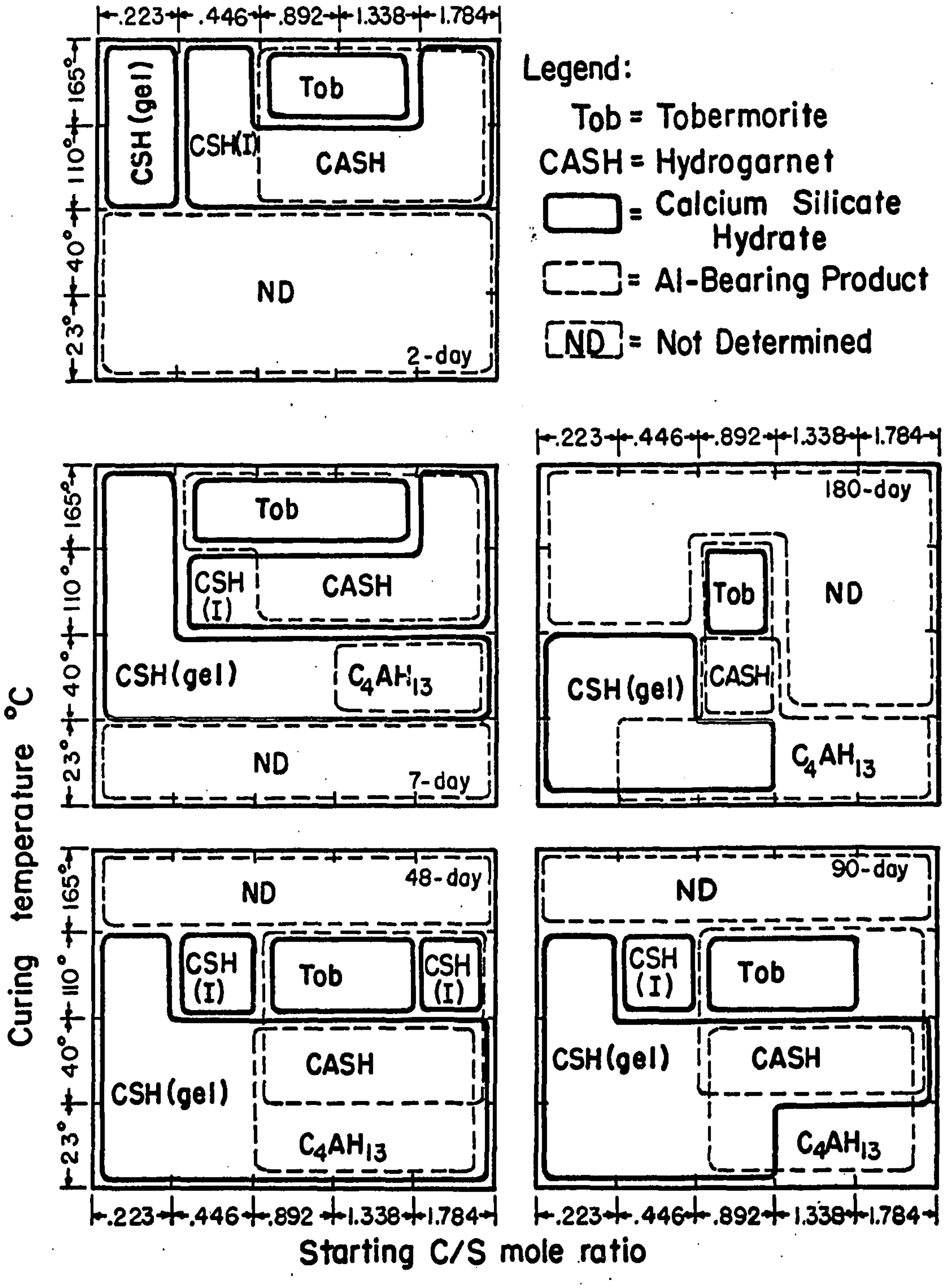

Figure 1. Reaction products of bentonite-Ca(OH)$_2$ pastes cured at different curing temperatures and periods

ratio is extremely low. Better crystalline products, such as CSH(I) or tobermorite, always replace CSH(gel) when both curing temperature and the starting C/S are high. Evidence of transformation of CSH(I) to tobermorite is seen with the progress of curing time. Tobermorites can only be found in the starting mixture having C/S ratios between 0.446 and 1.338 and at or above 110°C. No tobermorite is formed in the extremely lime-rich mixtures (C/S=1.784) at any temperature. The exact C/S ratio in the newly formed tobermorite structures is not known because of the complicated analytical process in determining the amounts of Al- and Fe-substitution in the tobermorite structure. Normally, without any substitution, it is said that tobermorites can be synthesized possessing C/S ranging from 0.80 to 1.08 (18).

Hydrogarnet can be found in relatively lime-rich mixtures cured at and above 40°C. This product can exist together with any other newly formed compounds. The lower the curing temperature, the longer it takes to form.

Calcium aluminate hydrate phases appear only at low curing temperatures with lime-rich mixtures. CSH(gel) may be found with these phases in the same mixture, but with prolonged curing at room temperature disappearance of the CSH (gel) phase is noticed, the C_4AH_{13} phases being the sole reaction product.

In brief, temperature, time, and compositional factors are inter-dependent one to another. With suitable composition, high temperature can accelerate the rate of formation of well-crystallized products, whereas the progress of curing may reveal the transformation process and show the final stable products in that particular curing temperature and composition.

Reaction products of bentonite-$Ca(OH)_2$-MgO pastes

Magnesium oxides were added in the bentonite-$Ca(OH)_2$ system in this series of studies in order to find the role of MgO in the soil-lime (pozzolanic) reactions. Two subseries: first, varying C/M mole ratios with (C+M)/S constant, and second, varying (C+M)/S mole ratios with C/M constant, were investigated.

Varied C/M, constant (C+M)/S The C/M mole ratios were varied from zero to infinity, while the ratio of combined moles of calcium oxide(C) and magnesium oxide(M) to the moles of silicon dioxide(S) was kept at a constant value of 0.892 in the bentonite-$Ca(OH)_2$-MgO mixtures. Table 5 reports the identified reaction products reacted from curing under different temperatures and periods. A conversion of MgO to $Mg(OH)_2$ was always observed so long as there was MgO present in the starting mixture. In general, CSH(gel), CSH(I) (probably also some CSH(II)), tobermorite, hydrogarnet, and

Table 5. Reaction products of bentonite-$Ca(OH)_2$-MgO ($\frac{C+M}{S}$ = 0.892) pastes

Curing temperature and period	C/M							
	0	0.25	0.5	1	2	4	∞	
Starting components	—	—	—	—	—	—	—	montmorillonite
	—	—	—	—	—	—	—	quartz
		—	—	—	—	—	—	$Ca(OH)_2$
	—	—	—	—	—	—		MgO
165°C curing 4 hours		—	—	—	—	—	—	montmorillonite
	—	—	—	—	—	—	—	quartz
	—	—	—	—	—	—		$Mg(OH)_2$
		- -	—					CSH(gel)
				—	—	—	—	CSH(I)
	—							chlorite
	—							serpentine
							—	hydrogarnet
16 hours		—	—	—	—	—		montmorillonite
	—	—	—	—	—	—	—	quartz
	—	—	—	—	—	—		$Mg(OH)_2$
		—	—	—	—	—	—	tobermorite
						—	—	hydrogarnet
	—							chlorite
	—							serpentine
36 hours		—	—	—	—			montmorillonite
	—	—	—	—	—	—	—	quartz
	—	—	—	—	—	—		$Mg(OH)_2$
		—	—	—	—	—	—	tobermorite
					—	—	—	hydrogarnet
	—							chlorite
	—							serpentine
81 hours		—	—	—	—			montmorillonite
		—	—	—	—	—	—	quartz
	—	—	—	—	—	—		$Mg(OH)_2$
		—	—	—	—	—	—	tobermorite
					—	—	—	hydrogarnet

Table 5 (Continued)

Curing temperature and period	0	0.25	0.5	1	2	4	∞	
	—							chlorite
	—							serpentine
150 hours		—	—	—				montmorillonite
		—	—	—	—	—	—	quartz
		—	—	—	—			$Mg(OH)_2$
		—	—	—	—	—	—	tobermorite
					—	—	—	hydrogarnet
	—							chlorite
	—							serpentine
110°C curing 2 days		—	—	—	—	—	—	montmorillonite
	—	—	—	—	—	—	—	quartz
	—	—	—	—	—	—		$Mg(OH)_2$
		- - -	- - -	—	—	—		CSH(gel)
							—	CSH(I)
							—	hydrogarnet
	—							chlorite
	—							serpentine
7 days		—	—	—	—	—		montmorillonite
	—	—	—	—	—	—	—	quartz
	—	—	—	—	—	—		$Mg(OH)_2$
		- - -	—	—	—			CSH(gel)
						—	—	CSH(I)
						—	—	hydrogarnet
	—							chlorite
	—							serpentine
28 days		—	—	—				montmorillonite
		—	—	—	—	—	—	quartz
	—	—	—	—				$Mg(OH)_2$
		—						CSH(gel)
			—	—	—	—	—	tobermorite
					—	—	—	hydrogarnet
	—							chlorite
	—							serpentine

Table 5 (Continued)

Curing temperature and period	C/M							
	0	0.25	0.5	1	2	4	∞	
90 days		—	—	—	—			montmorillonite
		—	—	—	—	—	—	quartz
	—	—	—	—	—			$Mg(OH)_2$
		—	—	—	—	—	—	tobermorite
					—	—	—	hydrogarnet
	—							chlorite
	—							serpentine
180 days				—				montmorillonite
				—				quartz
				—				$Mg(OH)_2$
		ND	ND		ND	ND	—	hydrogarnet
				—			—	tobermorite
	—							chlorite
	—							serpentine
40°C curing 7 days		—	—	—	—	—	—	montmorillonite
	—	—	—	—	—	—	—	quartz
				—	—	—	—	$Ca(OH)_2$
	—	—	—	—	—	—		$Mg(OH)_2$
		- -	- -	- -	- -	- -	- -	CSH(gel)
	—							chlorite
	—							serpentine
28 days		—	—	—	—	—	—	montmorillonite
	—	—	—	—	—	—	—	quartz
						—	—	$Ca(OH)_2$
	—	—	—	—	—	—		$Mg(OH)_2$
		- -	- -	—	—	- -	- -	CSH(gel)
					—	—	—	hydrogarnet
						—	—	C_4AH_{13}
	—							chlorite
	—							serpentine
90 days		—	—	—	—	—	—	montmorillonite
	—	—	—	—	—	—	—	quartz

Table 5 (Continued)

Curing temperature and period	C/M							
	0	0.25	0.5	1	2	4	∞	
	—	—	—	—	—	—		$Mg(OH)_2$
		- -	- -	—	—	- -	—	CSH(gel)
					—	—	—	hydrogarnet
						—	—	C_4AH_{13}
	—							chlorite
	—							serpentine
180 days		—	—	—			—	montmorillonite
	—	—	—	—			—	quartz
	—	—	—	—				$Mg(OH)_2$
		- -	—	—				CSH(gel)
							—	CSH(I)
					ND	ND	—	hydrogarnet
							—	C_4AH_{13}
	—							chlorite
	—							serpentine
23°C curing 28 days		—	—	—	—	—	—	montmorillonite
	—	—	—	—	—	—	—	quartz
				—	—	—	—	$Ca(OH)_2$
	—	—	—	—	—	—		$Mg(OH)_2$
		- -	- -	- -	- -	- -	- -	CSH(gel)
						—	—	C_4AH_{13}
	—							chlorite
	—							serpentine
90 days		—	—	—	—	—	—	montmorillonite
	—	—	—	—	—	—	—	quartz
				—	—	—	—	$Ca(OH)_2$
	—	—	—	—	—	—		$Mg(OH)_2$
		- -	- -	—	- -	- -	—	CSH(gel)
				—	—	—	—	C_4AH_{13}
	—							chlorite
	—							serpentine

Table 5 (Continued)

Curing temperature and period	C/M							
	0	0.25	0.5	1	2	4	∞	
180 days		—	—	—	—	—	—	montmorillonite
	—	—	—	—	—	—	—	quartz
					—	—	—	$Ca(OH)_2$
	—		—	—	—	—		$Mg(OH)_2$
		- -	- -	—	- -	—	—	CSH(gel)
			—	—	—	—	—	C_4AH_{13}
	—							chlorite
	—							serpentine

C_4AH_{13} phases were the new products found in bentonite mixtures containing MgO and $Ca(OH)_2$. The methods of identifying these products were explained in the previous section.

In mixtures containing MgO alone (C/M=0), transformation of montmorillonite to a chlorite-like mineral and an aluminum-substituted magnesium silicate hydrate similar to the 1-layer ortho serpentine was found. The process of identification of these products is explained in the following paragraphs.

The transformation of montmorillonite to a phyllite of a nonexpanding 14Å basal spacing[1] was noted by Caillere and Henin in treatment of montmorillonite with $MgCl_2$ and NH_4OH

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[1] The 14Å basal spacing was obtained when the sample was dried at 105°C, but air-drying gave a spacing of 15.2Å.

solutions (12). The product showed the characteristics of chlorite and vermiculite. Later, Caillere and Henin confirmed that the transformation was caused by precipitation of at least part of the magnesium hydroxide between the structural layers of montmorillonite. They concluded, through data obtained from X-ray, DTA, and other tests, that the mineral was to approximate chlorite without, however, being completely the same (10). The precipitation of magnesium hydroxide in between the structural sheets was found to be very rapid if not almost instantaneous.

The chlorite and serpentine minerals have often been classified together by mineralogists because of similarities in chemical and optical data, though crystallographers prefer to keep them separate in view of structural differences (6, 11). The conversion between serpentines and chlorites observed by several investigators rather support the former view (7, 65, 72). A model was suggested that some Si atoms are displaced and linked to the adjacent brucite-type layer, producing in effect serpentine structural units (7).

The above information is pertinent to the present studies. Results have shown that, independent of curing temperature and time, whenever MgO alone was added to the bentonite-water system, a conversion of MgO to $Mg(OH)_2$ occurred. At the same time a diffuse but stable 15.2Å basal spacing which, unlike the montmorillonite, would not expand in either water or in glycol or glycerine solution, and also a series of diffuse new peaks led by a longest spacing in the vicinity of 7Å were observed. The 15Å phase is believed to be chlorite-like mineral based on the studies by Caillere and Henin (10, 12). The 7Å phase corresponds to a 1-layer ortho serpentine, $(Mg_{6-x}Al_x)(Si_{4-x}Al_x)O_{10}(OH)_8$ $(x=3/4)$, but is believed to be very poorly crystallized because only few broad lines that correspond to the strong lines in serpentine were found (1, 6).

The final product of a reacted bentonite-MgO paste with M/S=1.63, which was cured at 165°C for 8 months, was nothing but a well-crystallized 1-layer ortho serpentine; the chlorite appeared to have all been converted into serpentine. For the same mixture cured at 23°C up to a year (Figure 2) and for the mixtures with M/S=0.892 cured at different temperatures up to 6 months (Table 5), the chlorites and serpentines formed were all identical to the early stage products of the mixture that eventually forms only the well-crystalline serpentine. It is thus believed that the formation of well-crystallized serpentine depends on the temperature as well as on the composition; only a combination of high M/S mole ratio and a high temperature can cause the formation.

The DTA patterns of reacted bentonite-MgO mixtures further demonstrate the transformation of montmorillonite to chlorite and the formation of serpentine. Figure 3 shows

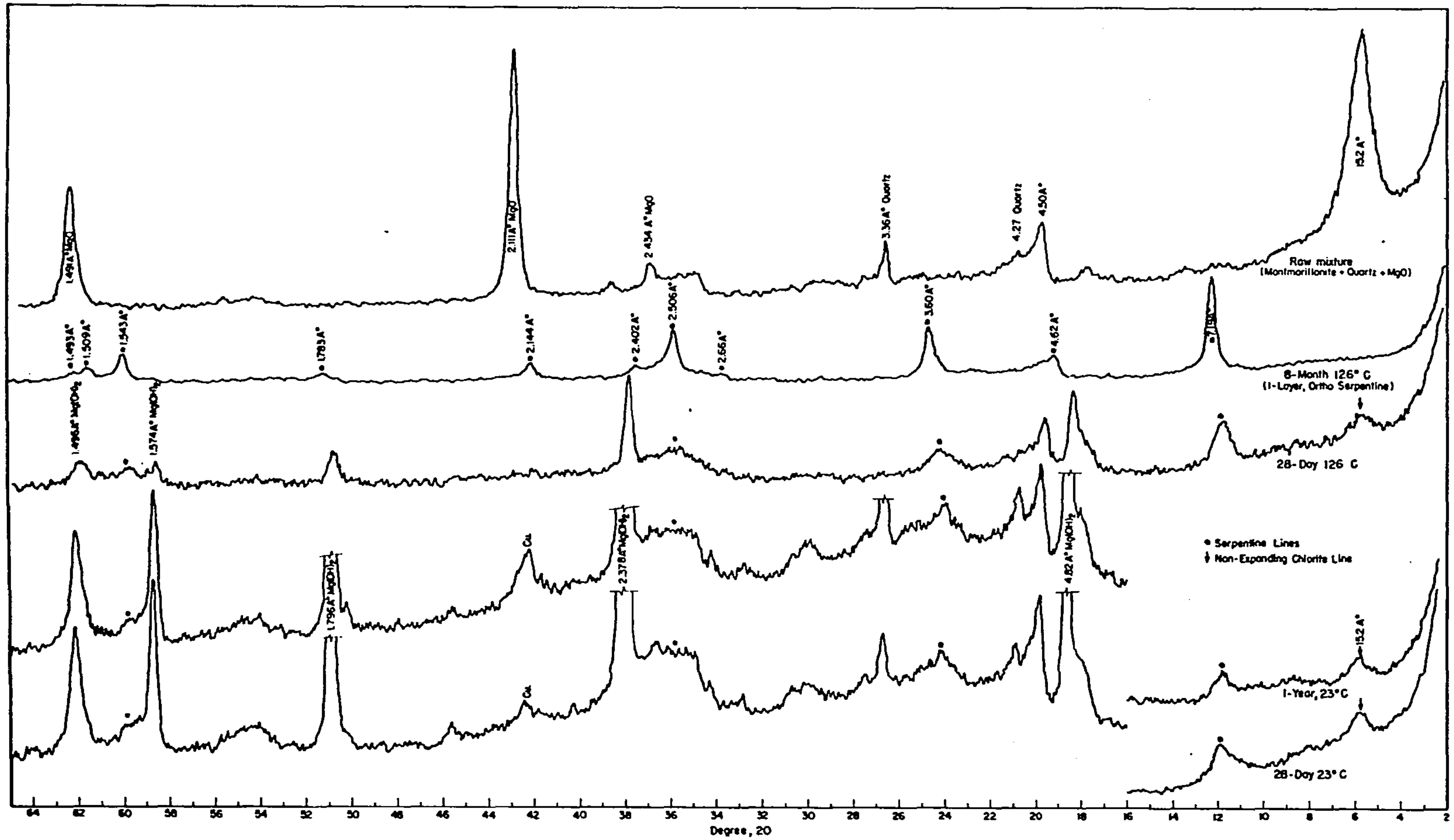

Figure 2. X-ray diffraction tracings of bentonite-MgO pastes (M/S=1.63)

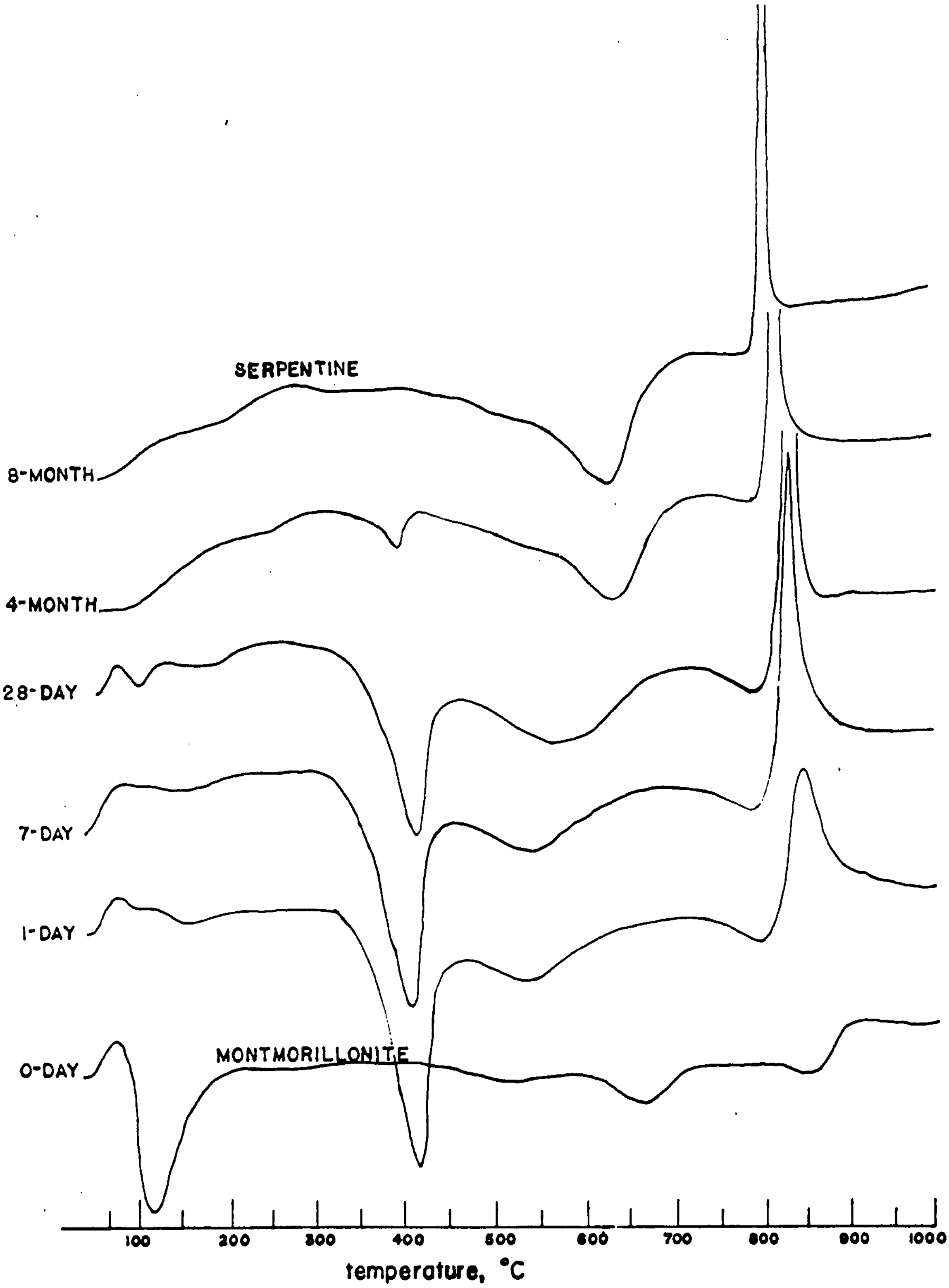

Figure 3. Differential thermal analysis tracings of bentonite-MgO mixtures (M/S=1.63), cured at 126°C for different periods

that only after 1-day curing at 126°C, the characteristic endothermic peak for montmorillonite at approximately 670°C has disappeared. The new pattern presents a strong endothermic peak at 410°C due to the dehydration of $Mg(OH)_2$, a broad endothermic peak at about 540°C region, and a strong exothermic peak at 840°C preceded by a weak endothermic peak at 800°C characterizing the existence of serpentine (11). The peaks corresponding to the chlorite are thought to have been overlapped by the serpentine peaks since a pattern for chlorites prepared from precipitation of $Mg(OH)_2$ in montmorillonite by Caillere and Henin showed only a weak endothermic peak in the region of 500-600°C and another weak exothermic peak at about 850°C (10, 12).

An interesting and worth-noting feature in Figure 3 is that the large, low-temperature endothermic peak at 110°C that signifies the loss of hygroscopic moisture in montmorillonite is absent in the cured mixtures where chlorites and serpentines are present. This indicates that there must be at least some alternation of the montmorillonite into a less "water-loving" mineral.

It is also seen in Figure 3 that gradual shifts of the broad endothermic peak at 540°C to higher temperature and the strong exothermic peak at 840°C to lower temperature have occurred with the progress of curing. Well-crystallized serpentine shows a large endothermic peak at 620°C and a very strong exothermic peak at 800°C.

The morphology of bentonite-MgO mixture (M/S=1.63) cured at 126°C for 7 days shows strong formation of fibrous phase under electron microscopic observation (Figure 4), which, with the aid from X-ray and DTA pattern, is believed to be a fibrous serpentine. However, the 8-month cured specimen, which showed the formation of well-crystallized 1-layer ortho serpentine under X-ray and DTA examinations, exhibits essentially plates and elongated sheets (Figure 5). This coincides with the known facts that 1-layer ortho serpentines are platy (6). The change of morphology of serpentines from the early fibrous to the final platy forms has been attributed to the gradual substitution of aluminum ions in the crystal lattice.

Again, part of the results in Table 5 is presented into graphical forms (Figure 6). The graphs were plotted using curing temperature against the starting C/M mole ratio of the bentonite-$Ca(OH)_2$-MgO mixtures, with respect to each curing period. It was hoped to see whether if there is an optimum C/M ratio in dolomitic limes that would favor the formation of pozzolanic reaction products, namely, hydrated calcium silicates and calcium aluminates.

It appears in Figure 6 that the rates of formation of calcium silicate and calcium aluminate hydrates depend simply

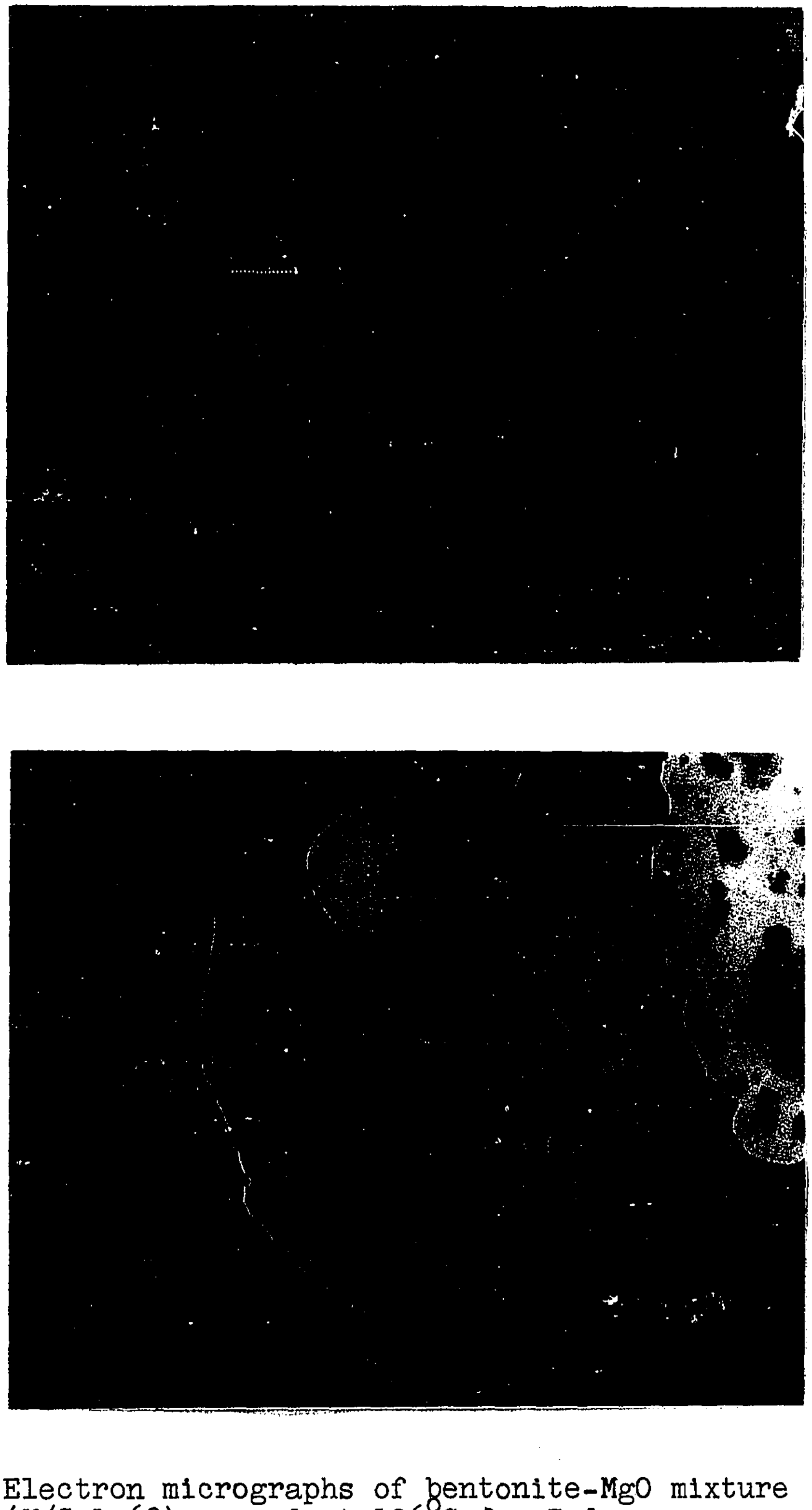

Figure 4. Electron micrographs of bentonite-MgO mixture (M/S=1.63), cured at 126°C for 7 days

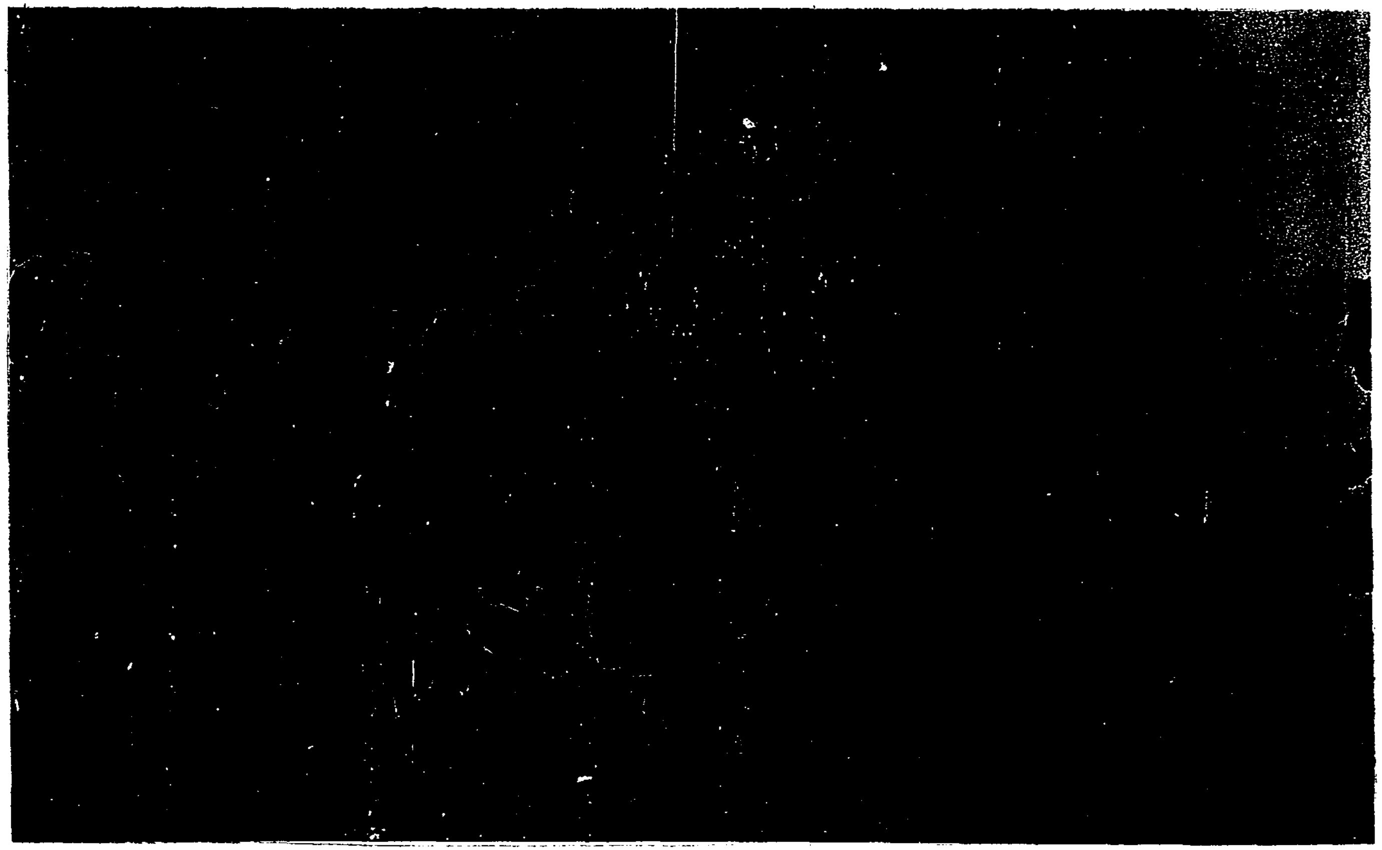

Figure 5. Electron micrograph of bentonite-MgO mixture (M/S=1.63), cured at 126°C for 8 months

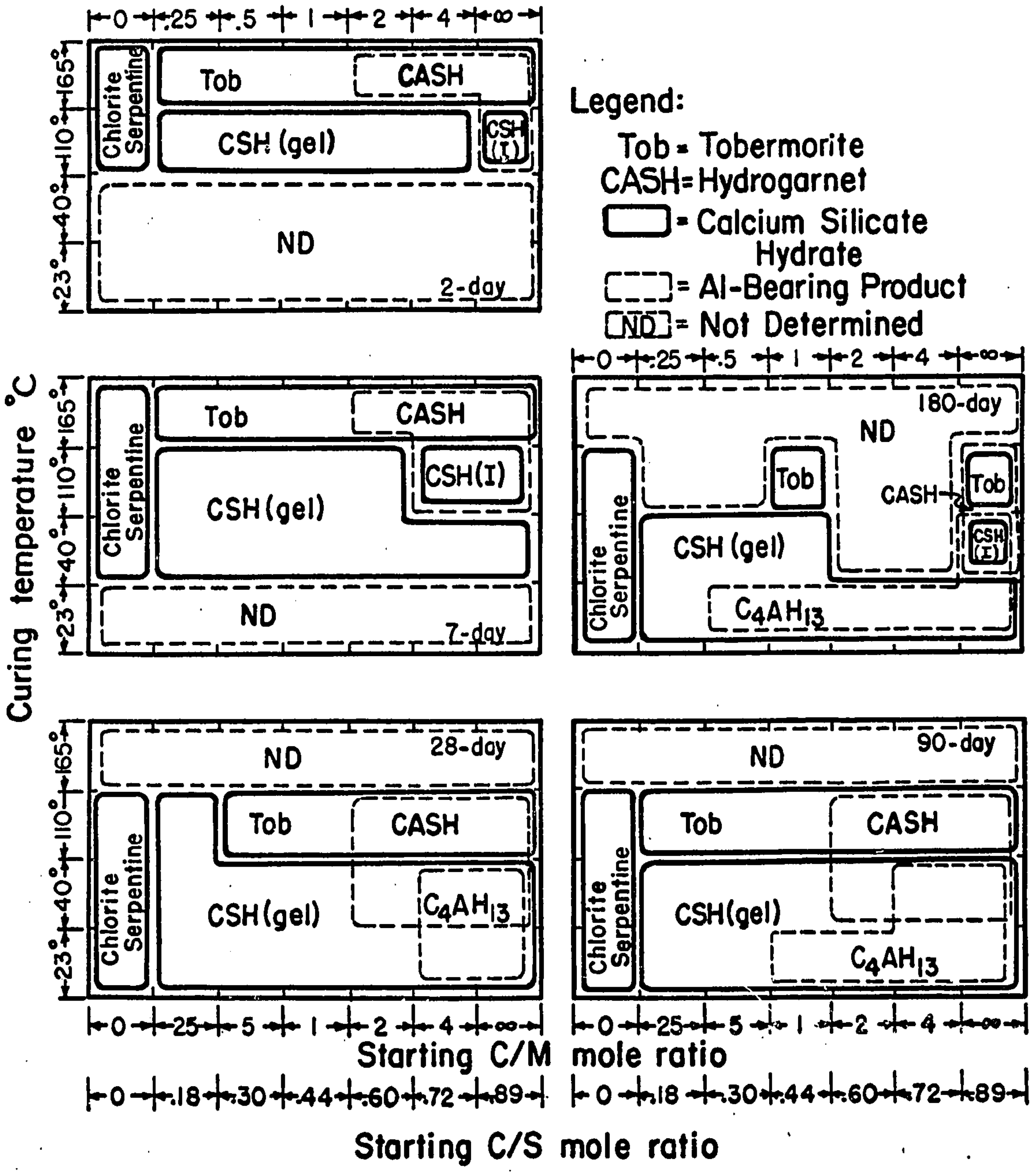

Figure 6. Reaction products of bentonite-$Ca(OH)_2$-MgO $(\frac{C+M}{S}=1)$ pastes cured at different curing temperatures and periods

on the amounts of calcium ions present, and on the temperature and period of curing, as discussed in the previous section on bentonite-$Ca(OH)_2$ mixtures (Figure 1). A scale expressed in C/S mole ratios was thus drawn in addition to the corresponding C/M mole ratio scale in Figure 6. In comparing this figure with Figure 1, it is clearly seen that with the same C/S ratio, despite of the presence of various amounts of MgO, the pozzolanic reactions in these two separate systems at low temperatures are practically identical. However, it has been observed in the bentonite-$Ca(OH)_2$-MgO mixtures cured at and above 110°C that tobermorites appear in mixtures with starting C/S mole ratio as low as 0.18, while in bentonite-$Ca(OH)_2$ mixtures this ratio is 0.446. This phenomenon probably indicates that large amounts of magnesium ions may have entered the tobermorite structures and thus made more calcium ions available for further pozzolanic reactions. Nevertheless, as far as the low temperature curing conditions are concerned, the reaction products have been all alike in the bentonite-$Ca(OH)_2$ and bentonite-$Ca(OH)_2$-MgO systems, i.e., there appears no optimum C/M ratio in favor of pozzolanic reactions.

It should be noted in Table 5 and Figure 6 that as long as calcium hydroxides are present in the bentonite-MgO mixtures, there is no conversion of montmorillonite to chlorite and no new formation of magnesium compounds, except the hydration of MgO; the formation of calcium silicate and calcium aluminate hydrate seems to have the priority. Perhaps, the relative chemical activity of the $Ca(OH)_2$ and MgO compounds are responsible for this.

Constant C/M, varied (C+M)/S This subseries was performed as a further check on the role of MgO in pozzolanic reactions. The C/M mole ratio was kept at a constant value of one to simulate the composition of commercial dolomitic lime, and the total amounts of calcium oxide(C) and magnesium oxide(M) were varied in respect to the amount of silicon dioxide(S) present in the bentonite. Results obtained under various curing conditions are presented in Table 6, and some parts of the results are also presented in graphical forms (Figure 7). The methods of identification of the reaction products have been discussed in the previous sections. Well-crystallized 1-layer ortho serpentines have also been found in mixtures of high (C+M)/S ratios cured at high temperatures. No magnesium silicate or magnesium aluminate hydrate was found in any of the mixtures cured at low temperatures.

As far as the formation of pozzolanic reaction products is concerned, again MgO shows no apparent effect at low curing temperatures. In comparing Figure 7 with Figure 1, it is seen that with the same starting C/S mole ratio the rates of formation of hydrated calcium silicate and calcium aluminate hydrates are all alike in the bentonite-$Ca(OH)_2$ systems with and without MgO. Nevertheless, bentonite-

Table 6. Reaction products of bentonite-$Ca(OH)_2$-MgO (C/M=1) pastes

Curing temperature and period	0.223	0.446	0.892	1.338	1.784	
Starting components	———	———	———	———	———	montmorillonite
	———	———	———	———	———	quartz
	———	———	———	———	———	$Ca(OH)_2$
	———	———	———	———	———	MgO
165°C curing 4 hours	———	———	———			montmorillonite
	———	———	———	———	———	quartz
		———	———	———	———	$Mg(OH)_2$
	- - -	- - -				CSH(gel)
			———	———	———	CSH(I)
					———	hydrogarnet
					———	serpentine
16 hours	———	———	———			montmorillonite
	———	———	———	———	———	quartz
		———	———	———	———	$Mg(OH)_2$
	- - -	- - -				CSH(gel)
			———	———	———	tobermorite
				———	———	hydrogarnet
					———	serpentine
36 hours	———	———	———			montmorillonite
	———	———	———	———		quartz
		———	———	———	———	$Mg(OH)_2$
	- - -	- - -				CSH(gel)
			———	———	———	tobermorite
				———	———	hydrogarnet
				———	———	serpentine

Table 6 (Continued)

Curing temperature and period	0.223	0.446	0.892	1.338	1.784	
81 hours	——	——	——			montmorillonite
	——	——	——	——		quartz
		——	——	——	——	$Mg(OH)_2$
	- - -	——				CSH(gel)
			——	——	——	tobermorite
				——	——	hydrogarnet
				——	——	serpentine
150 hours	——	——	——			montmorillonite
	——	——	——			quartz
		——	——	——	——	$Mg(OH)_2$
	- - -					CSH(gel)
		——	——	——	——	tobermorite
				——	——	hydrogarnet
				——	——	serpentine
110°C curing 2 days	——	——	——	——		montmorillonite
	——	——	——	——	——	quartz
		——	——	——	——	$Mg(OH)_2$
		- - -	——	——	- - -	CSH(gel)
				——	——	hydrogarnet
7 days	——	——	——	——		montmorillonite
	——	——	——	——	——	quartz
		——	——	——	——	$Mg(OH)_2$
	- - -	- - -	——		——	CSH(gel)
				——		tobermorite
				——	——	hydrogarnet

Table 6 (Continued)

Curing temperature and period	0.223	0.446	0.892	1.338	1.784	
28 days	—	—	—			montmorillonite
	—	—	—	—		quartz
		—	—	—	—	$Mg(OH)_2$
	- - -	- - -				CSH(gel)
			—	—	—	tobermorite
				—	—	hydrogarnet
					—	serpentine
90 days	—	—	—			montmorillonite
	—	—	—			quartz
		—	—	—	—	$Mg(OH)_2$
	- - -	—				CSH(gel)
			—	—	—	tobermorite
				—	—	hydrogarnet
				—	—	serpentine
180 days	ND	ND	—	ND	ND	montmorillonite
			—			quartz
			—			$Mg(OH)_2$
			—			tobermorite
40°C curing 7 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
		—	—	—	—	$Mg(OH)_2$
			—	—	—	$Ca(OH)_2$
		- - -	- - -	- - -	- - -	CSH(gel)

Table 6 (Continued)

Curing temperature and period	0.223	0.446	0.892	1.338	1.784	
					—	C_4AH_{13}
28 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
		—	—	—	—	$Mg(OH)_2$
				—	—	$Ca(OH)_2$
	- - -	- - -	—	—	—	CSH(gel)
					—	C_4AH_{13}
90 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
		—	—	—	—	$Mg(OH)_2$
					—	$Ca(OH)_2$
	- - -	- - -	—	—	—	CSH(gel)
				—	—	hydrogarnet
				—	—	C_4AH_{13}
180 days	—	—	—			montmorillonite
	—	—	—			quartz
		—	—	ND	ND	$Mg(OH)_2$
	- - -	- - -	—			CSH(gel)
23°C curing 28 days	—	—	—	—	—	montmorillonite
	—	—	—	—	—	quartz
	—	—	—	—	—	$Mg(OH)_2$
			—	—	—	$Ca(OH)_2$

Table 6 (Continued)

Curing temperature and period	0.223	0.446	0.892	1.338	1.784	
		- - -	- - -	- - -	- - -	CSH(gel)
				———	———	C_4AH_{13}
90 days	———	———	———	———	———	montmorillonite
	———	———	———	———	———	quartz
	———	———	———	———	———	$Mg(OH)_2$
			———	———	———	$Ca(OH)_2$
	- - -	- - -	———	- - -	- - -	CSH(gel)
			———	———	———	C_4AH_{13}
180 days	———	———	———	———	———	montmorillonite
	———	———	———	———	———	quartz
		———	———	———	———	$Mg(OH)_2$
				———	———	$Ca(OH)_2$
	- - -	- - -	———	- - -	- - -	CSH(gel)
			———	———	———	C_4AH_{13}

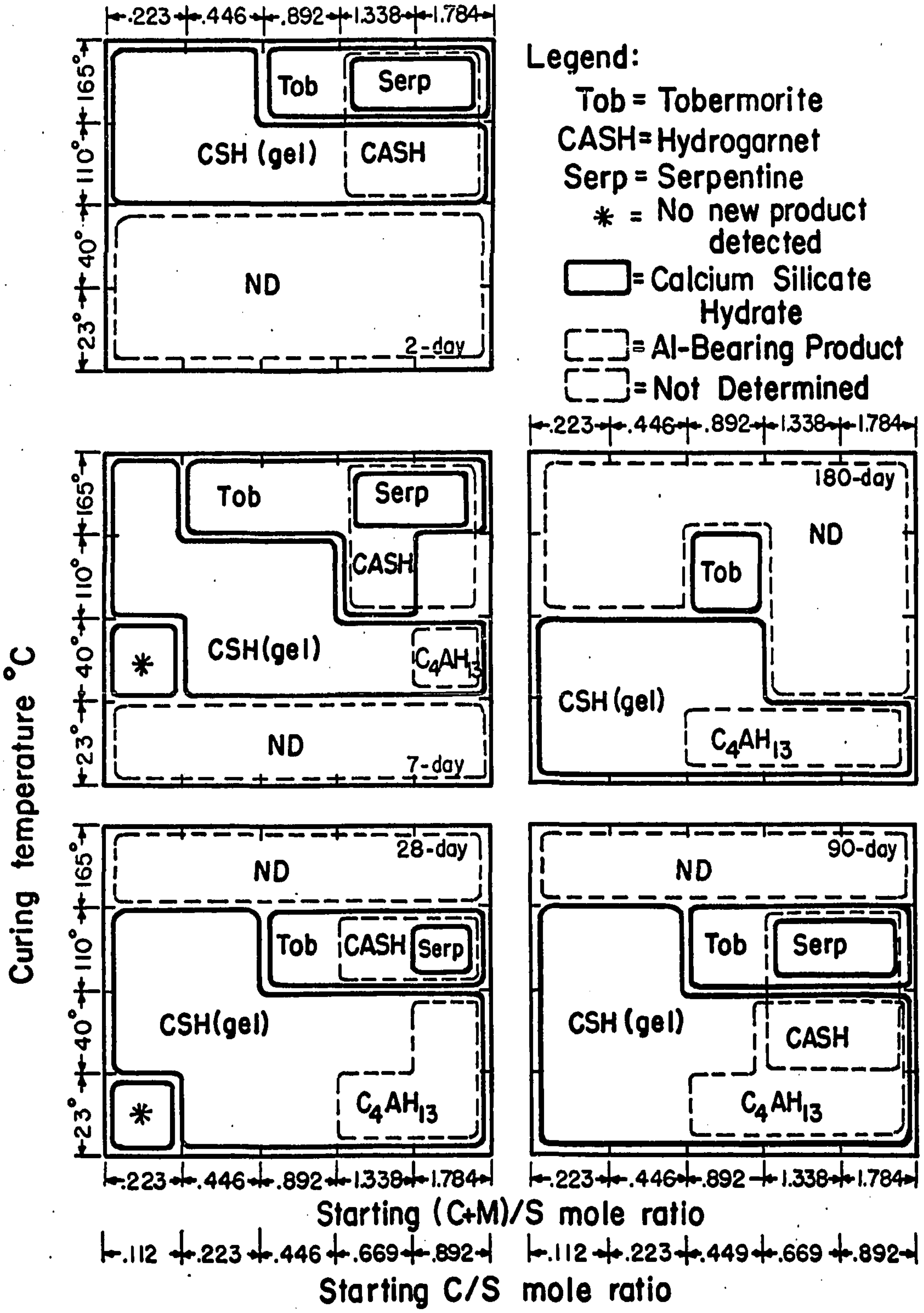

Figure 7. Reaction products of bentonite-Ca(OH)$_2$-MgO (C/M=1) pastes cured at different temperatures and periods

$Ca(OH)_2$-MgO mixtures cured at high temperatures again may form tobermorites at a starting C/S ratio as low as 0.223, as compared with 0.446 in the bentonite-$Ca(OH)_2$ mixtures.

When the mole ratio of (C+M)/S in Figure 7 is equal to that of C/S in Figure 1, the rates of the formation of calcium silicate hydrates of the former at 165°C curing is no less than that of the latter. It is believed that high-temperature curing makes substitution of calcium ions by magnesium possible in well-crystallized hydrates, and thus more calcium can be available for reaction. In comparing the same mixtures cured at 110°C, however, the bentonite-$Ca(OH)_2$-MgO system shows slower rates of forming better crystalline products than the bentonite system with $Ca(OH)_2$ alone. This is because the condition of curing may not allow for fast and extensive substitution of Ca^{++} by Mg^{++} in the silicate structures and the amount of $Ca(OH)_2$ is thus insufficient for formation of well-crystallized phases. At curing temperatures below 40°C, on the other hand, there is apparently no difference in reaction rates since the reactions are very slow at room temperature, and CSH(gel) is the first phase to form. High $Ca(OH)_2$ content favors the formation of C_4AH_{13} and hydrogarnet phases, but their effect on strengths is believed to be small because they are basically weak cements (4, 55).

In brief The pozzolanic reactions between clay and $Ca(OH)_2$ at room temperature and 40°C are slow and do not seem to be affected by the presence of magnesium oxides. At high curing temperatures, however, the presence of MgO may accelerate the rate of pozzolanic reaction, forming a well-crystallized calcium silicate hydrate at very low starting C/S ratio. This suggests that substantial amounts of magnesium ions can substitute for calcium ions in the tobermorite structure, and thus make more calcium ions available for more pozzolanic reactions. This evidence is contradictory to that assumed by Diamond, that the magnesium ion may substitute for silicon in the tobermorite structure (18).

Reaction products of bentonite-$Ca(OH)_2$-$Mg(OH)_2$ pastes

This series of studies was made to simulate the pozzolanic reactions between clay and dolomitic dihydrate lime. The (C+M)/S mole ratios in the starting bentonite-$Ca(OH)_2$-$Mg(OH)_2$ mixtures were kept at a constant value of 1.63, while the C/M values were at 0 and 0.6. Reaction products found through curing at various temperatures and periods have been tabulated in Table 7.

Figure 8 presents X-ray diffraction tracings of the C/M=0 mixtures (i.e., C+M/S=M/S=1.63). For mixtures cured at room temperature (23°C), the 15.2Å peak is still characteristic of unaltered montmorillonite that expands upon treating

Table 7. Reaction products of bentonite-$Ca(OH)_2$-$Mg(OH)_2$ ($\frac{C+M}{S}$ = 1.63) pastes

Curing temperature and periods	C/M	
	0	0.60
Starting components	montmorillonite (M) quartz (Q) $Ca(OH)_2$ $Mg(OH)_2$	M Q $Ca(OH)_2$ $Mg(OH)_2$
165°C curing 1 day	Q $Mg(OH)_2$ chlorite serpentine	M Q $Mg(OH)_2$ tobermorite
126°C curing 1 day	Q $Mg(OH)_2$ chlorite serpentine	M Q $Mg(OH)_2$ CSH(I)
7 days	Q $Mg(OH)_2$ chlorite serpentine	M Q $Mg(OH)_2$ tobermorite
8 months	$Mg(OH)_2$ chlorite serpentine	$Mg(OH)_2$ tobermorite serpentine
70°C curing 3 days	Q $Mg(OH)_2$ chlorite serpentine	
23°C curing 7 days	M Q $Mg(OH)_2$	M Q $Mg(OH)_2$ C_4AH_{13}(Tr.)

Table 7 (Continued)

Curing temperature and periods	C/M 0	 0.60
28 days	M Q $Mg(OH)_2$	M Q $Ca(OH)_2$ $Mg(OH)_2$ C_4AH_{13} CSH(gel)
2 months		M Q $Mg(OH)_2$ C_4AH_{13} CSH(gel)
1 year	M Q $Mg(OH)_2$ serpentine	

with water or glycol or glycerine solution, and there is no 7Å serpentine peak insight. Even in the mixture that was cured up to a year at room temperature only a weak hump is visible in the vicinity of 7Å in the X-ray diffraction pattern, and the 15Å peak still expands to some extent in water. For mixtures cured at elevated temperatures, chlorites and poorly crystallized serpentines were always formed. A fairly well-crystallized serpentine has been observed in a mixture cured at 126°C for 8 months. The very low solubility of the

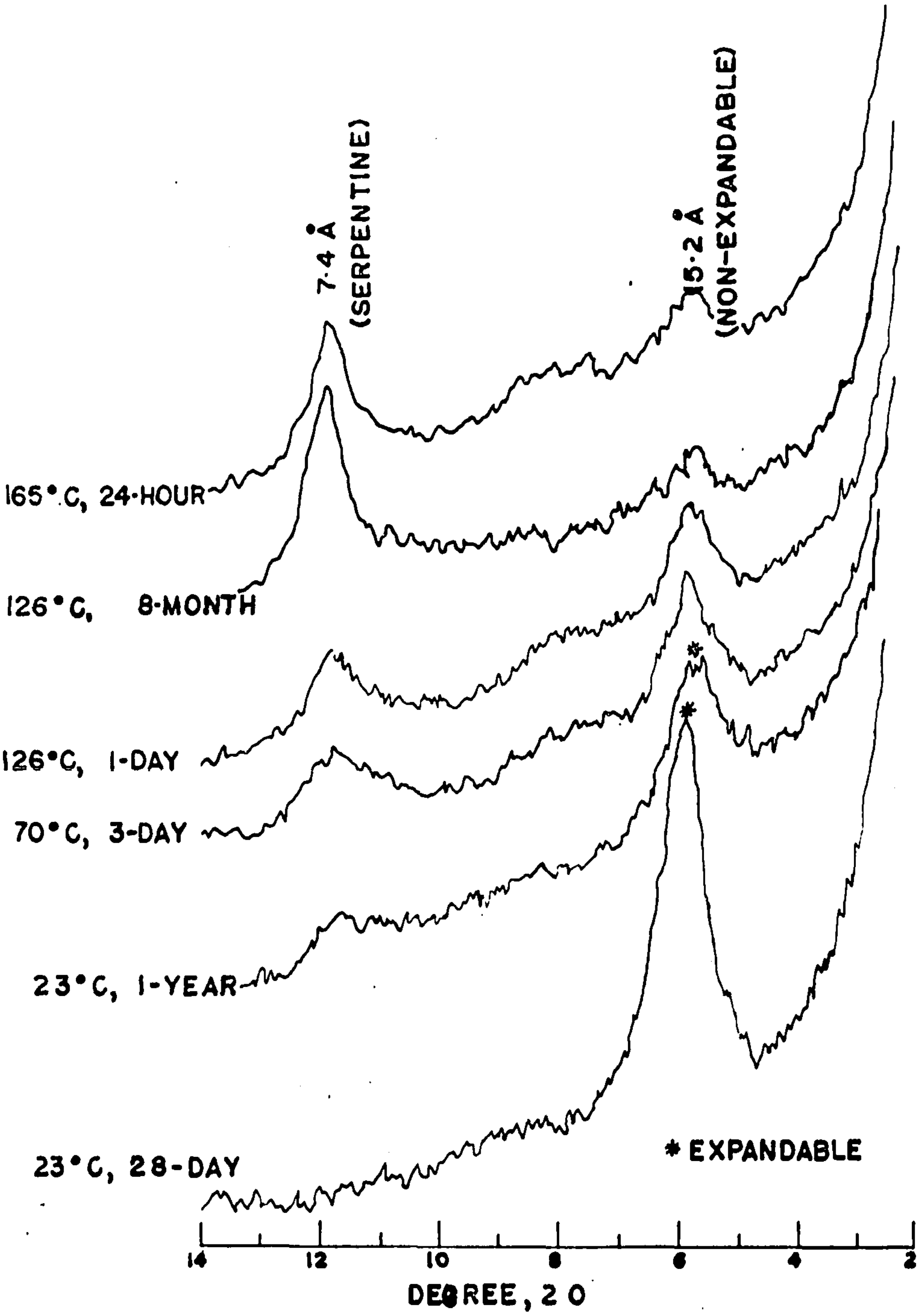

Figure 8. X-ray diffraction tracings of bentonite-$Mg(OH)_2$ mixtures (M/S=1.63)

$Mg(OH)_2$ at room temperature is believed to be responsible for these results. The reprecipitation of $Mg(OH)_2$ in between the structural layers of montmorillonite is therefore very slow due to the low solubility of the $Mg(OH)_2$, and the transformation of montmorillonite to chlorite will probably take a long time. However, at elevated temperatures because of the increased solubility, magnesium hydroxide behaves like magnesium oxide in the respect that precipitation of $Mg(OH)_2$ is much more rapid which, in turn, makes the formation of chlorite possible.

In comparing the reaction products of the series having C/M=0.60(C/S mole ratio also equals to 0.60) in Table 9 with the equivalent series in Figures 1, 6, and 7, the sequence of formation of hydrated calcium silicates and calcium aluminates has been found essentially similar. When $Mg(OH)_2$ is present in the bentonite-$Ca(OH)_2$ system, there does not seem to be any restraint on the pozzolanic reactions between $Ca(OH)_2$ and clay. Hydrated calcium silicates and calcium aluminates can form readily, depending on the temperature and time of curing and on the amount of calcium oxide present, as discussed in the previous sections.

Hydraulic properties of the chief components in hydrated limes

Strickly speaking, the term hydraulic refers only to "hardening under water"; however, the type of hardening derived from the hydration of portland cement mortar in concrete has also often been called as hydraulic in recognition of the undisputed role played by the water in the process of hardening. In the present study, the hydraulic properties were evaluated by compacting sand-additive mortars. Hardening of the mortars through the interaction between the additive and the water is therefore also characterized as hydraulic.

Hydraulic properties of MgO It is clearly seen from Table 9 that magnesium oxide, if not heated to too high a temperature, i.e., with small crystallite size (Table 8) possesses distinct hydraulic properties, whereas magnesium hydroxide or calcium hydroxide do not show any hydraulic properties, although carbonation may contribute significant hardening. Figure 9 presents a representative part of these results in a graphical form. MgO in its reactive state may give the compacted sand-MgO mixture a strength 10 to 20 times higher than that of sand-$Ca(OH)_2$ or sand-$Mg(OH)_2$ mixtures under CO_2-free or ordinary atmospheric curing conditions.

$Mg(OH)_2$, $Ca(OH)_2$, and reactive MgO all reached very high strengths within 7 days curing under a CO_2-saturated atmosphere. X-ray data indicate that the formation of magnesium carbonate or calcium carbonate was responsible for the hardening. Figure 10 shows the formation of $MgCO_3.3H_2O$

Table 8. Average crystallite sizes and their limits of uncertainty in Angstroms

Additive	Calcining temp. °C	Average crystallite sizes of starting materials Å[a]			Average crystallite sizes of resulted $Mg(OH)_2$, Å[a]					
					CO_2-free curing		Atmospheric curing		CO_2-saturated curing	
		(200)[b]	(001)[b]	(100)[b]	(001)[b]	(100)[b]	(001)[b]	(100)[b]	(001)[b]	(100)[b]
MgO	600	255.4 ±1.6			369.9 ±2.0	659.7 ±10.6	347.2 ±3.2	515.2 ±11.9	235.6 ±5.0	392.6 ±7.5
	850	576.7 ±2.7			611.0 ±5.5	681.0 ±2.7	434.5 ±2.6	550.6 ±4.2	--[c]	
	1000	1278 ±16			734.9 ±17.0	739.8 ±11.4	429.8 ±6.2	669.9 ±12.1	--[c]	
	1100	1719 ±22			--[d]		--[d]		--[c]	
	1350	2438 ±20			--[c]		--[c]		--[c]	
$Mg(OH)_2$	reagent		267.3 ±2.5	667.4 ±6.0						
$Ca(OH)_2$	reagent		462.1 ±5.4	955.4 ±13.5						

[a] The range of uncertainty is calculated from 95% confidence limits of peak broadening from 5 measurements, expressed in ± Angstroms.

[b] The size measured is normal to the particular crystal plan.

[c] No $Mg(OH)_2$ formed.

[d] The $Mg(OH)_2$ formed is too weak to be measured.

Table 9. Hardening of compacted sand-additive specimens

Additive	Average crystallite sizes of MgO Å	Unconfined compressive strengths, psi					
		CO_2-free curing		Atmospheric curing		CO_2-saturated curing	
		2-day	7-day	2-day	7-day	2-day	7-day
MgO	255.4	500	620	800	1260	1120	1720
	576.7	820	1050	820	1400	3000	3660
	1278	56	780	157	730	2500	4300
	1719	20	170	130	220	510	1800
	2438	10	15	15	40	300	1600
$Mg(OH)_2$ (Reagent)		100	220	290	310	4640	6070
$Ca(OH)_2$ (Reagent)		50	55	60	110	1020	1320
Portland cement ("Type I")		-[a]	2473	-[a]	-[a]	-[a]	-[a]
Tobermorite (Synthetic)		-[a]	45	-[a]	70	-[a]	105

[a] Not determined.

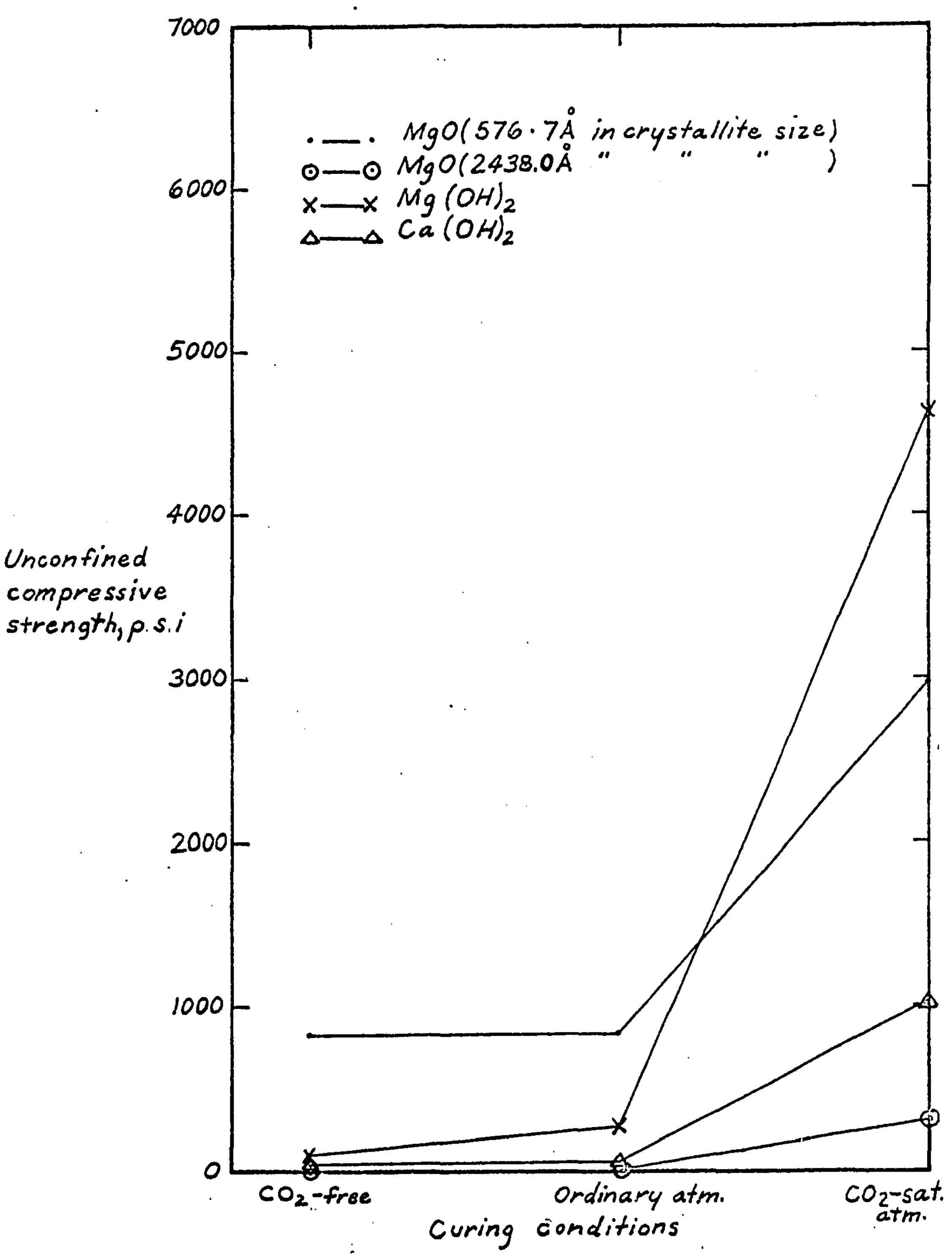

Figure 9. Hydraulic properties of magnesium oxides, magnesium hydroxide, and calcium hydroxide, with room-temperature curing

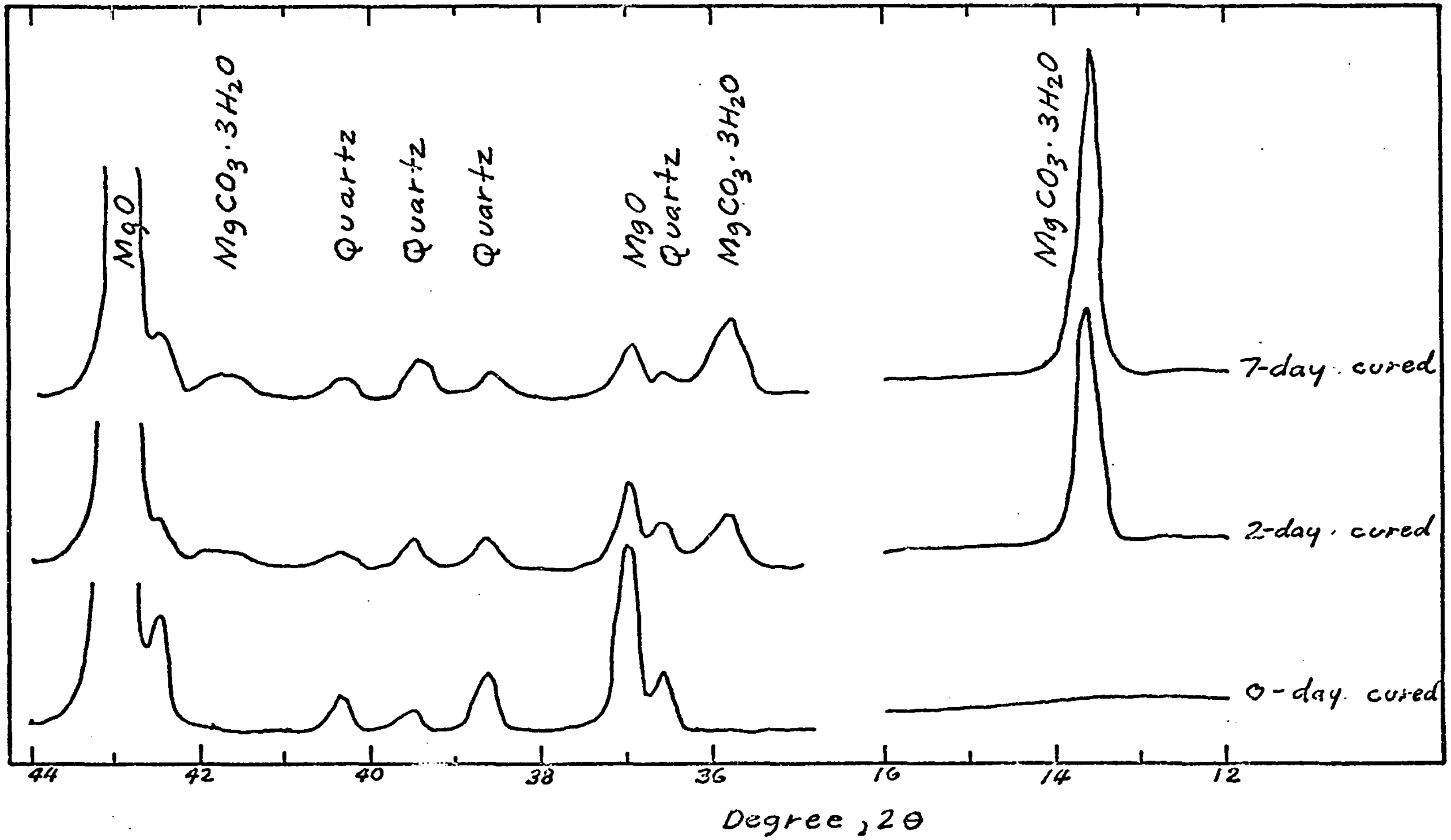

Figure 10. X-ray diffraction tracings of strength test specimens made with sand and MgO (1278Å in crystallite size), cured under a moist CO_2-saturated atmosphere

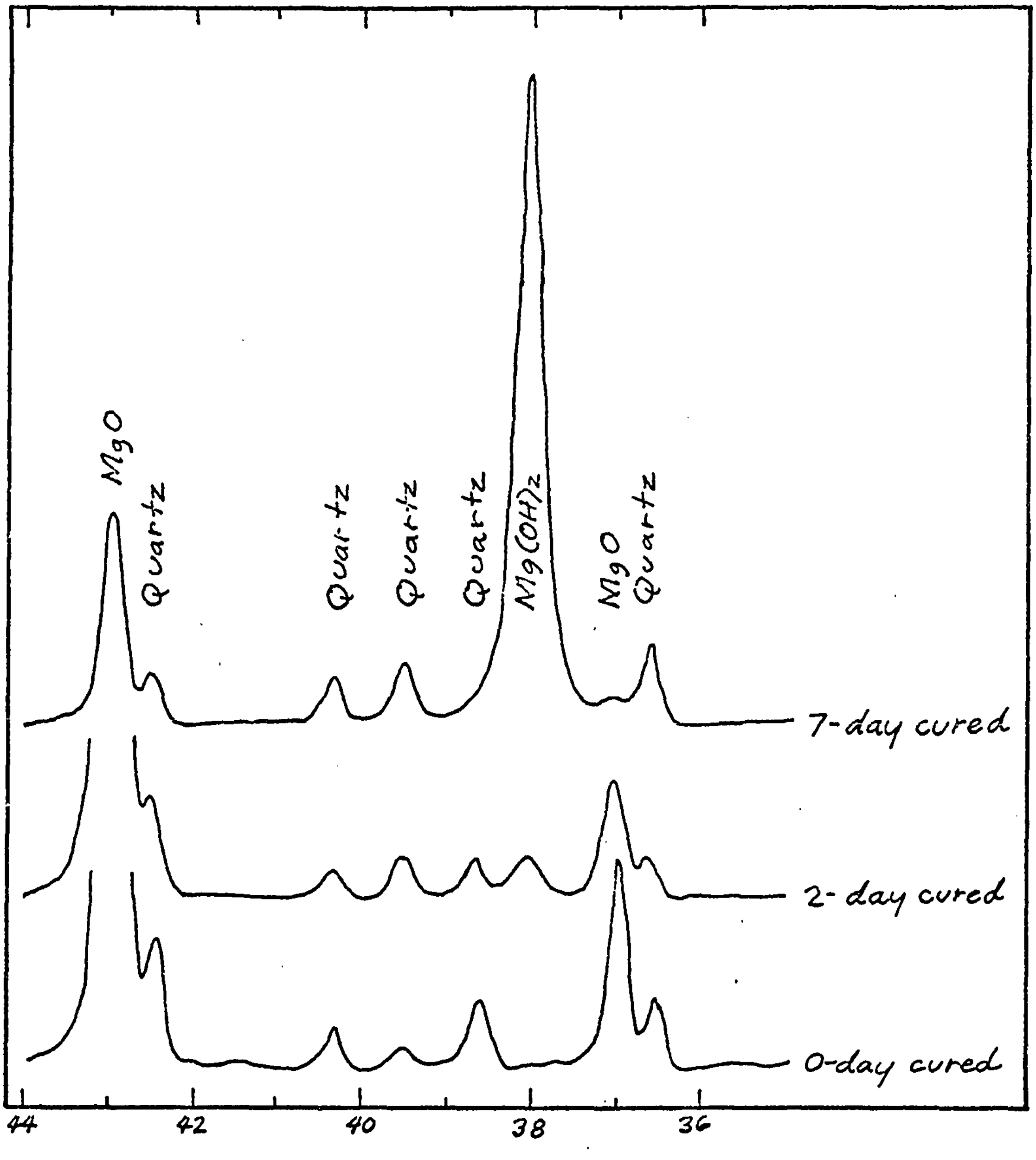

Figure 11. X-ray diffraction tracings of strength test specimens made with sand and MgO (1278Å in crystallite size), cured under a moist CO_2-free atmosphere

at the expense of MgO in compacted sand-MgO strength test specimens.

In the absence of CO_2, the fast and strong hardening properties of sand-MgO specimens were attributed to the formation of $Mg(OH)_2$. Figure 11 reveals the gradual conversion of a "not-so" active MgO to $Mg(OH)_2$ by X-ray diffraction tracings, examined at the end of various curing periods. The process of hydration was nearly completed within 2 days for very active MgO, while the unreactive ones, i.e., "dead-burned" with large crystallite size, did not show any sign of hydration even up to 7 days of curing, as will be shown later in Figure 17. Consequently, the strength gains between the 2-day and 7-day curing were small for the reactive MgO, and there were very little or no strength gains for the unreactive ones.

It is noted in Table 9 that the most reactive MgO used (calcined at 600°C with a crystallite size of 255.4 Å) did not give the highest strength, although almost all the MgO had been hydrated into $Mg(OH)_2$ within 2 days (Figure 17). This is almost certainly due to the extreme reactivity, which caused immediate hydration of MgO when mixed with water and sand. The hydration made the mixture very gluey and it was almost impossible to mold a physically sound specimen. The strength obtained was thus drastically reduced due to the physical defects in the specimens.

The CO_2 content present in the ordinary atmosphere did not seem to cause carbonation of magnesium compounds up to 7 days of curing, as Figure 12 shows no traces of such formation in addition to the newly formed $Mg(OH)_2$. The strength gained are therefore also attributed to the hydration of MgO, such as in the case of curing under CO_2-free atmosphere. Nevertheless, the strength obtained when cured under ordinary atmosphere is higher than that when cured under a CO_2-free condition. This may be because the $Mg(OH)_2$ crystallite sizes formed were smaller in the ordinary atmospheric curing condition than that of CO_2-free condition (Table 8). This will be discussed below.

Since $Ca(OH)_2$ and $Mg(OH)_2$ do not possess hydraulic properties, the limited strengths of the CO_2-free or ordinary atmosphere cured sand specimens containing these additives are believed to be contributed by the surface tension forces of the thin water films within the mix and the interlocking between particles. There were trace amounts of $CaCO_3$ formed in the sand-$Ca(OH)_2$ specimens cured under ordinary atmosphere. The $CaCO_3$ conceivably contributed to some strength gains.

Reactivity of MgO The specific surface of a material is usually a relative indication of reactivity, i.e., the higher the surface area per unit weight of material, the higher is its reactivity. The increase in specific surface

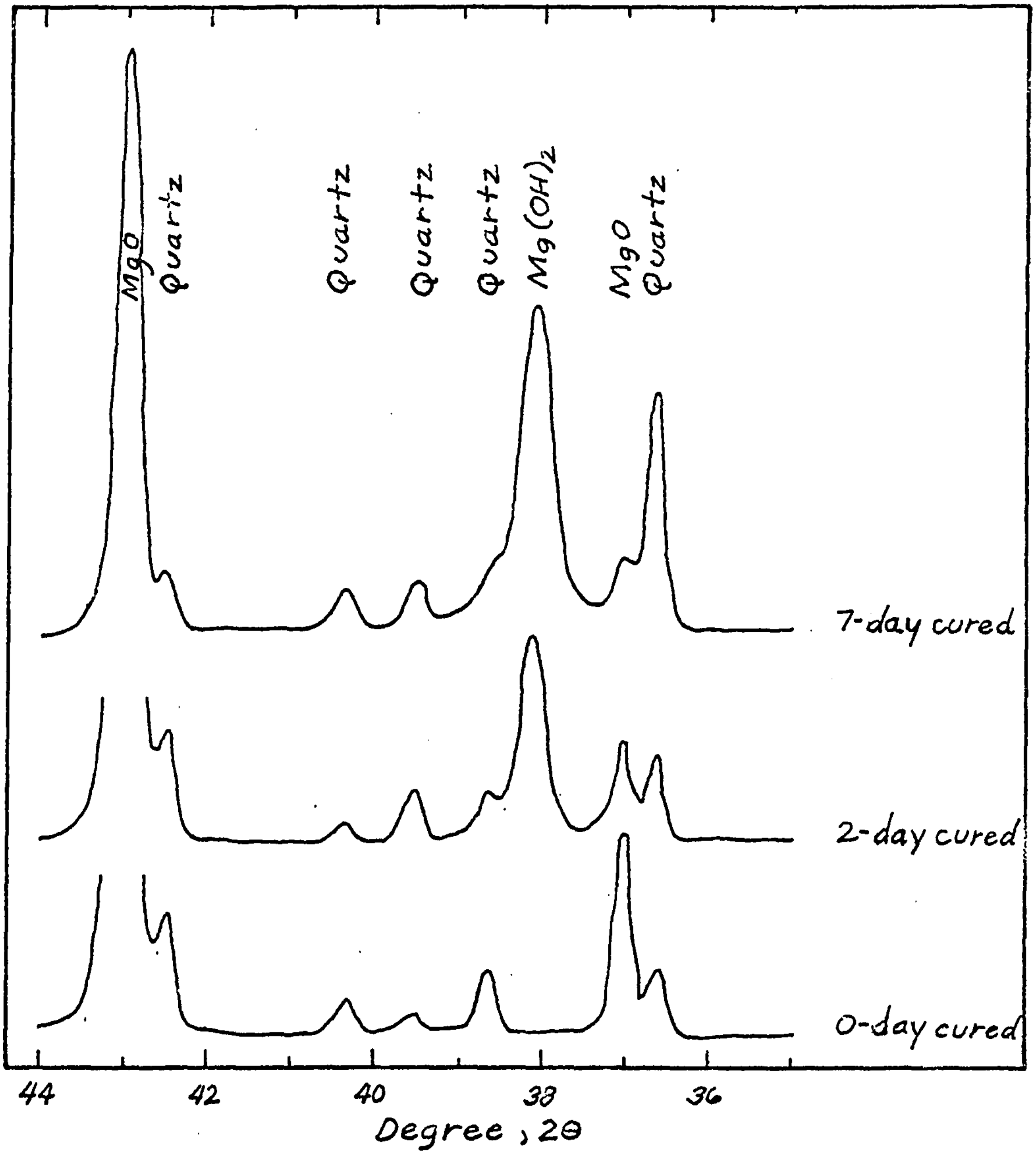

Figure 12. X-ray diffraction tracings of strength test specimens made with sand and MgO (1278Å in crystallite size), cured under a moist, ordinary atmosphere

of MgO is related to the decrease in crystallite size, and small crystallite size possesses higher rate of hydration (28, 32, 71). Magnesium oxides of different reactivities were made in the present investigation by calcining $Mg(OH)_2$ in different temperature for 48 hours. The effect of temperature on the MgO crystallite sizes is shown in Figure 13.

The influence of MgO crystallite sizes on the unconfined compressive strengths of compacted sand-MgO specimens cured under CO_2-free, ordinary, and CO_2-saturated atmosphere is shown in Figures 14, 15, and 16, respectively.

Figure 14 indicates that strength decreases with the increase in MgO crystallite size. The reason for the lower strength obtained with the most reactive MgO (255.4 Å in crystallite size) was stated in the previous section. Corresponding X-ray tracings of strength test specimens made with sand and MgO of different reactivities reveal that the magnitude of strength gain depends upon the amount of $Mg(OH)_2$ formation (Figure 17). There was no strength gain for specimens made with sand and large crystallites of MgO because the MgO was extremely hard-burned, hard-burning by definition meaning the MgO would not hydrate. Figures 15 and 18 present results obtained from curing under ordinary atmosphere, which are identical to those obtained from CO_2-free curing.

Hard burning of MgO also hinders the rate of carbonation. Strength data correlate very well with the amount of mag-

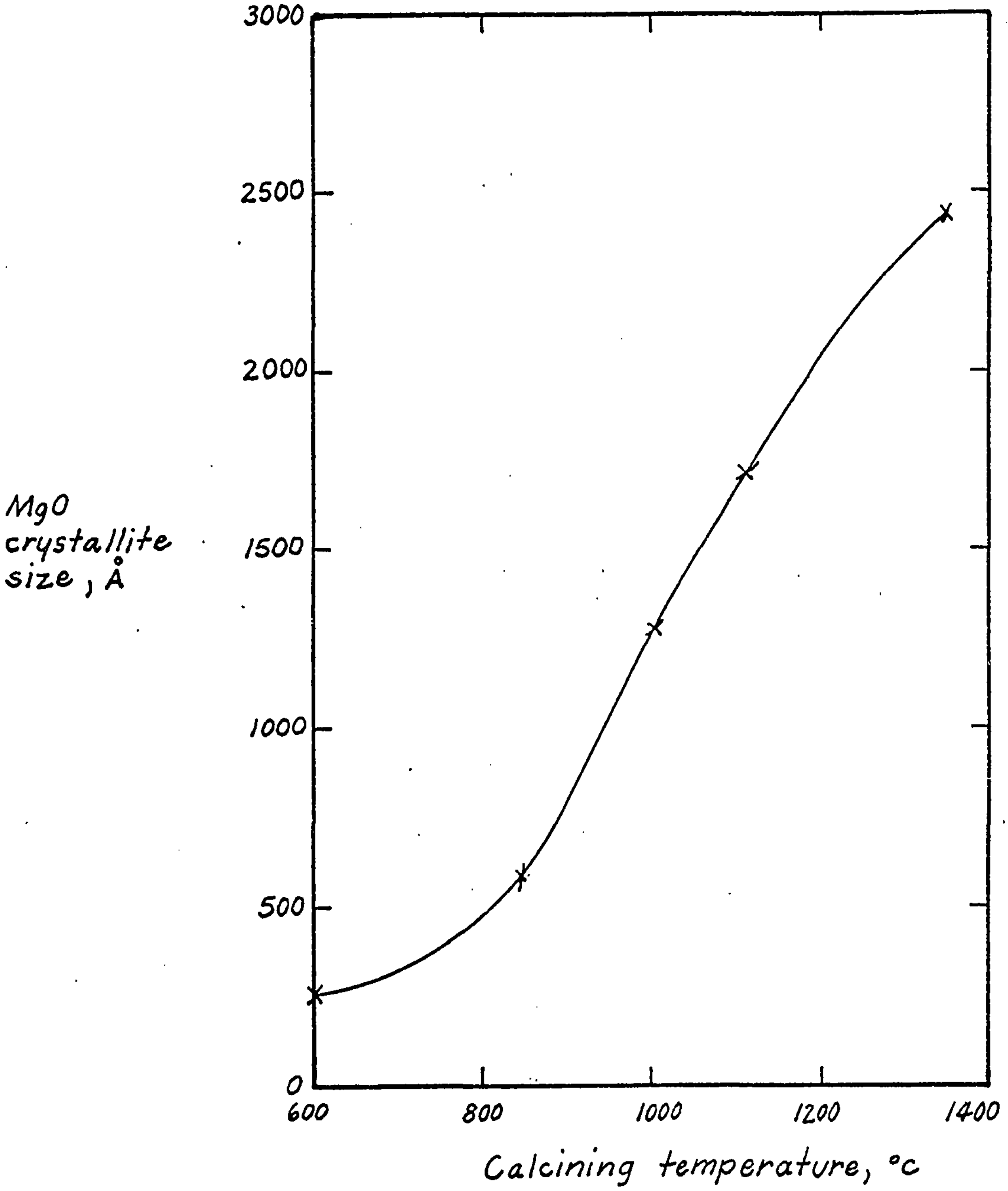

Figure 13. Effect of calcining temperature on the average crystallite size of MgO

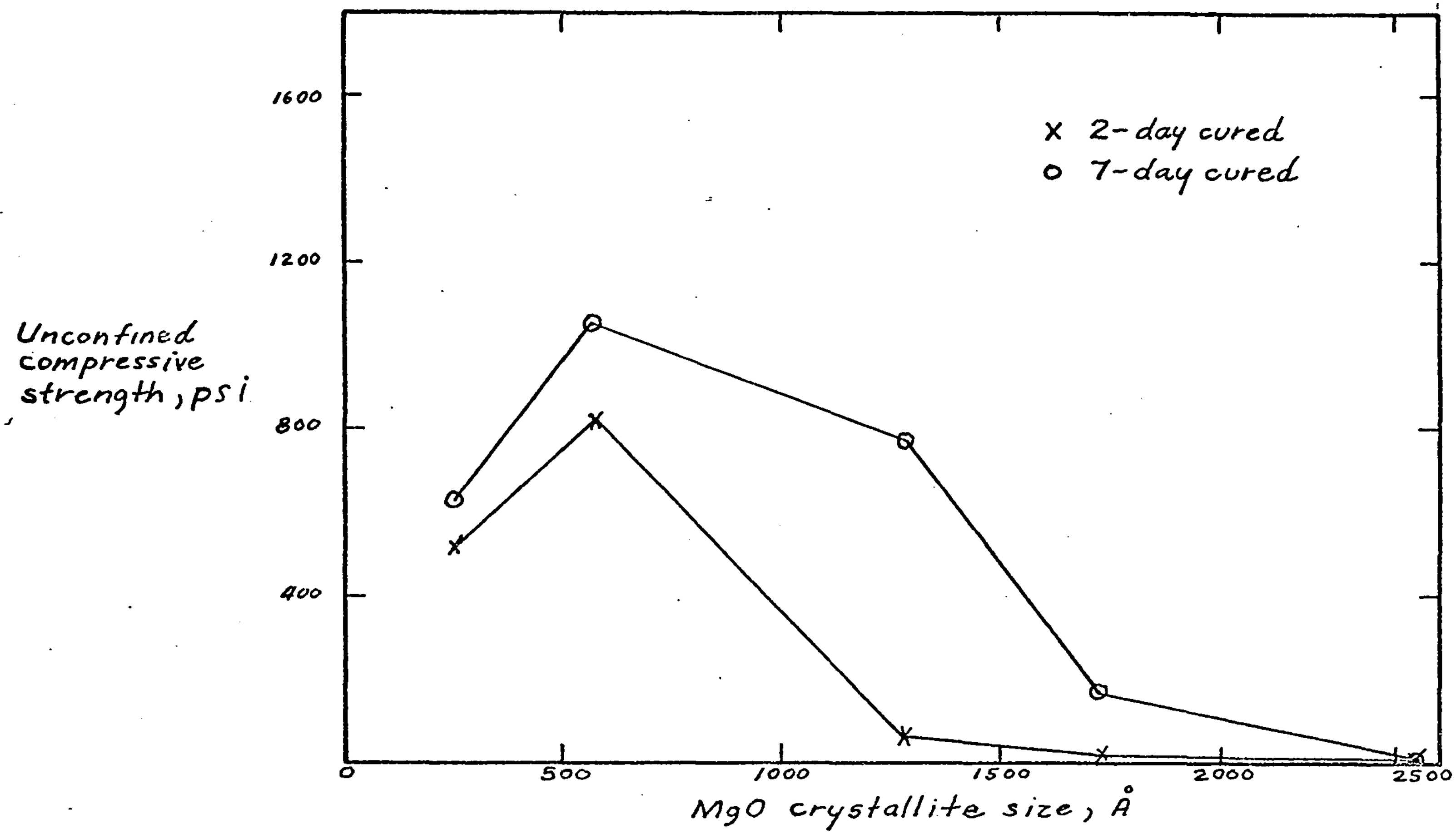

Figure 14. Influence of MgO crystallite size on the unconfined compressive strengths of compacted sand-MgO specimens, cured under a moist, CO_2-free atmosphere

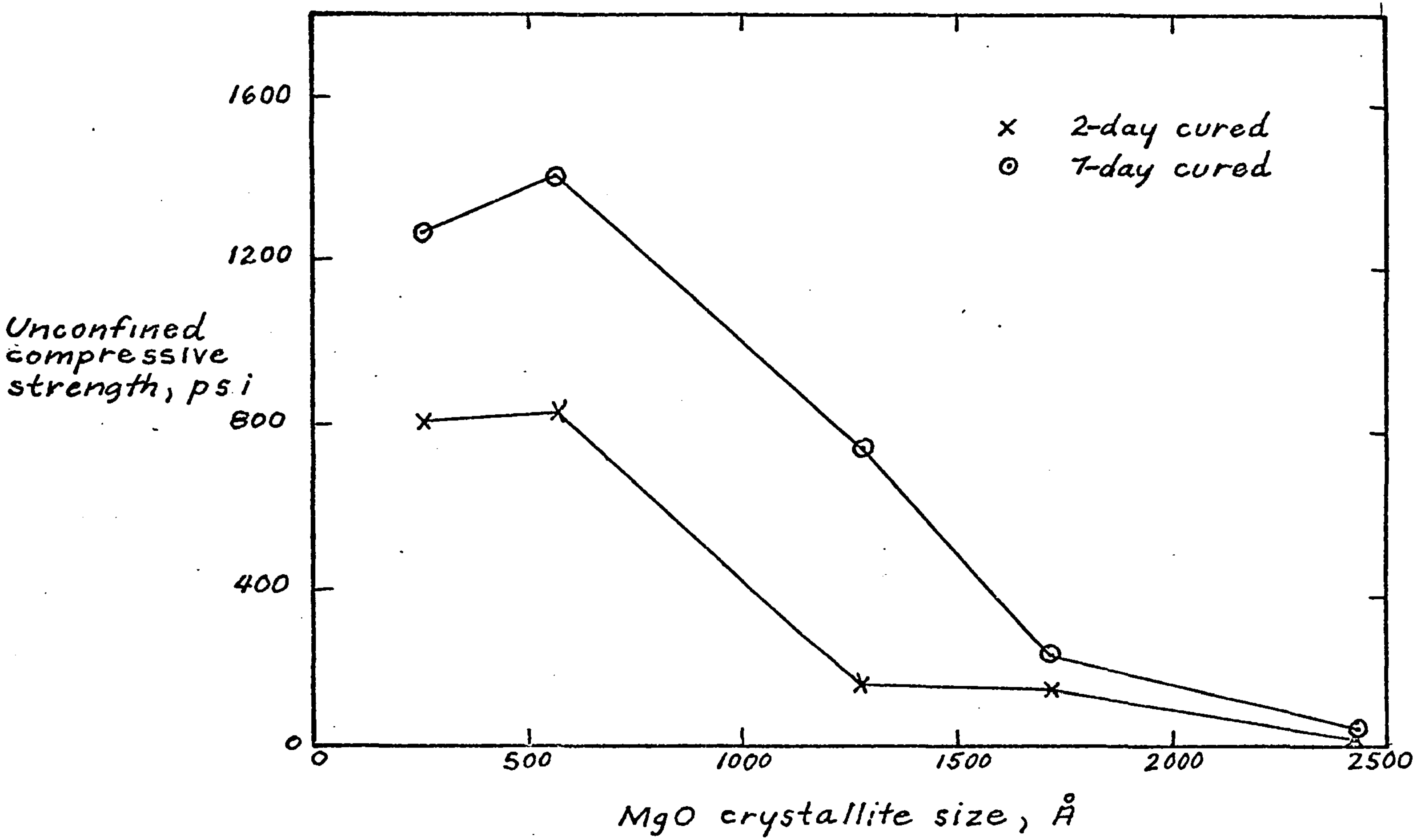

Figure 15. Influence of MgO crystallite size on the unconfined compressive strengths of compacted sand-MgO specimens, cured under a moist, ordinary atmosphere

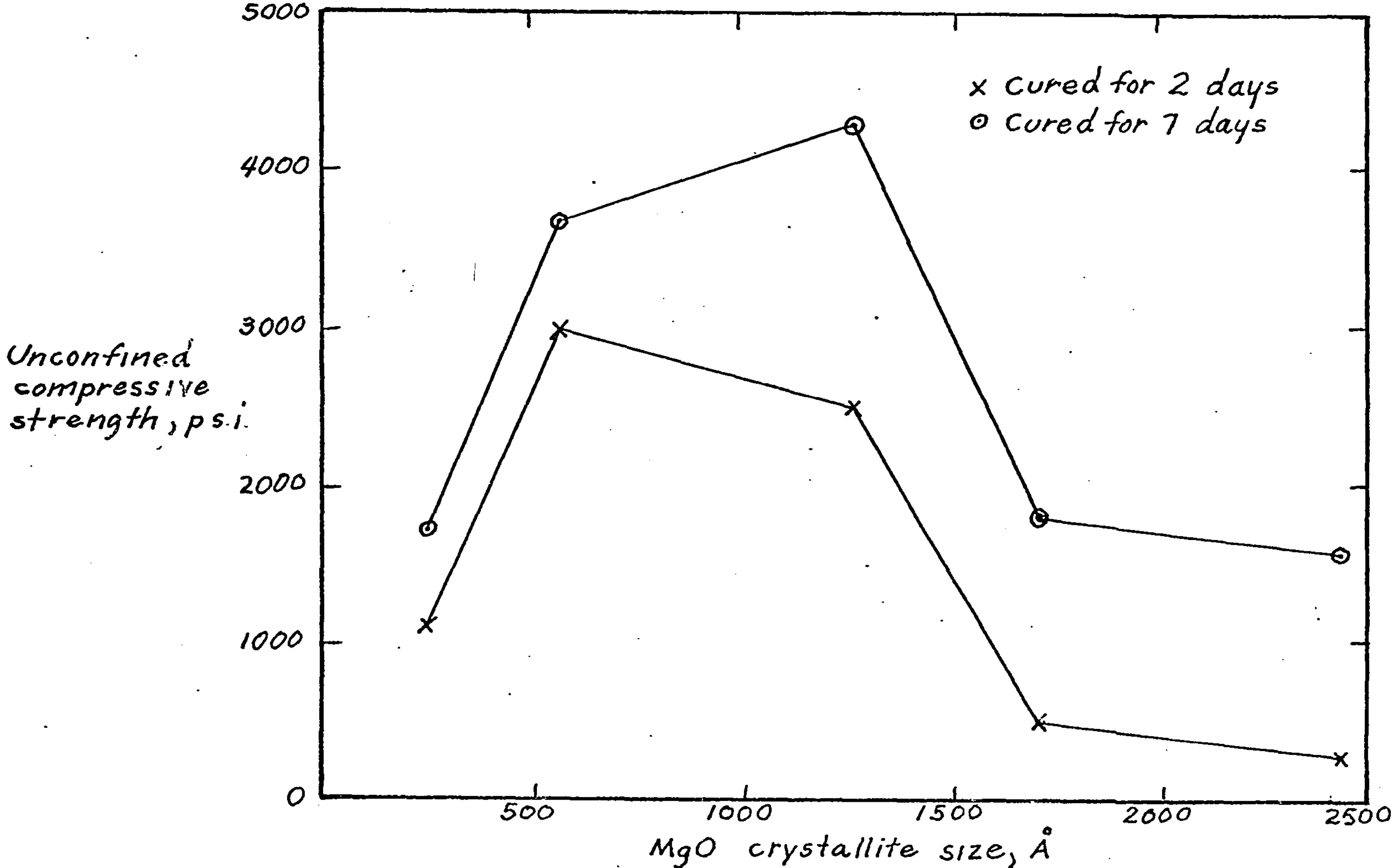

Figure 16. Influence of MgO crystallite size on the unconfined compressive strengths of compacted sand-MgO specimens, cured under a moist CO_2-saturated atmosphere

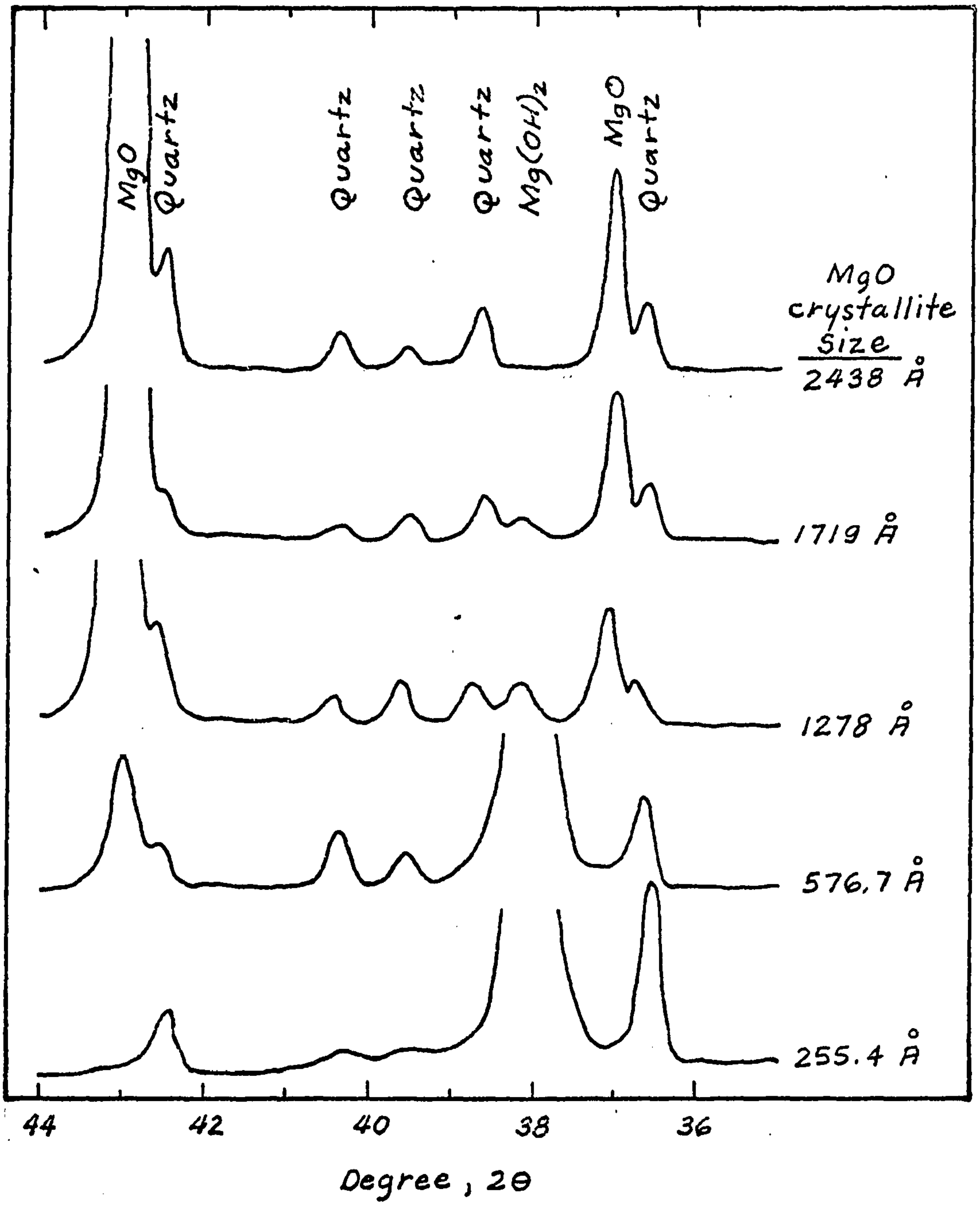

Figure 17. X-ray diffraction tracings of strength test specimens made with sand and MgO of different reactivities, cured under a moist CO_2-free atmosphere for 2 days

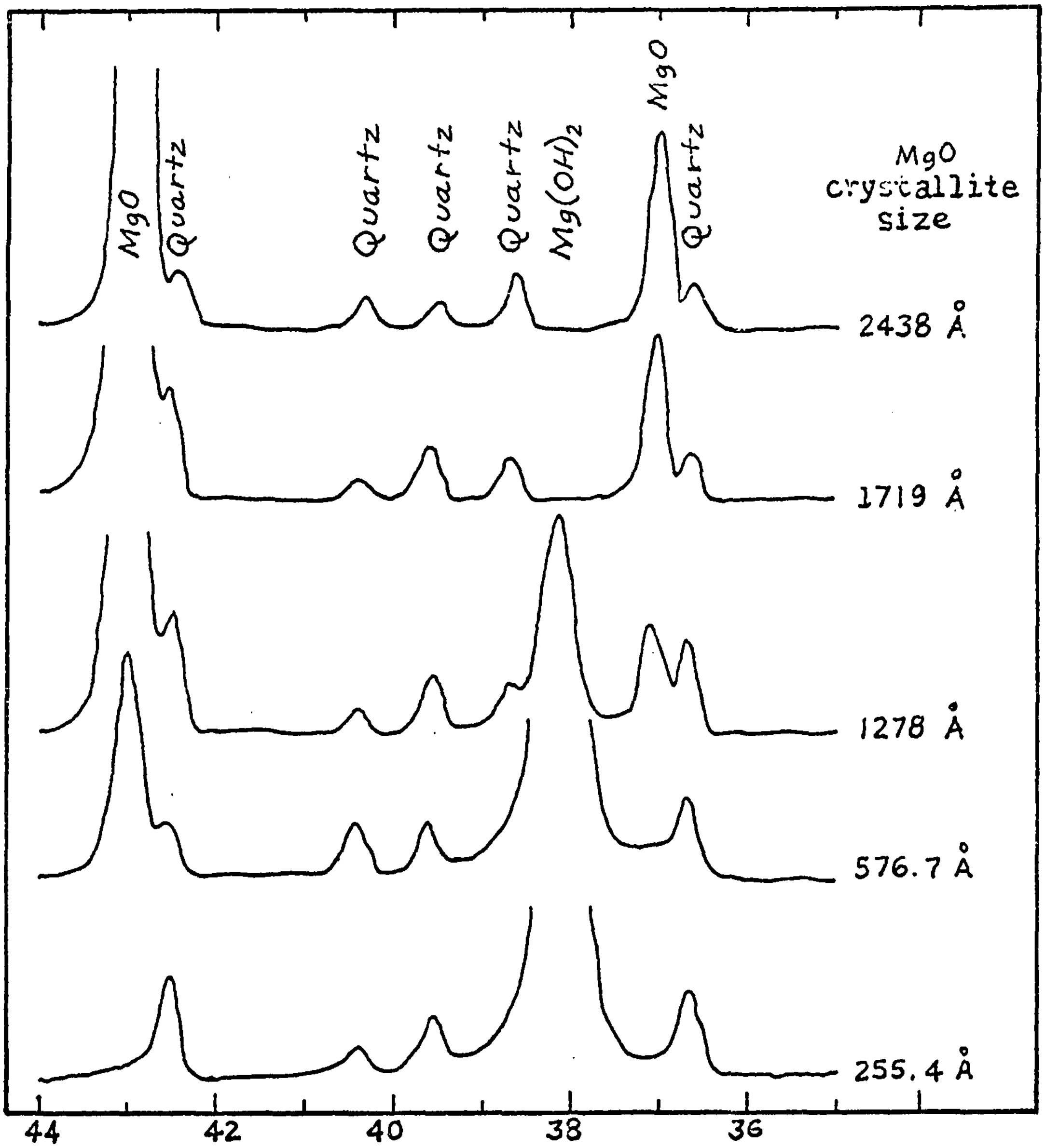

Figure 18. X-ray diffraction tracings of strength test specimens made with sand and MgO of different reactivities, cured under a moist, ordinary atmosphere for 2 days

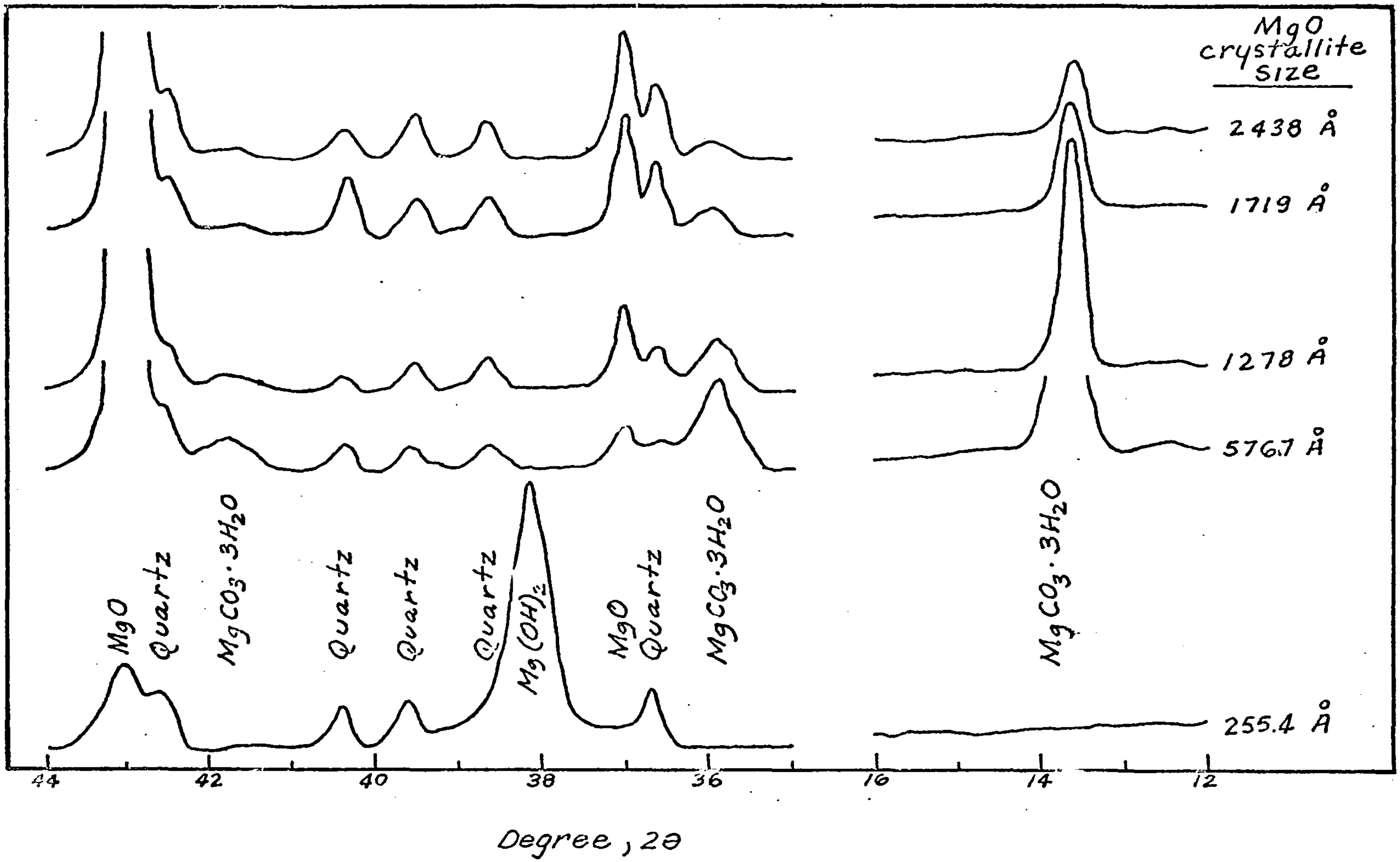

Figure 19. X-ray diffraction tracings of strength test specimens made with sand and MgO of different reactivities, cured under a moist, CO_2-saturated atmosphere for 2 days

nesium carbonate formation (Figures 16 and 19). It is noted in Figure 19, however, that the most active grade MgO (255.4Å in crystallite size) was partly hydrated into $Mg(OH)_2$ rather than being carbonated even up to 7 days under CO_2-saturated curing condition. The result was checked and rechecked, but no mistake was found and no explanation could be given. It is suspected, however, that this very active MgO has such an intensive force to hydrate, and the great affinity for water keeps the surface of the MgO particles practically dry at all times and thus hinders carbonation. It is generally known that carbonation occurs only in wet conditions so that CO_2 and water can form carbonic acid, the carbonic acid, in turn, attacking the $Ca(OH)_2$ or $Mg(OH)_2$ to form carbonates. Nevertheless, it is evident that the rate of hydration of this MgO was also reduced under CO_2-saturated conditions (Figure 19), since under CO_2-free and ordinary curing atmospheres this grade of MgO was completely hydrated within 2 days. A very thin carbonate skin formed on the particle may have reduced the availability of water for hydration.

The mechanisms of hydraulic hardening will be discussed in latter sections. The extremely small crystallite size and high specific surface of the resulted hydration product are believed primarily responsible. A study on the factors influencing the crystallite size of the hydrated product should be worthwhile, since Table 8 seems to show that the starting

MgO crystallite sizes as well as the curing conditions (presumably the amcunt of CO_2 present in the curing atmosphere) have exerted obvious influence on the crystallite sizes of the $Mg(OH)_2$ formed.

Discussion

Pozzolanic reactions

The results indicate that the pozzolanic reactions between $Ca(OH)_2$ and clay are very slow at room temperature in comparison with the rate of hydration of portland cement. However, the X-ray data suggest that rate of the lime-clay reactions can be greatly accelerated at higher temperatures. It is thus reasonable that high temperature curing should yield higher early strengths in soil-lime mixtures, as indeed it does (17,61).

The presence of MgO in lime does not appear to affect the reaction at room temperature or a little above. However, when the curing temperatures is above 110°C, X-ray data indicate that MgO favors the formation of well-crystallized calcium silicate hydrate, even at a very low C/S mole ratio in the starting bentonite-$Ca(OH)_2$ mixtures. The latter suggests that magnesium substitutes for calcium in the octahedral layer in the tobermorite structures, thus making more Ca^{++} available for further reaction. This hypothesis deviates from the assumption made by Diamond (18) who suggested that Mg substitutes for silicon in the tetrahedral layer in the tobermorite structure. It is more likely, according to Pauling's rule of crystal coordination, that Mg++ fits into a oxygen or a hydroxyl octahedral rather than a tetrahedral coordination due to the size of the Mg++ ion.

Tobermorites, the well-crystallized member of the hydration products of portland cement, have reported specific surfaces ranging from 25 to 90 m^2/g whereas the less crystalline members in this family show: CSH(I), 135 to 380 m^2/g; CSH(II), about 300 m^2/g; CSH(gel), 150 to 500 m^2/g (18). Materials possessing these extremely large surface areas are colloidal or gel-like in nature, and are glue-like substances.

The cohesive nature of the colloids is explained by their surface forces. Each solid body owes its stability to the presence of molecular forces of mutual attraction between the individual constituent units. Inside the body of a solid material these forces act equally in all directions, but at a surface unbalanced attractive forces exist and tend to attract and hold other materials. If a colloidal substance is formed, the tremendous surface area which it possesses comes into play, with the result that water molecules are drawn to the surface of the particles and held there strongly (adsorbed) thereby reducing very considerably the usual mobility of water (i.e., increasing its viscosity). Furthermore, the above effect is accompanied by inter-linking and cross-linking of the constituents of the solid material as a result of the inter-growth of crystals, so that a framework is developed which still further stiffens the mass.

In the case of the hydration of portland cement, the increase in surface area may be in the order of about a thousand times through the formation of calcium silicate hydrates. The calcium aluminate hydrates are of comparatively large crystals which can be picked under light microscope (30, 31, 39), and therefore contribute little to the development of new surface area and strength (4, 17). Since it is evident that just as the increase of specific surface leads to cementation in cement pastes, the formation of pozzolanic reaction products in soil-lime mixture would lead to the same effect, although due to the limited extent of reaction the increase in surface area probably is not so extensive.

The creation of new surfaces was believed to be essential in producing strengths. To check on this, an experiment was performed whereby synthetic tobermorite powder ground finer than 74 microns was mixed with sand, compacted and cured. The strength obtained was very low (Table 9). The reasons for the low strength can be explained as follows: first, owing to the extremely low solubility of calcium silicate hydrate (78), there was practically no recrystallization of tobermorite to form new surfaces and to furnish undisrupted crystalline bonds; secondly, the surface reactivity of the aged tobermorite was lower than that of freshly formed according to the theory by Weyl (85), which states that slight atomic rearrangements on the mineral surface after the formation tend to minimize the surface energy; thirdly, the aged tobermorite was present in the form of agglomerates of particles which drastically reduced the amount of the original surface area available. Therefore, due to the absence of the process of crystallization and the loss of surface reactivity, tobermorite, the strength-contributing mineral in concrete, cannot be reused as an additive to reproduce hydraulic strengths. The same reasons can be used to explain why $Ca(OH)_2$ and $Mg(OH)_2$ do not possess hydraulic properties, as will be pointed out in the following discussion.

Hydraulic properties of magnesium oxide

Magnesium oxide, if not previously heated to too high a temperature, possesses distinct hydraulic properties (Table 9). Sintering of this compound results in an unreactive product of large crystal size and high density. The larger the crystallite size, the slower the rate of hydration, and extremely hard-burned magnesium oxide may take a very long time to become hydrated. The process of ordinary hydration yields crystallites of colloidal magnesium hydroxide (Table 8). The mechanism involved in yielding high strength is therefore similar to that of the pozzolanic reaction products. Magnesium hydroxide, on the other hand, does not possess any hydraulic properties, so its role is similar to that of tobermorite reused as an additive to reproduced hydraulic strength, as discussed in the previous paragraph.

The hydration of magnesium oxide can be a relatively fast process occurring in a matter of hours or days. The high early-strength of soil stabilized by dolomitic monohydrate lime is thus believed to be mainly contributed by the hydration of MgO in the lime. Due to the inconsistancy in the practice of different lime manufacturers, the dolomitic monhydrate limes are most likely to be subjected to variation in properties of the MgO component in lime because of the different degree of calcination. In a previous study (81) we found that different commercial dolomitic monohydrate limes showed significant variation in the production of early-strengths, while the various high-calcium hydrated limes showed very uniform strength properties. The best dolomitic monohydrate lime was found to have the smallest MgO crystallite size, and the poorest had the largest.

Pozzolanic reaction is a relatively slow process at room temperature, but is the principal source of prolonged hardening in soil-lime stabilization, continuing so long as there are unreacted $Ca(OH)_2$ and clay in the system. Hydrated magnesium oxide, i.e., magnesium hydroxide, may also react with clay to form serpentine type of magnesium silicate hydrates, but X-ray data show the formation to be very slow and limited in the presence of $Ca(OH)_2$ (Tables 6 and 7).

Magnesium oxide, in its reactive state, has been proved to be an excellent soil stabilizer by itself. Particularly with sand, the strengths obtained are comparable with those from use of portland cement (Table 9). In fine-grained soils, especially with the montmorillonitic clay, MgO may cause transformation of the clay to a non-expansive chloritic mineral (Table 6 and Figure 2). In the meantime the hydration of MgO provides cementation. Nevertheless, the amount of MgO required to obtain satisfactory strength in very fine-grained soil can be very large because of the large surface area of the soils to be covered by the $Mg(OH)_2$ crystallites, and the difficulties in obtaining an uniform mixing of the sticky mass. A joint use of small amount of $Ca(OH)_2$ followed by a large proportion of MgO is believed to be a more ideal stabilizer for very fine-grained soils.

Based on the above speculations the cementation ability of MgO was further tested for stabilization of an extremely wet, highly sensitive allophane soil from Japan[1]. Various stabilizers, including lime and quicklime, had been tried on

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[1] Handy, R. L. and Demirel, T. Ames, Iowa, Iowa State University of Science and Technology. Stabilization of an allophane soil. Private communication. 1964.

this soil without success. The addition of 10% MgO yielded marked improvement.

Magnesium hydroxide does not possess any hydraulic property (Table 9), and the presence of this compound in lime will therefore reduce the effective amount of MgO for cementation or $Ca(OH)_2$ for pozzolanic reactions. It is reasonable that dolomitic dihydrate lime shows the poorest strength gaining properties among all types of hydrated limes. Precautions should then be taken not to overhydrate the dolomitic monohydrate lime during manufacture, in order to take advantage of the hydraulic property of MgO for soil stabilization.

Carbonation

It has been known that the hardening of lime mortar in plastering is caused by the carbonation of lime by carbon dioxide in the air (4, 17, 54). In the present studies it has also been demonstrated that the strength of sand-lime specimens was significantly increased when cured under CO_2-saturated or under the ordinary laboratory atmosphere. Because of its very low surface area, sand does not readily enter into pozzolanic reactions, and the strength obtained was attributed to the formation of calcium carbonates. However, it has been generally accepted that carbonation is detrimental to the long-term soil-lime strength, for CO_2

steals lime away and prevents it from entering pozzolanic reaction with soil clay.

An experiment was performed to test this assumption. 10% $Ca(OH)_2$ was added to bentonite and compacted into miniature samples at the optimum moisture content. The samples were then cured separately under vacuum, ordinary, and CO_2-saturated moist atmospheres for 7 and 28 days. X-ray examinations were followed after each curing period.

Extensive carbonation of the $Ca(OH)_2$ was detected in 10% $Ca(OH)_2$-bentonite samples cured under CO_2-saturated atmosphere. Slight carbonation was found in samples cured in the open air, while no carbonates were found in vacuum cured specimens. Table 10 shows the strengths obtained under the various curing environments.

Table 10. Effects of carbonation on soil-lime strengths

Curing conditions	Unconfined compressive strength, psi 7-day	 28-day
Vacuum	240	370
Ordinary atmosphere	250	320
CO_2-saturated atmosphere	100	220

Data in Table 10 indicate that carbonation of $Ca(OH)_2$ yields low strength in clay stabilized by lime, and pozzolanic reaction products appear to be much stronger cementing agents than calcium carbonate. The strength of the specimen cured under ordinary atmosphere was comparable to that of the vacuum cured, probably because this relatively low CO_2 content in air was unable to penetrate the compacted, dense mass in a relatively short periods. X-ray examinations on the outer and inner portion of the specimens confirmed that there was much more calcium carbonate formed at the outside portion of the specimen than at the inside. The detrimental effect of carbonation was more pronounced after longer curing, as carbonation penetrated deeper into the specimen.

Carbonation of MgO or $Mg(OH)_2$ also yields high strength in sand cured under CO_2-saturated atmosphere (Table 9). However, no carbonation was detected when the magnesium compounds were cured under ordinary atmospheric conditions, and the process must be extremely slow. It is thus concluded that carbonation of MgO or $Mg(OH)_2$ generally is not a strength-contributing factor in soil-lime stabilization.

STRENGTH STUDIES

Objectives

In previous Iowa State University soil-lime publications the superior strength characteristics of dolomitic monohydrate lime have been noted principally under room temperature curing conditions over relatively short periods of time (less than 3 months). The response of soil plus different types of limes under various curing temperatures has not been studied, except one dealed with high-calcium hydrated lime only (61). The analytic results in this thesis allow one to predict the effects of curing temperatures and time on the strength characteristics of different types of lime with soil.

Under low temperatures of curing, due to the slow rate of pozzolanic reaction between $Ca(OH)_2$ and soil, the presence of active MgO in lime should contribute a substantial portion of the early strength. At elevated temperatures the rate of pozzolanic reaction is greatly accelerated, and the proportion strength contributed by the hydration of MgO should thus become relatively insignificant. One may then expect that high-calcium lime may be just as good as, or may be even better than, dolomitic monohydrate lime in obtaining soil-lime strengths at higher curing temperatures.

The following study was designed to confirm or disapprove the above hypothesis. The results may also serve as a guide for practical applications.

Materials and Procedures

A Wisconsin stage loess soil, representative of the major surface deposits in western Iowa, was used for the strength studies. This soil contains approximately 12% 2-micron clay, predominantly montmorillonite, and 87% silt between 2-74 microns in size. The physical and chemical properties of this soil have been reported (83).

The limes used were synthesized from reagent grade chemicals. In addition to the use of $Ca(OH)_2$, MgO, and $Mg(OH)_2$ alone in the soil, dolomitic monohydrate limes of varied C/M mole ratios (0.2, 0.6 and 2) were made in order to see the strength characteristic of these limes under various curing temperatures.

Cylindrical samples (2 in. diameter x 2 in. height) were used to study the effects of temperature on soil-lime strengths. The Iowa State compaction apparatus was employed to compact the soil-lime mixtures at an optimum moisture content for maximum density, whereby a constant compacting energy was applied to the mixture through use of a drop-hammer. The density obtained was near to the standard AASHO density.

Details of the apparatus and the procedures on molding have been listed elsewhere (53, 56, 67).

The soil was mixed with the correct weight of lime and sufficient water to bring the mixture to the optimum moisture for compaction. The limes were added in 2, 5, 8 and 12% of the dry weight of the soil. Molded samples were wrapped in waxed papers to prevent the carbonation of lime and the loss of moisture during curing, and then cured at different temperatures for various periods up to 3 months.

Since the temperatures in the field may range from below freezing up to as high as 60^oC, the temperatures chosen were -5^oC, 5^oC, 23^oC, (the standard curing temperature in laboratory experiment), 40^oC and 60^oC. The -5^oC and 5^oC samples were cured in temperature-controlled refrigerators, whereas the 23^oC curing was performed in a room of 90-100% relative humidity. The 40^oC and 60^oC curing were conducted in the electric ovens. No significant loss of moisture was noted to occur from any of the samples cured at 40^oC up to 3 months and 60^oC up to 28 days. Samples cured at 60^oC for 3 months often develop cracks due to excessive heat and drying action, and the physical damages are believed to have critical effects on the strengths obtained. Hence, no strength data are presented on the specimens cured at 60^oC for 3 months.

After curing, the samples were allowed to adjust to room temperature and immersed in distilled water for 24 hours before testing in unconfined compression.

Results and Discussion

The effect of increased curing temperature is to increase the strength of the soil at any curing interval (Figures 20, 21, 22 and 23). However, calcium hydroxides are very sensitive to temperature of curing, while the temperature effects on MgO and $Mg(OH)_2$ are comparatively moderate. Except at 2% lime content, MgO always gave a faster and higher strength gain than $Ca(OH)_2$ when the curing temperature was $23^{o}C$ or lower. When curing temperatures exceeded $23^{o}C$, $Ca(OH)_2$ gained strength at a much faster rate. Even when curing temperatures are lower than $23^{o}C$, $Ca(OH)_2$ may eventually catch up to the strength obtained by MgO at longer curing time.

The amount of strength-gain with $Mg(OH)_2$ was always very poor in comparison to that with $Ca(OH)_2$ and MgO.

In comparing the strength of soil-dolomitic monohydrate limes with that of soil-$Ca(OH)_2$, it is seen that dolomitic monohydrate limes gave high strength properties at low curing temperatures. Furthermore the mole ratios of calcium oxide to magnesium oxide in the lime do not appear to be critical in producing the better strengths at low temperatures. High curing temperatures cause rapid increases in strength of

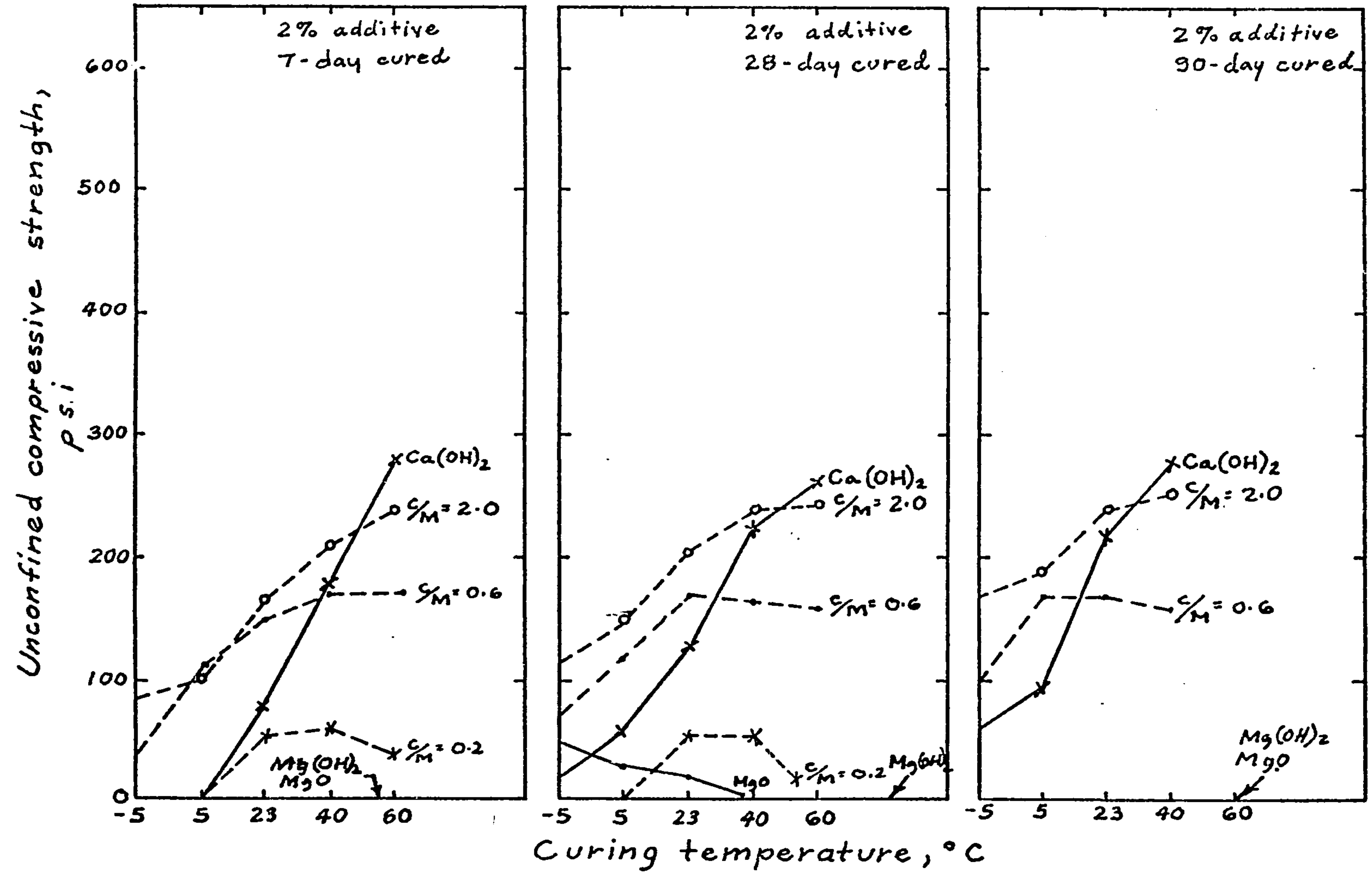

Figure 20. Effects of curing temperature on soil-lime strengths

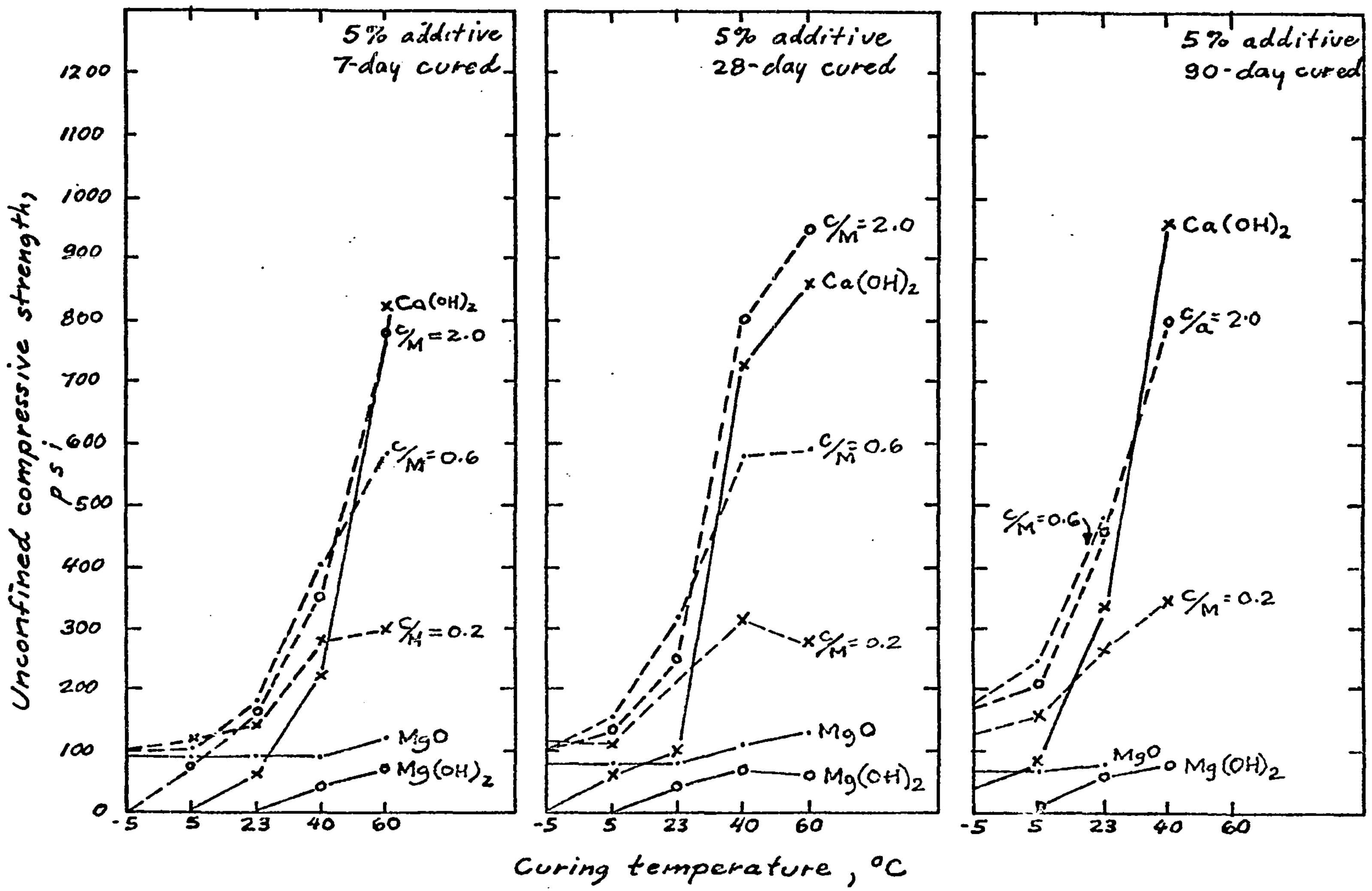

Figure 21. Effects of curing temperature on soil-lime strengths

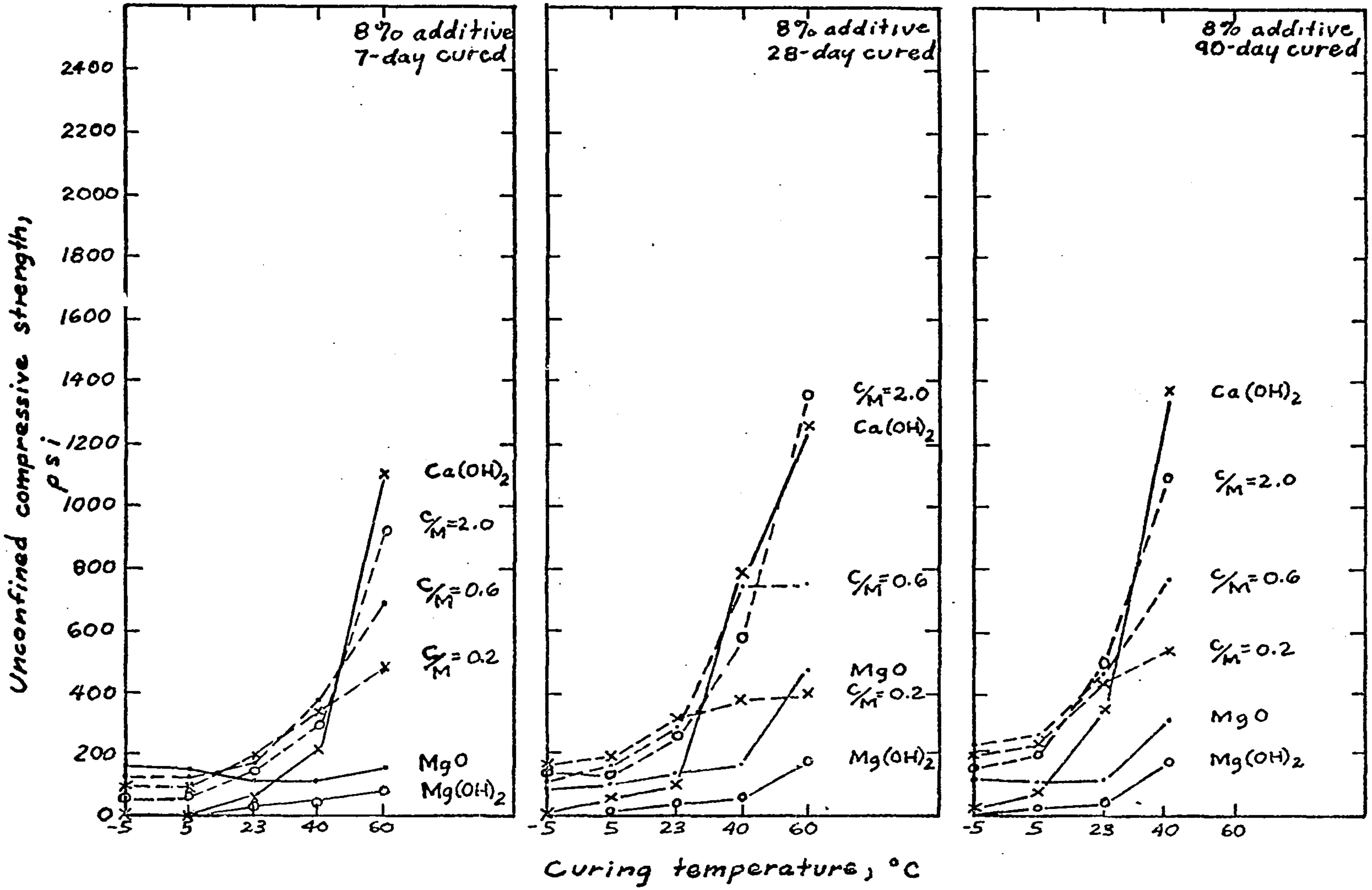

Figure 22. Effects of curing temperature on soil-lime strengths

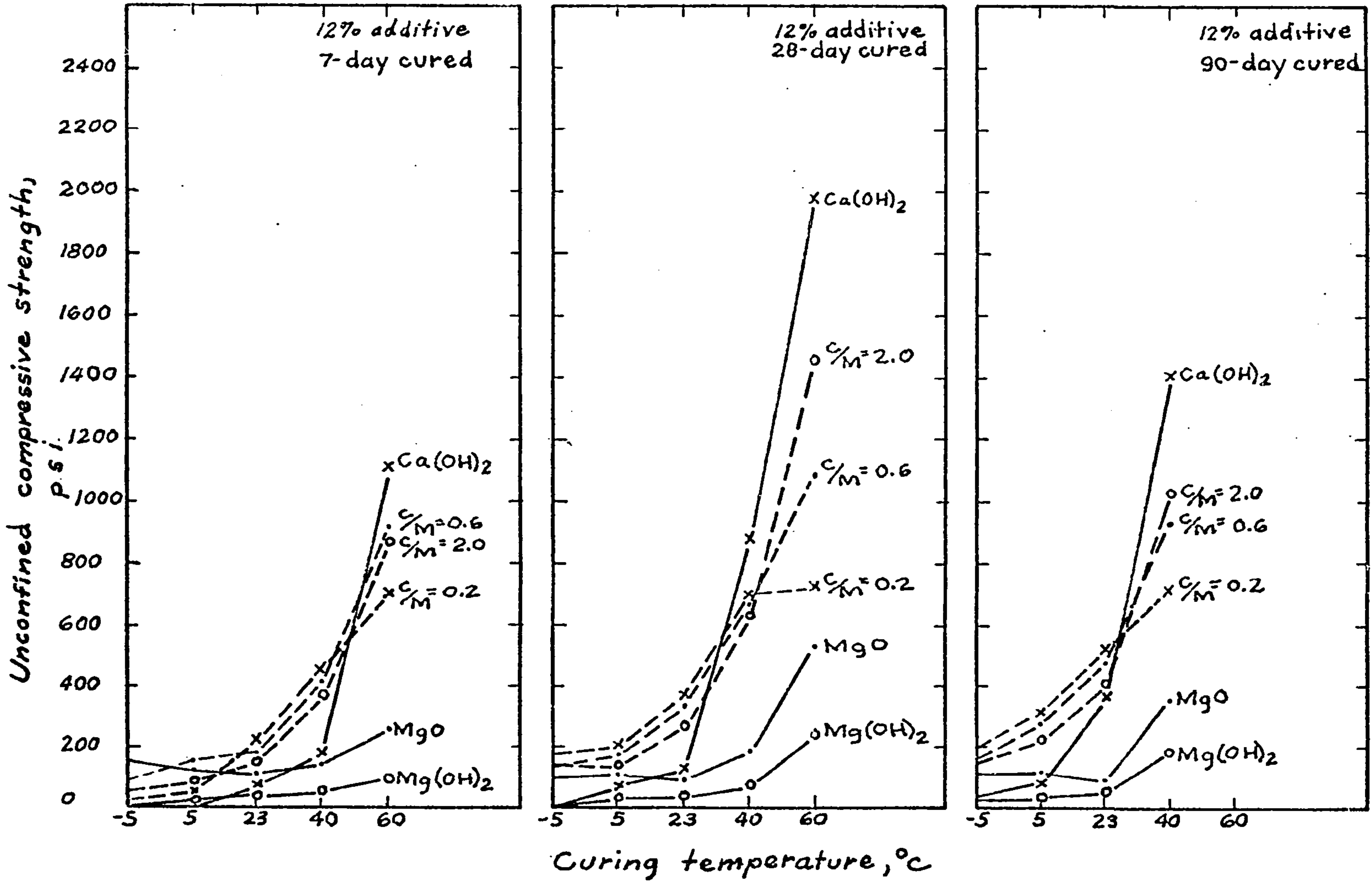

Figure 23. Effects of curing temperature on soil-lime strengths

dolomitic monohydrate limes, but the rate of increase depends upon the amount of calcium hydroxide in the lime, i.e. the higher the C/M mole ratio, the more the strength gain is accelerated at high curing temperatures.

Figure 24 translates the 8% additive data of Figure 22 into iso-strength contours on temperature-logarithmic time plots. In plotting the contours, interpolation of strengths follows the relationship obtained through the strength-temperature and strength-time curves. A tightening of the iso-strength lines above a certain temperature or after a certain time may indicate a speed-up of the reaction product formation, or occurrence of a new reaction.

When 8% MgO alone is used in the soil (Figure 24a), an early strength is already evident at low curing temperatures, due to the hydration of MgO. This hydraulic strength remains essentially constant over a wide range of curing temperatures, and only when the curing temperature is above 40°C do the soil-MgO mixtures start to show a moderate increase in strength, believed to be due to formation of serpentine minerals. Soil stabilized with $Mg(OH)_2$ alone shows the same trend at higher temperatures, but at low temperatures there is practically no strength because of the lack of hydraulic properties of this compound (Figure 24b).

When 8% $Ca(OH)_2$ alone is used in the soil (Figure 24c), the early strength obtained at low temperatures is very low,

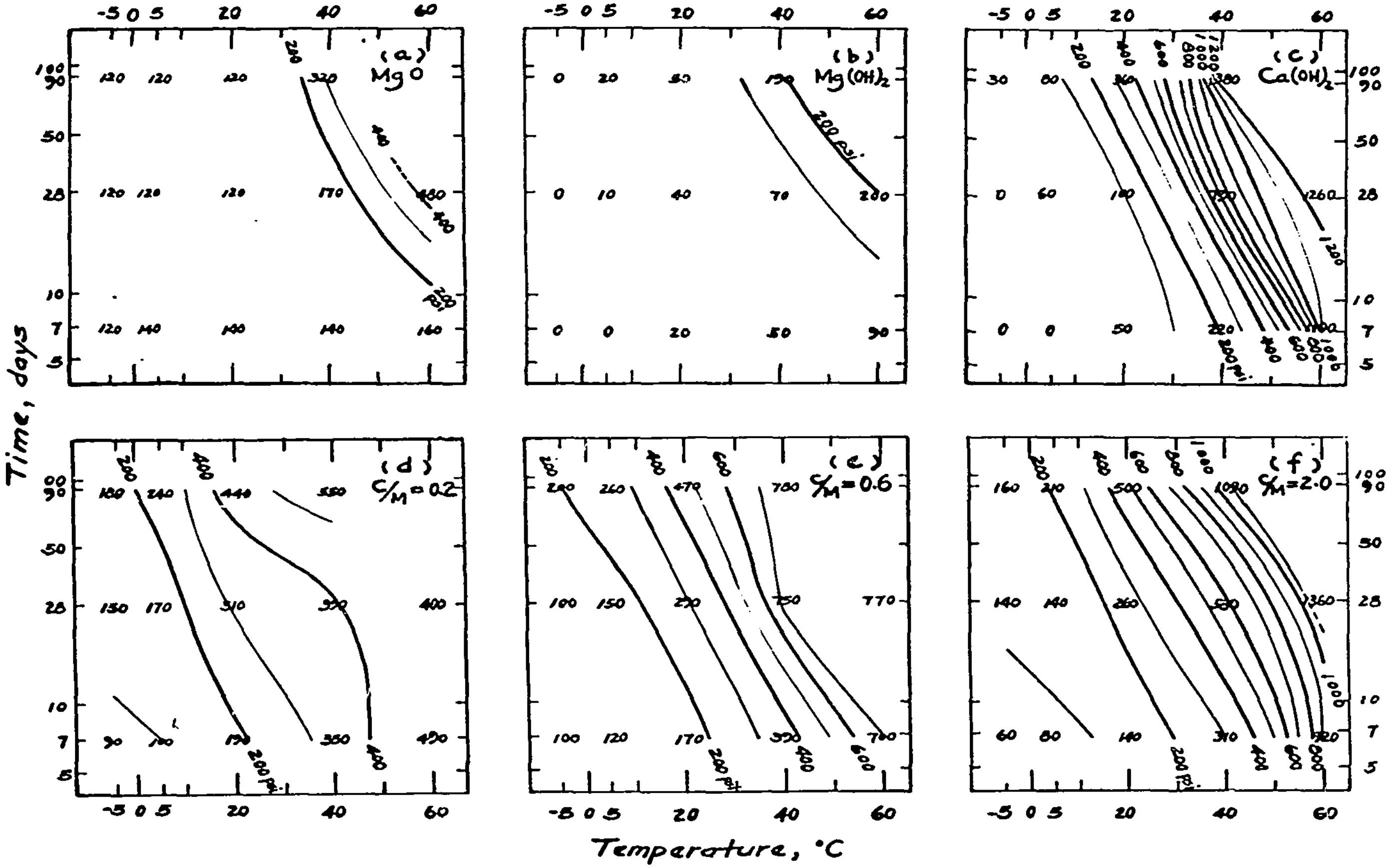

Figure 24. Logarithmic time-temperature plots of iso-strength contours (8% additive)

indicative of slow pozzolanic reaction. However, when curing temperature is higher than room temperature (23°C), especially above 30°C, the rate of pozzolanic reaction is greatly accelerated, as shown by the rapid increase in strength with increased temperatures and time and tightening of the iso-strength contours. Judging from the amount of increase in strength, the pozzolanic reaction products apparently are much better cementing agents than the serpentine minerals.

The contour plots of soil stabilized with dolomitic monohydrate limes show, in general, a combination of influences of the $Ca(OH)_2$ and MgO patterns (Figure 24d, e, and f). The high-early strengths at low temperatures are believed to be mainly contributed by the hydraulic properties of MgO, while at the higher temperatures, pozzolanic reaction products come into play. The higher the proportion of $Ca(OH)_2$ in the dolomitic monohydrate lime, the more vigorous are the pozzolanic strength gains.

It should be remembered that there is probably no strength contributed by the formation magnesium silicates in the soil-dolomitic lime stabilization, since the analytic studies in this thesis have shown that in the presence of $Ca(OH)_2$, magnesium oxide does not react with the clay unless temperatures are higher than 110°C and the total $Ca(OH)_2$ and MgO contents are very high.

CONCLUSIONS

The role of magnesium oxide in soil-lime stabilization was studied through the examination of pozzolanic reaction products and the hydraulic properties of the chief components in hydrated limes. These results were presented in the analytic part of this thesis. In the second part of this thesis, soil-lime strengths obtained after curing at various temperatures were found to coincide, in general, with the reaction trends shown in the analytic studies.

Based on these investigations the following conclusions were reached:

1. The process of hydration of MgO into $Mg(OH)_2$ is hydraulic in nature. The hydraulic hardening of MgO in dolomitic monohydrate lime is relatively fast and is believed to contribute a major portion of the early strengths in soil-dolomitic lime stabilization.

2. The formation of pozzolanic reaction products between $Ca(OH)_2$ and soil is slow at room temperature, and can be greatly accelerated at elevated curing temperatures. The essential effects of $Ca(OH)_2$ at room temperature are to flocculate the clay, and to contribute to long-term pozzolanic strengths.

3. At elevated temperatures, pozzolanic reactions involving high-calcium hydrated lime gain strength very fast,

exceeding the gains with dolomitic monohydrate lime.

4. MgO does not show any apparent effect on the rate of pozzolanic reactions at room temperature. However, when curing temperature is high, e.g., over 100°C, MgO may accelerate the rate of formation of well-crystallized calcium silicate hydrates.

5. It is anticipated that long-term strength of high-calcium hydrated lime is no less, or may be even better, than that of dolomitic monohydrate lime.

6. The difference in rates of strength gains with different types of limes suggests that soil stabilized with high-calcium hydrated lime should be constructed in warm regions or in the summer season, whereas with dolomitic monohydrate lime, the construction may be scheduled in late fall or used in a cooler climate.

7. Carbonation of $Ca(OH)_2$ also contributes to strengths in soil-lime stabilization. Nevertheless, this reaction is undesirable where clay is present, because carbonates are weaker cements than the products of pozzolanic reactions. Carbonation of magnesium compounds under ordinary atmosphere appears to be very slow, and it is concluded that little or no strength is contributed by magnesium carbonate.

8. Magnesium hydroxide is not hydraulic, and its presence in lime reduces the effective amount of MgO and $Ca(OH)_2$ available for cementitious reactions. Hence,

dolomitic dihydrate lime generally shows poor strength gaining properties.

9. The addition of an active magnesium oxide to a montmorillonite changes the clay into a material which is non-expansive in character, and form hydrated magnesium silicates similar to the serpentine minerals. However, in the presence of $Ca(OH)_2$, these reactions are hindered by the pozzolanic reactions between the $Ca(OH)_2$ and the clay.

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ACKNOWLEDGMENTS

The subject matter of this report was obtained under Project 531-S of the Iowa Engineering Experiment Station, Iowa State University. Project 531-S is under contract with the Iowa Highway Research Board of the Iowa State Highway Commission at their project HR-106.

The author is deeply grateful to Dr. R. L. Handy, his major professor, for the help, guidance, and unfailing encouragement throughout the investigation. The author also extends sincere thanks to Dr. C. Ho and Dr. T. Demirel for their assistance and friendly counsel during the investigation.

The autoclave used in the reaction product studies was loaned from Dr. G. Burnet of Chemical Engineering, and the electric furnace used for MgO studies was loaned by Dr. T. D. McGee of Ceramic Engineering. The electron micrographs presented in this report were prepared under the supervision of Dr. E. A. Rosauer of Ceramic Engineering. The author wishes to express his special appreciation for their most kind assistance.

Most of all, the author wishes to record his gratitude to his wife, Cynthia, whose encouragement and understanding were never lacking.

During the period of his graduate study at Iowa State University, the author is deeply indebt to many teachers and friends for assisting him to achieve the overall program of study; among those specially helpful were the late Dr. D. T. Davidson, Dr. R. L. Handy, Dr. T. Demirel, and Dr. M. Mateos.