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EFFECT OF TEMPERATURE ON PHASE COMPOSITION AND MICROSTRUCTURE OF ARTIFICIAL POZZOLANA-CEMENT PASTES CONTAINING BURNT KAOLINITE CLAY

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ABSTRACT

The influence of high temperature on the phase composition and microstructure of cement paste is vital for fire-resistance studies. Pozzolana tends to improve the microstructure of cement paste, due to its reaction with hydrated products. This study aimed to investigate experimentally the change occurring in the phase composition and microstructure of burnt kaolinite cement pastes after being exposed to high temperatures. The kaolinite clays were thermally activated by firing at 850°C for 2 h. The ordinary Portland cement (OPC) was partially substituted for by 0, 10, 20, and 30% of activated kaolinite clay by weight. The treatment temperature varied from 100 to 600°C by increment of 100°C a period of 3 h. The phase composition and microstructure measures were performed by means of differential thermal analysis and scanning electron microscopy. The results of this investigation show recrystallization and carbonation of $Ca(OH)_2$; they also show a deformation of C-S-H and C_4AH_{13} phases. *© 1998 Elsevier Science Ltd*

Introduction

Fire is one of the natural hazards that attack building constructions. The damage to buildings due to their continuous exposure to fire is caused by high temperatures. The chemical processes stimulated by temperature in the particular phases of cement paste have a significant influence on the thermal deformations that occur (1). Vaporization of free moisture at around 100°C, dehydration of calcium hydroxide (CH) at temperatures above 350°C, and partial volatilization of C-S-H at 500°C or higher are responsible for buildup of internal pressure in concrete and loss of ignition of its hydrates (2). The pozzolanic material (silica fume) has been shown to improve the microstructure of cement paste in concrete by densifying the cement paste matrix and the porous paste aggregate interfacial zone (3–5). The cement hydrates, as well as the C-S-H phases produced as a result of consumption of free$Ca(OH)_2$ by active silica fume, are deposited within the pore system and around the grains of the concrete constituents, leading to a more dense structure of concrete specimens

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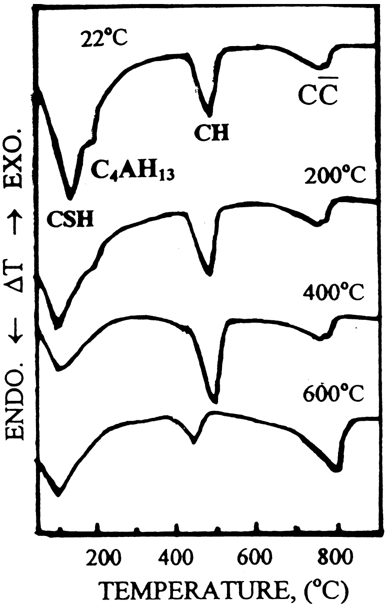


FIG. 1.
DTA thermograms of sample containing 0% kaolinite.

containing silica fume (6). The use of thermal-activated kaolinite clay as a pozzolan in cement paste prolonged the initial and final setting times and improved the microstructure of the formed hydrates (7).

Experimental Work

The cement pastes were prepared using ordinary Portland cement (OPC) that had been partially substituted for by thermally-activated kaolinite clay (burnt at 850°C for 2 h) with ratios of 0, 10, 20, and 30% by weight. The oxide composition of OPC has been found to be: CaO, 63.8%; SiO_2, 21.75%; Al_2O_3, 6.86%; Fe_2O_3, 1.78%; MgO, 2.74%; SO_3, 1.46%; and ignition loss, 1.8%. The chemical composition of kaolinite clay used in this study was found to be: SiO_2, 44.2%; Al_2O_3, 37.75%; Fe_2O_3, 0.93%; TiO_2, 1.85%; K_2O, 0.72%; SO_3, 0.57%; Na_2O, 1.15%; K_2O, 0.72%; and ignition loss, 13.01. The pastes were prepared using the standard water of consistency for water/solid ratios 0.255, 0.263, 0.275, and 0.287 for 0, 10, 20, and 30% burnt kaolinite clay, respectively. After 28 days of curing under water, the hardened cement specimens were dried at a temperature of 1005°C for 24 h in an electric furnace. Then, they were kept for 3 h in each of the investigated temperatures, in the range of 200 to 600°C in intervals of 100°C. The thermally-treated specimens were cooled together with the furnace to the indoor room air temperature and then were given to structural tests. Scanning electron microscopy and differential thermal analysis were used for identification of the changes occurring in the microstructure of the formed and/or decomposed phases.

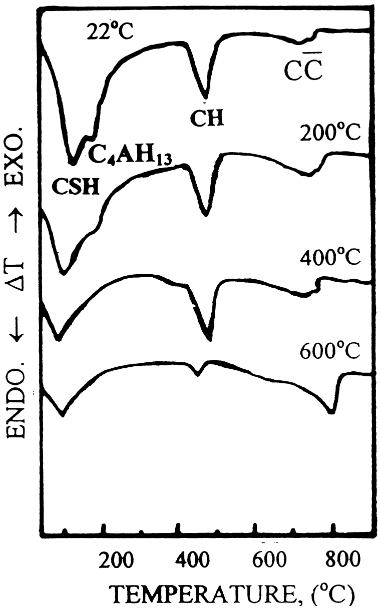


FIG. 2.
DTA thermograms of sample containing 10% kaolinite.

Results and Discussion

Figures 1–3 show the DTA thermograms of the various heat-treated kaolinite-cement pastes. The results indicate the existence of four endothermic peaks. The first peak, located at about 135°C, characterizes the calcium silicate hydrates, mainly C-S-H(I); minor amounts of ettringite, $C_3A{\cdot}3CaSO_4{\cdot}2H_2O$, also decompose below this temperature. The second endothermic peak, observed at about 175°C, represents the decomposition of calcium aluminate hydrate, mainly as C_4AH_{13}. The third endothermic peak, located at about 480°C, represents the decomposition of CH. The last endothermic peaks appeared at 740°C and 765°C, and represent the decomposition of amorphous $CaCO_3$ and its crystalline form, respectively. The mean feature of the thermograms, characterized by a decrease in the peak area of the CH phase and an increase in the peak area of C-S-H(I) and C_4AH_{13} phases as the amount of burnt kaolinite clay, increased from 0 to 20% for controlled samples (thermally-treated at 22°C). The decrease of the $Ca(OH)_2$ endotherm is actually the result of consumption of the free lime obtained during cement hydration by burnt kaolinite to form hydrated phases, leading to an increase of the endotherms of C-S-H(I) and C_4AH_{13}. It is also clear that the endotherm of the CH phase increases and the endotherm of C-S-H(I) and C_4AH_{13} decreases as the temperature of thermal-treatment increases up to 400°C. The increase in CH peak areas is a result of recrystallization of the amorphous part of $Ca(OH)_2$, but the decrease in peak areas of C-S-H(I) and C_4AH_{13} may be due to partial decomposition of these phases at 400°C. Evidently, the $CaCO_3$ endotherm increases as the temperature of thermal-treatment increases; this may be due to the physico-chemical processes connected with the liberation of water from 200–500°C, which accelerate $Ca(OH)_2$ carbonation kinetics. This is indicated by a partial decrease in the $Ca(OH)_2$ content, which tends to increase the $CaCO_3$ content.

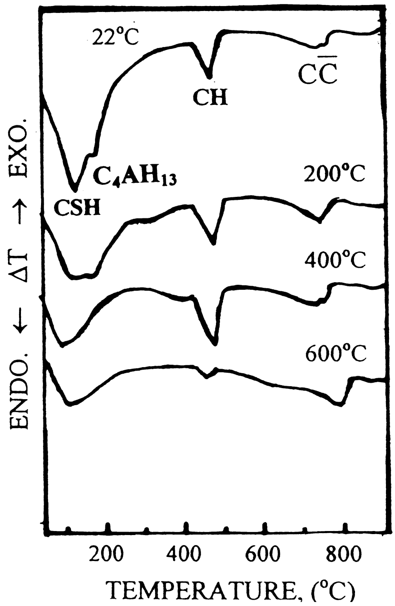


FIG. 3.
DTA thermograms of sample containing 20% kaolinite.

Figure 4 shows the relation between weight loss and temperature of thermally-treated kaolinite-cement pastes. In general, the weight loss increases with increasing temperature of thermal treatment, a result which is mainly associated with liberation of water from the decomposition of $Ca(OH)_2$ and the other formed cement hydrates. Apart from physico-

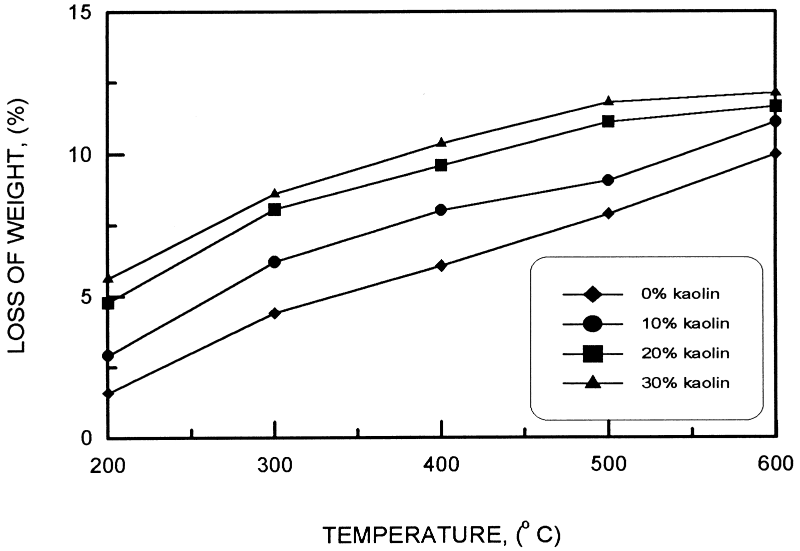


FIG. 4.
Change of weight loss of kaolinite-cement paste with temperature.

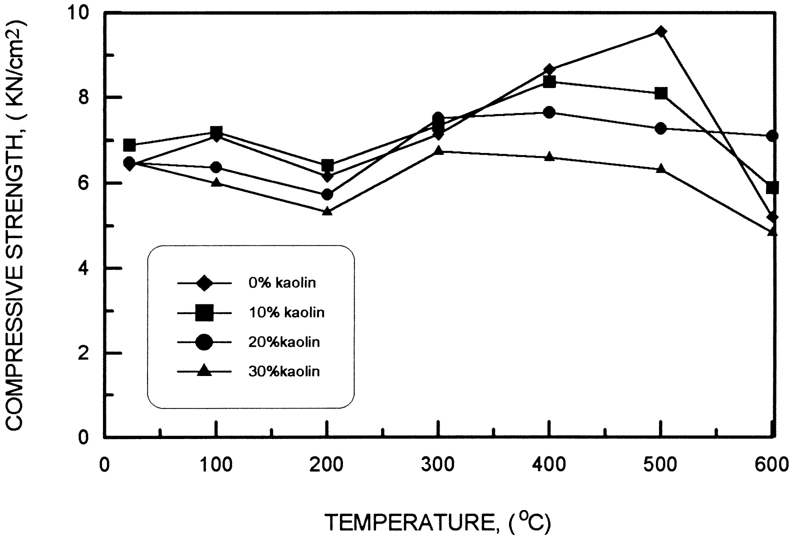
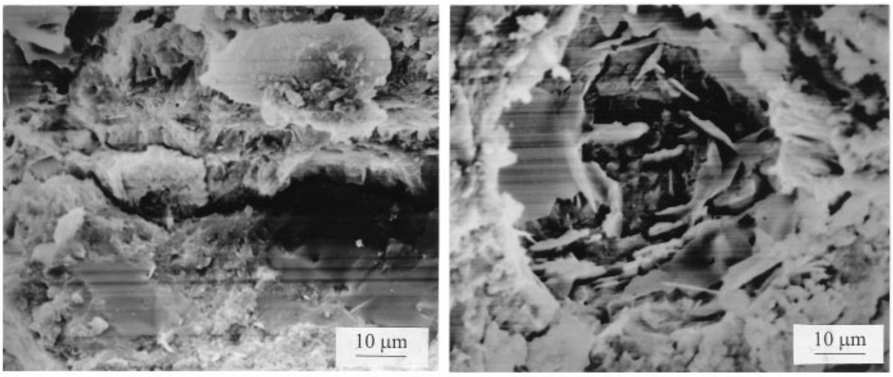


FIG. 5.
Variation of burnt kaolinite-cement paste compressive strength with temperature.

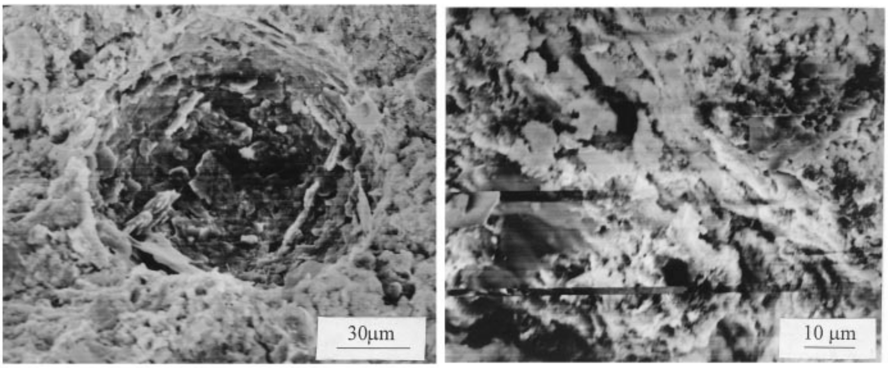
chemical processes connected with the liberation of water from cement pastes in the temperature range 200–500°C, a partial carbonation of $Ca(OH)_2$ was observed. This is indicated by a decrease in the $Ca(OH)_2$ content with the consequent increase in the $CaCO_3$ content as observed in the DTA thermograms (Figs. 1–3).

Figure 5 illustrates the relation between compressive strength of various cement pastes and temperature of thermal treatment. There appears a decrease in compressive strength with increasing temperature up to 200°C; then the strength increases as the temperature increases up to 500°C for the samples containing 0 and 10% burnt kaolinite. The compressive strength of the sample containing 20% burnt kaolinite is thermally stable in the temperature range from 200–600°C; but the sample containing 30% burnt kaolinite clay is thermally stable up to 500°C. The initial decrease of compressive strength in the temperature range 22–200°C can be attributed to the swelling of water layers in the paste, which causes a sort of weakening of bonds (8). The increase in compressive strength with temperature may be due to additional hydration of unhydrated cement grains as a result of steam effect under the condition of the so-called internal autoclaving; it is also due to the pozzolanic reaction of burnt kaolinite with free lime to produce more C-S-H phases which deposit in the pore system. Evidently, the partial substitution of OPC by 20% of burnt kaolinite clay improves the compressive strength of cement paste by 27% more than that of the controlled sample at 600°C. Therefore, the artificial pozzolana (burnt kaolinite) improved the fire resistance of cement paste up to 600°C.

Figure 6 shows the SEM micrographs of kaolinite-cement paste containing 20% burnt kaolinite clay for the unheated specimens as well as the thermally-treated specimens at 200°C, 400°C, and 600°C. The micrographs of unheated samples (cured at 22°C) consist mainly of ill-crystallized and fibrous particles of calcium silicate "gel," amorphous and well-crystallized calcium hydroxide as well as calcium aluminate hydrate. It is used as a reference to the samples exposed to high temperatures in this study. The morphology of



burnt kaolinite-cement paste (unheated) **burnt kaolinite-cement paste heated at 200°C**



burnt kaolinite- cement paste heated at 400°C **burnt kaolinite- cement paste heated at 600°C**

FIG. 6.
SEM micrographs of thermally-treated cement pastes containing 20% burnt kaolinite clay.

hydrates after exposure at 200°C is characterized by well-formed crystals (platy crystals) that are deposited in the pore system with no apparent cracks; the calcium hydroxide phase appears according to a well-crystallized habit, stacked as parallel layers. The morphology of hydrates after exposure at 400°C and 600°C shows a massive structure: platy lick calcium silicate hydrates that are arranged in a layered structure. Microcracks make their appearance for the specimens treated at 600°C.

Conclusions

The main conclusions derived from this study may be summarized as follows:

1. The thermal treatment of kaolinite-cement paste increases $Ca(OH)_2$ carbonation kinetics.
2. The replacement of OPC by 20% of thermally-activated kaolinite in cement paste increases its thermal stability against temperature increase up to 600°C.

3. The improvement in compressive strength of pozzolana-cement paste containing burnt kaolinite clay is 27% at 600°C.
4. Microstructural analysis reveals that a massive structure of calcium silicate hydrates is observed for samples exposed to heat up to 600°C.

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