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# POZZOLANIC REACTIONS OF SIX PRINCIPAL CLAY MINERALS: ACTIVATION, REACTIVITY ASSESSMENTS AND TECHNOLOGICAL EFFECTS

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## ABSTRACT

Six standard clays, before and after calcination at 3 or 4 temperatures and being mixed with $Ca(OH)_2$ [CH] in the presence of simulated cement pore solution, and with ordinary Portland cement, respectively, were studied in detail. Chemical compositions of most clays conform well to the requirement in ASTM C 618. Water demand of clay-containing mortar varies, depending on the crystal chemistry of raw clays, and on the specific surface area of calcined clays. Measurements of XRD background or alkali soluble Si are rapid methods in evaluation of the pozzolanic activity of clays. Compressive strength of mortars based on the raw clays is affected by structure of clays. Calcination increases the pozzolanic activity of clays and the compressive strength of the Portland cement - clay mortars. A close correlation exists between compressive strength of mortars and particle size distribution of the dehydroxylated clays. The most common reaction products of clay - CH mixtures are C-S-H[2] and $C_4AH_x$, while $C_2ASH_8$ and $C_3AH_6$ were also detected with clays rich in Al.

## Introduction

Clays have been used as pozzolanic materials for thousands of years (1). In spite of heavy competition from industrial by-products, clays are still good alternatives as mineral additives or blendings for concrete in many places of the world.

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[2] Cement abbreviations: C = CaO, A = $Al_2O_3$, S = $SiO_2$, H = $H_2O$, $\bar{S}$ = $SO_3$, $\bar{C}$ = $CO_2$

Numerous papers on pozzolanic activity of calcined clays have been published, in which attention was paid especially to the technological properties of the clay-containing mortars (2-10). The present investigation concentrated primarily upon the connections between the mineralogy of a broad spectrum of starting clays, effects of calcination and the optimum calcination temperature with respect to technological properties for clay based mortars.

## Materials and Experimental Methods

Five so called standard clay minerals were obtained from American Clay Minerals Society: illite (IMt-1), Ca-montmorillonite (STx-1), Na-montmorillonite (SWy-1), mixed layer mica/smectite (Sny-1) and sepiolite (SepSp-1). Kaolinite was supplied by the Royal Porcelain Factory (Denmark). The samples were calcined at three to four temperatures according to their thermal reactions revealed by DTA and TG. All samples, untreated and calcined, were mixed with CH in the presence of simulated cement pore solution, and with ordinary Portland cement (OPC), respectively. The calcined clays and the reaction products were studied by XRD, DTA, SEM, EPMA, as well as alkali and acid solubility tests. Technological properties of the raw and calcined clay-containing mortars including flow of fresh mortar and compressive strength were studied. The mortars have the ratio of cement : clays : sand = 70 : 30 : 300 (in weight). Mini-RILEM prisms ($2X2X15cm^3$) (11) were cast and cured in water at 40°C for 2, 7, 28 and 91 days for compressive strength tests. Detailed descriptions of experimental methods are in (12).

## Results and Discussions

### 1. Chemical properties of the clay additives

In relation to the ASTM C 618 (13) which stipulates that the sum of $SiO_2+Al_2O_3+Fe_2O_3$ in a natural pozzolan to be used in concrete must exceed 70.0 wt%, clays usually present a satisfactory chemical composition. This sum for the investigated clays is: kaolin 82.0, illite: 80.6, mixed layer mica/smectite: 88.1, Na-montmorillonite: 86.4, and Ca-montmorillonite: 86.7 wt%. The 2:1 structured clays such as montmorillonites and illite are Si rich, with Si/Al ratio above 2.0. However, the synthetic mixed layer mica/smectite is extraordinarily rich in Al which not only occupies all octahedral positions and 1/5 of the tetrahedral positions but also occupies some interlayer positions as a charge-balancing cation (14-15). It has Si/Al ratio similar to that for the 1:1 structured kaolinite, i.e. about 1.1. It is obviously not realistic to apply the compositional ASTM requirement to sepiolite which is a magnesium silicate with only traces of Al content.

The ASTM requirement for a natural pozzolan to contain less than 3.0% moisture and exhibit less than 10.0% loss on ignition may be a tough threshold for untreated clays which are characterized by high absorption. Their contents of moisture and loss on ignition may differ substantially from these values depending on the atmospheric humidity. Practically, the moisture/weight loss criteria can only be applied after the clays have be pre-treated at temperatures over 100°C.

### 2. Water retention capacity of clays and water demand of clay- containing mortars

The water/(cement+clay) ratio (W/C) was investigated based on the mortars with a consistency of 100% flow (ASTM flow table). The considerable variations in the water demand for the mortars containing different types of clays (Fig. 1) obviously correlate with the structural

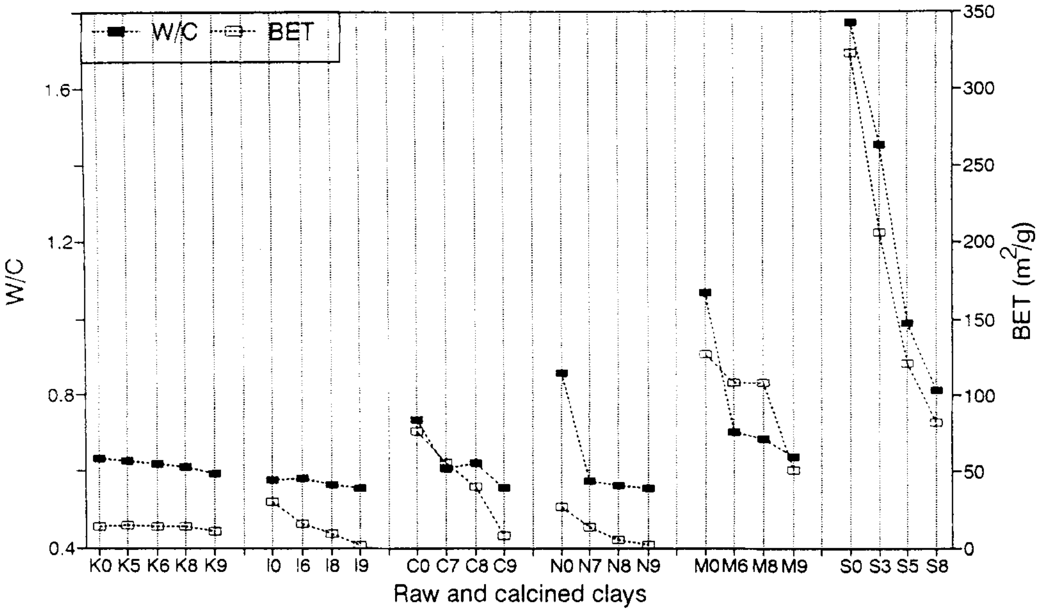

FIG. 1.

W/C: Water/(cement+clay) ratio of the mortars (flow=100%), and BET specific surface area of the used clays (nitrogen absorption). Connection lines between data points do not have physical meaning.

Abbreviations in all the Figs: K=kaolinite, I=illite, C=Ca-montmorillonite, N=Na-montmorillonite, M=mixed layer mica/smectite and S=sepiolite. Numbers beside these letters indicate the calcination temperature rounded down to the nearest hundred degrees (°C), e.g. K5=kaolin calcined above 500°C. 0 indicates clay without calcination.

properties of these clays. The W/C of the sepiolite-containing mortar is as high as 1.7 due to its zeolite-like structure that can absorb water up to about 20 wt% of its own mass (16). The water is firmly held at the edges of crystal ribbons and in the channels of sepiolite structure. The relation between water demands and clay structure can be confirmed also by comparing the water-demands of untreated Na- and Ca-montmorillonites. The former has only about one third of the specific surface area of the latter (Fig. 1) but its water demand is higher than the latter due to the limited water absorption by Ca-montmorillonite (3-4 layers of water in the interlayer space) versus unlimited swelling (particle dispersion in water) for the Na-montmorillonite (17).

The retention of a substantial amount of water in the structures of clay minerals causes high W/C for the clay-containing mortars. However, this part of water will have different physical properties from those of free water (18) and is not "effective" in the term of cement and concrete chemistry (19). Its possible negative effects on the microstructure and durability of the hardened mortar and concrete, and the possible positive effects in facilitating chemical and physical reactions of mortars and concretes remain to be evaluated.

For the expandable clays such as Na- and Ca- montmorillonites and mixed layer mica/smectite, the water-demand curves show a marked decrease from the untreated sample to the dehydroxylated one. On the other hand, for the non-expandable clays such as kaolinite and illite (12, 20) and for the calcined samples this change is rather gradual, displaying better correlation with the changes in their specific surface area (BET) than for the expandable ones (Fig. 1).

When in contact with water during gauging, untreated clays adsorb moisture immediately to various extent depending on their crystal chemistry, whereas, in agreement with Grim (21), the rehydration capacities of the calcined clays are substantially diminished or destroyed by calcination at the temperature of dehydroxylation and beyond (Fig. 1 and 2).

It is noticeable that the W/C ratio of mortars shows a broad linear correlation ($r^2$=0.89) with the specific surface area (BET) of the raw and calcined clays contained in them, with the most pronounced deviation for raw Na-montmorillonite (Fig. 2). It suggests that the internal surfaces of clays, including those in the channels of sepiolite, are measurable by $N_2$ absorption method although it was suggested before that the access of $N_2$ to the tunnels of sepiolite is far from complete (22).

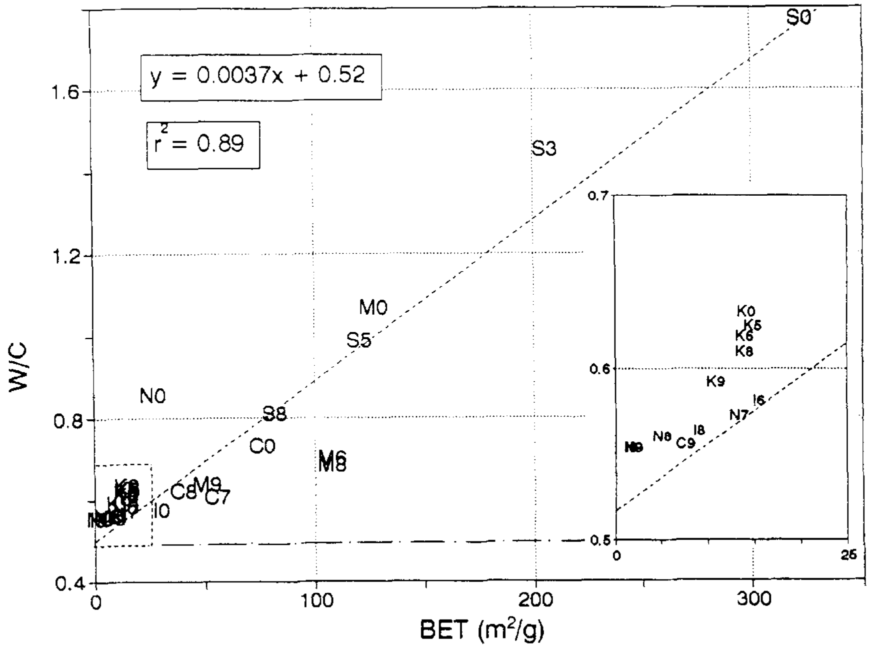

FIG. 2.

W/C of the mortars containing raw or calcined clays vs. the specific surface area (BET) of these clays. Abbreviations are explained in Fig. 1.

## 3. Measurement of pozzolanic activity of raw and calcined clays

Our study confirms that calcination that results in damaging and destroying the crystal structures of clays is very effective in activating pozzolanic properties of clays. They can be evaluated by two fast methods that do not involve addition of CH, cement pore solution or cement:

(1) *The amount of XRD amorphous phase.*

Its increase with calcination temperature can be illustrated by calcined kaolin (Fig. 3). After dehydroxylation of kaolin at 550°C, the XRD powder pattern shows a pronounced diffuse band at 20 - 30° 2Θ whose intensity increased to 180% of the original background value. It increased further to 195% at 800°C but dropped abruptly to 145% at 950°C when the formation of mullite took place. For Na-montmorillonite, the diffuse background increased to 155% after calcination

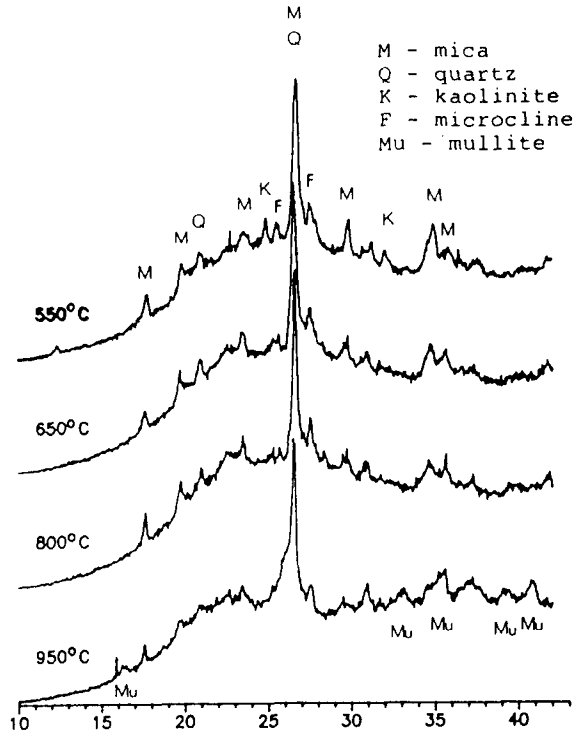

FIG. 3.

XRD powder patterns of calcined kaolin. Monochromatized Cu-Kα radiation (50 kV and 30 mA).

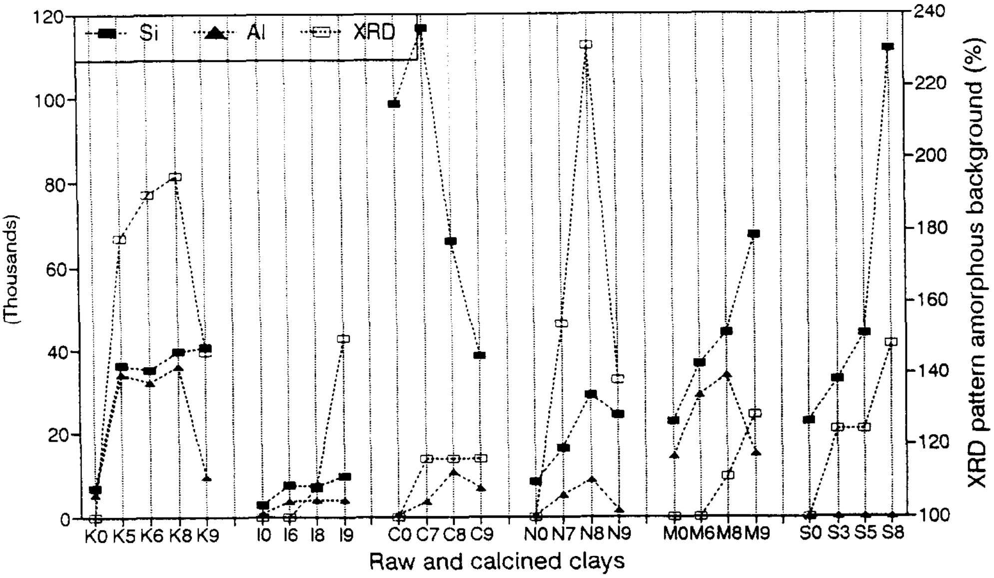

FIG. 4.

Alkali (0.5N NaOH) soluble Si and Al, and development of the amorphous background of XRD powder patterns for raw and calcined clays (background of untreated clays put to 100%). Connection lines between data points do not have physical meaning. Abbreviations are in Fig. 1.

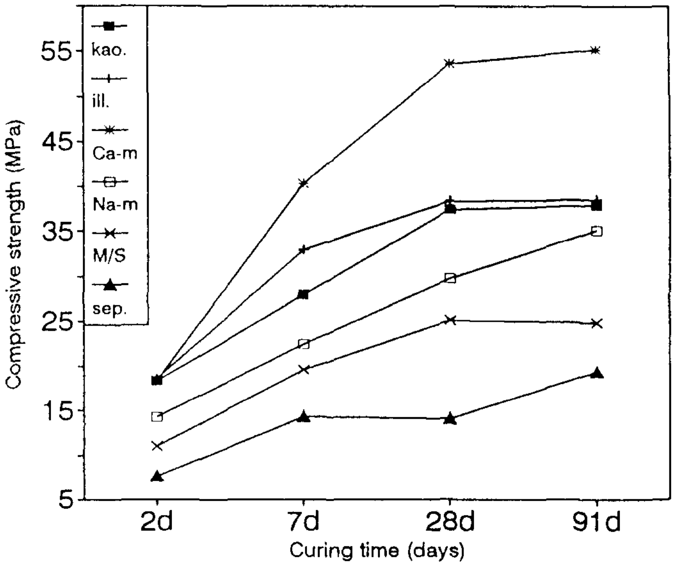

Fig. 5.
Compressive strengths of the mortars containing untreated clays. Abbreviations are in Fig. 1.

at 740° and to 230% at 830° but a sharp drop followed, to 135% at further calcination at 920° due to crystallization of $\gamma$-$Al_2O_3$ at the expense of amorphous substance (Fig. 4). For illite, the increase in XRD background during calcination is modest: a slight increase at 650°C, 10% at 790°C and by 55% at 930°C (Fig. 4) while the intensity of (001) reflection of illite decreases accordingly.

Kaolin and Na-montmorillonite represent clays with a sharp increase in the contents of amorphous phase with temperature, followed by a sharp drop; for other clays the increase is less abrupt and no drop was observed at the temperatures of the order of 800-900°C. Ca-montmorillonite (Fig. 4) represents an intermediate case; its reaction may be overshadowed by the considerable amount of opal (25 wt%) impurity in the original sample.

(2) *The amount of alkali-soluble Al and Si*, which reflect the contents of active aluminosilicates in a material ready to react with lime (23).
In the present investigation, the soluble Al and Si values obtained with the test method described in (23) are 0.5% and 0.7% respectively for raw kaolinite (Fig. 4). They increased to 3.4% and 3.6% after calcination at 550°C and remained at the same order of magnitude during further calcination to 800°C. At 950°C the amount of Al dropped abruptly to 1.0% while Si still increased to 4.1% because the new crystalline phase, mullite ($A_3S_2$), consumes 3 times more Al than Si.

For Na-montmorillonite, soluble Al and Si in the raw samples are 0.02% and 0.8%, respectively. They increased by 36.3 and 2.5 times the original value, respectively, at the optimum temperature of 830°C. The alkali-soluble Al and Si for raw illite are 0.08% and 0.28% respectively. In this case, the increment is 3.8 and 1.6 times the original values respectively, at 650°C and 4.3 and 2.4 times at 930°C.

For most of the clays soluble Al starts to decrease earlier than Si, due to the high temperature-formation of $\gamma$-$Al_2O_3$ or alumina rich phases (mullite) that precedes formation of silica-rich phases. The unusually high amount of soluble Si in Ca-montmorillonite and its decrease already at 730°C confirm the presence of important amounts of amorphous silica impurity in STx-1.

## 4. Compressive strengths and hydraulic index of clay-containing mortars

To overcome the problems arising from the above discussed large variation in W/C ratio, when comparing different mortars Feret's formula (24) was applied to adjust all the measured compressive strengths of values of mini-RILEM prisms to the water content W/C=0.5:

$$\sigma=K^*[(C+P)/(C+P+V)]^n$$

where $\sigma$ is compressive strength; C, P and V are the volumes of cement, pozzolan (clay) and water, respectively, in the mixture; K and n are constants. The generally used value of *n* equal to 2 was adopted in the present investigation.

The adjusted compressive strengths of mortars based on the untreated clays are included in Table 1 and shown in Fig. 5. The strengths decrease in a sequence: Ca-Mont. > illite ≥ kaolin > Na-mont. > mixed layer > sepiolite. This sequence is obtained for any curing time between 2 and 91 days (at 40°C), indicating that it is a rather stable feature.

The sequences can be correlated to the different bonding forces between structural layers or sheets of the different clay minerals and to their clay-cement adhesion properties, showing the importance of untreated clay particles for the resulting compressive strength of the mortar. The high position of the untreated Ca-montmorillonite in this sequences is attributed to the fairly high content of amorphous $SiO_2$ with pozzolanic properties. Except for the anomalous result for Ca-montmorillonite, the resulting values range between 20 and 56% of compressive strength for pure OPC (28 days).

TABLE 1

Compressive strengths of mortars containing untreated and optimally calcined clays and reference materials

| Sample | Optimum T (°C) | CS (MPa) U | O | CS/OPC(%) U | O | CS/550°C-kaolin U | O (%) |
|---|---|---|---|---|---|---|---|
| kaolin | 650 | 37.5 | 84.6 | 54 | 122 | | 108 |
| illite | 930 | 38.5 | 54.6 | 56 | 79 | | 70 |
| Ca-mont. | 830 | 53.6 | 86.7 | 77 | 125 | | 111 |
| Na-mont. | 830 | 29.8 | 78.1 | 43 | 113 | | 100 |
| mixed layer | 960 | 25.2 | 77.9 | 36 | 113 | | 99 |
| sepiolite | 830 | 14.2 | 58.3 | 20 | 84 | | 74 |
| silica fume | | 78.4 | | 113 | | 100 | |
| slag | | 77.0 | | 111 | | 98 | |
| fly ash | | 61.1 | | 88 | | 78 | |
| OPC | | 69.2 | | 100 | | 89 | |

CS=Compressive strength; U=uncalcined clay - cement mortar
O=optimally calcined clay - cement mortar.
Mini-RILEM prisms, cured in water at 40°C for 28 days.

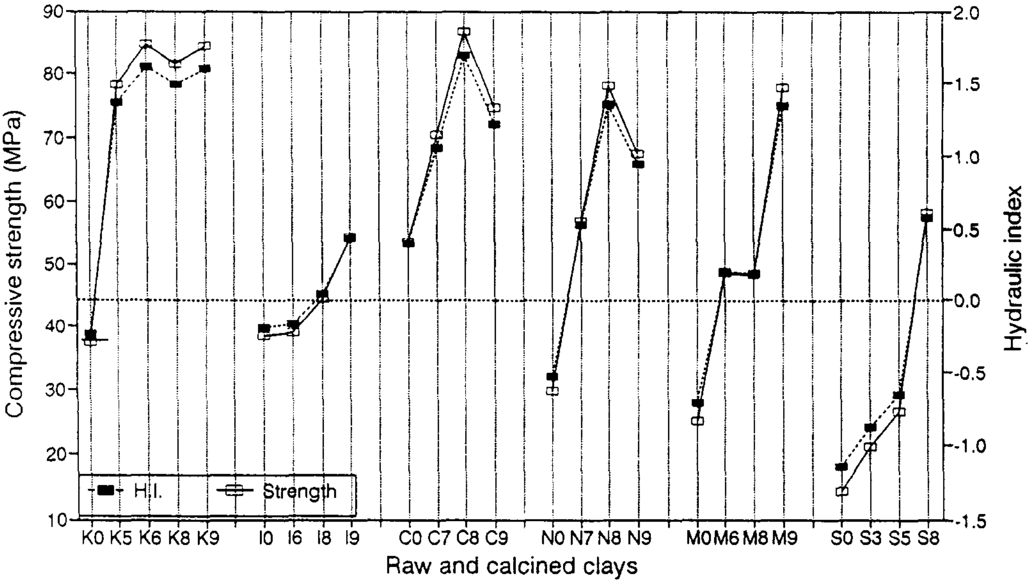

FIG. 6.

Compressive strengths and hydraulic index of the mortars containing raw and calcined clays. Prisms were cured for 28 days in water at 40°C. Abbreviations are in Fig. 1. Connection lines between data points do not have physical meaning.

Calcination is crucial for developing pozzolanic activity in clays. Dehydroxylation substantially increases the compressive strengths of the resulting mortar. The end of dehydroxylation reaction revealed by DTA in the present investigation: kaolin, 650°C; illite, 650°C; Ca-montmorillonite, 730°C; Na-montmorillonite, 740°C; mixed layer clay, 560°C; and sepiolite, 830°C. A well controlled optimal calcination temperature can bring the compressive strengths of the majority of resulting mortars above that of the reference OPC mortar (Table 1 and Fig. 6).

For kaolin, calcination at 550°C increases its compressive strength to 113% of pure OPC. It remains in this range during further calcination up to 950°C. Therefore it is economical to treat kaolin at 550°C to obtain a fairly good pozzolan.

Illite remains a generally poor pozzolan even though the highest calcination temperature of 930°C increased its activity considerably. Still, the maximum compressive strength of its mortar reaches only 70% of that for 550°C kaolin.

Ca-montmorillonite shows high compressive strength, constantly superior to that of Na-montmorillonite at every calcination temperature. This is probably due to the content of amorphous $SiO_2$, active at lower calcination temperatures, combined with particle size distribution and other factors. It is practically important that, unlike kaolinite, increasing calcination temperature past dehydroxylation at about 730°C to 830°C, increases the compressive strength for both montmorillonite types significantly. However, overheating to 930°C is connected with a substantial loss of mortar strength.

Mixed layer mica/smectite with $NH_4^+$ as cation did not show sufficient compressive strength until 960°C, despite dehydroxylation and deamination at 560°C. Calcination at 830°C, at which sepiolite is dehydroxylated, doubled the compressive strength of sepiolite and finally brought it to 84% of that of OPC.

For illite, mixed layer M/S and sepiolite, the highest compressive strength of the resulting mortars is achieved only after the clay admixtures had been calcined at the highest temperatures. These temperatures correspond to the complete destruction of the clays, as indicated by the XRD analysis.

Compressive strengths of all investigated raw and calcined clay-containing mortars (Fig. 6) are parallel to the development of XRD diffuse background and alkali soluble Si (Fig. 4). Active Si from amorphized clays reacts with CH to form C-S-H, which is the main strength contributor in the hardened mortars. Although compressive strength results from a combination of many factors, data in Figs 4 and 6 show that for the same type of clay, it is the pozzolanic activity that dominates the interacting system and controls the technical behavior of the mortars.

However, when we consider the body of the investigated clays as a whole, no simple relation exists between compressive strengths and the value for alkali soluble Si or the XRD background (cross-comparisons are difficult to make for the latter). Obviously, the differences in crystal structures, chemistry, and/or particle properties of different type of clays are equally important as differences in pozzolanic activity in influencing the compressive strength of the resulting mortars.

The hydraulic index, H, was calculated for mortars based on untreated or calcined clays as follows:

$$H = \frac{\sigma_x - \sigma_{x,inert}}{\sigma_0 - \sigma_{x,inert}} \times 100\%$$

where $\sigma_x$ is compressive strength of the tested sample, $\sigma_0$ is that of reference OPC and $\sigma_{x,\mathrm{inert}}$ is the strength of the OPC mixed with a completely inert component in the same replacement percentage as for the tested samples. Here the latter value was taken to be equal to 63% of pure reference OPC, corresponding to the effect of dilution calculated by Feret's formula. When H is equal to 0, the mixed component is completely inert, whereas when it is equal to 1, this component has the same activity as reference cement (25). Fig. 6 shows that most of the untreated clays are inferior to an inert component, probably due to the weak cohesion and cleavages of clay minerals from which fracturing propagates, and to the adverse effects of the flaky shapes on the structure of concrete (19). Moukwa et al (9) attributed the low compressive strength to the interference of water molecules on the clay surfaces.

## 5. Particle size distribution of clays and the compressive strength of corresponding mortars

Particle size distribution (PSD) is an important parameter in cement and concrete industry because it affects the reaction kinetics and the pore structures of mortars or concrete. After slight (standardized) pulverization the raw and calcined clays show a considerable variations in the particle size distribution. With exception of kaolin, all clays attain on dehydroxylation a certain degree of agglomeration that is apparently preserved to higher temperatures. Plotting the percentage of 45 μm residue (determined by laser diffractometry) against the compressive strength (Fig. 7) indicates a broad negative linear correlation ($r^2$=0.66) between these two parameters for all dehydroxylated clays as well as the reference samples of fly ash, silica fume, slag and OPC. This correlation does not hold for the untreated clays; they stay at low strength values despite their low 45 μm residues. Their low reactivities and excellent cleavage are the principal factors determining their positions in the diagram.

The lower boundary of the correlation band in Fig. 7 is determined by the clays dehydroxylated at lowest temperatures and those with reactivity falling around 900°C, the upper boundary by the most reactive clays, annealed at 800-900°C. The width of the correlation band for calcined clays is smaller than or comparable to the strength difference connected to the particle size effects.

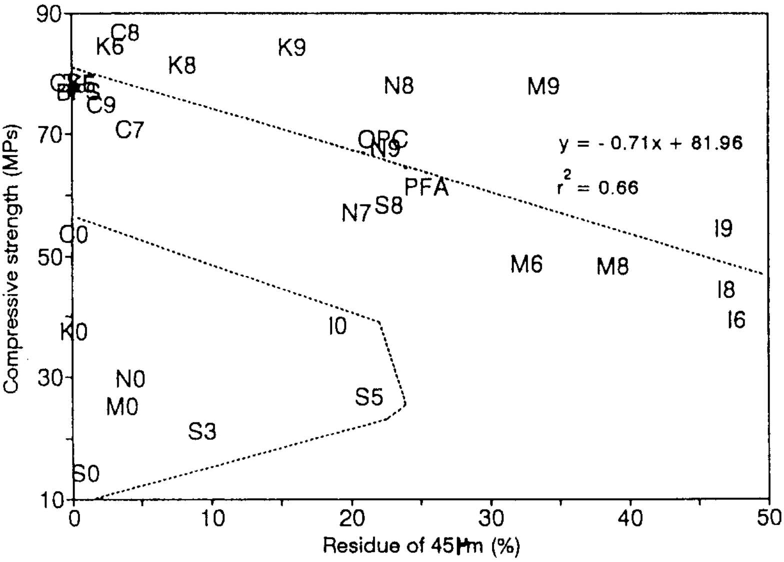

FIG. 7.

Compressive strengths of the mortars containing raw and calcined clays or reference materials vs. particle size of these materials (determined by laser diffractometry, expressed as percentage of the 45 μm residue). Abbreviations in Fig. 1. and CSF = condensed silica fume, BFS = blast furnace slag and PFA = pulverized fly ash.

## 6. Reaction products of clays and calcium hydroxide

The quantity of reaction products or the remnants of starting material, i.e. CH and clays, reflect the intensity of pozzolanic reaction in the CH-clay-water system. When raw and calcined clays are mixed with CH and simulated cement pore solution (which contains 43 mM Na, 95 mM K, and has pH=13.2), the most dominating reaction products are C-S-H and $C_4AH_x$ in various concentration, indicating that both Si and Al from the clay participate in pozzolanic reaction. The content of reacted Al is generally low. Gehlenite hydrate ($C_2ASH_8$) was observed by EPMA in kaolinite pellets immersed in the CH solution at 40°C for 7 days; hydrogarnet ($C_3AH_6$), with various degree of substitution $(OH)_4 \leftrightarrow SiO_4$, was detected by both XRD and EPMA in the mixed layer clay -- CH mixture reacted for 150 days at 40°C. Both clays have Al content higher than the other clays discussed.

## Conclusions

Most of clays have the sum of major chemical components, $SiO_2+Al_2O_3+Fe_2O_3$ exceeding 80%. They conform with the ASTM requirements of this sum being > 70% for a natural pozzolan to be used in blended hydraulic cements.

Water demand for a given consistency of clay-containing mortars varies considerably, depending on the water retention capacity that in turn is determined by the crystal chemistry of clay minerals. It decreases in the sequence: sepiolite > Na-montmorillonite > Ca-montmorillonite > mixed layer mica/smectite > non-expandable clays. Water/(cement+clay) ratio shows a broad linear correlation with the specific surface area (BET) of all clays.

The XRD background and alkali soluble Si of the pozzolanic clays reflect closely the thermal decomposition and pozzolanic activity of these materials. However, their connection with the compressive strengths of the resulting mortar may be outweighed by the influence of particle size distribution, especially when different types of materials are compared.

The sequence of compressive strength of mortars containing untreated clays is: Ca-montmorillonite (+ amorphous $SiO_2$) > illite ≥ kaolinite > Na-montmorillonite > mixed-layer clays > sepiolite. Proper calcination is an effective means for increasing the pozzolanic activity of clays. The optimal calcination temperatures for achieving the highest compressive strength are: Ca-montmorillonite, 830°C, kaolinite 650°C, Na-montmorillonite 830°C, mixed-layer clay 960°C. The compressive strengths (28 days at 40°C) of these clays - cement mortars are 112-130% of plain OPC mortar. Illite and sepiolite mortars lie at about 80-84% of the OPC strength even at the optimum calcination temperatures.

The dominating products of reaction between clays and CH are C-S-H and $C_4AH_x$ in various concentrations, while with the clays rich in Al (kaolinite and mixed layer clay), gehlenite hydrate and hydrogarnet were detected.

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