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MICROSTRUCTURE AND HYDRATION CHARACTERISTICS OF ARTIFICIAL POZZOLANA-CEMENT PASTES CONTAINING BURNT KAOLINITE CLAY

M. Saad Morsy*, S.A. Abo El-Enein, and G.B. Hanna***
*Building Research Center, P.O. Box 1770, Cairo, Egypt
**Faculty of Science, Ain Shams University, Cairo, Egypt

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ABSTRACT

The reaction of pozzolana with the lime liberated during the hydration process of Portland cement modifies some properties of cement and resulting concrete. This study aimed to investigate experimentally the change occurring in the phase composition and microstructure of pozzolanic cement pastes containing activated kaolinite clay. The artificial pozzolana (burnt kaolinite clay) were thermally activated by firing at 850°C for two hours. The ordinary Portland cement (OPC) was partially replaced by different amounts of activated kaolinite clay by weight. The changes in the electrical conductivity were reported during setting and hardening processes after gauging with water. The change occurring in the phase composition and microstructure of cement pastes were investigated by differential thermal analysis and scanning electron microscopy. The results of this investigation show that, the thermal activated kaolinite clay prolonged the initial and final setting times and reduced the porosity, it also improved the microstructure of the formed hydrates by recrystallization of hydrated calcium silicates (mainly as CSH-(I)) together with the formation of hexagonal calcium aluminate hydrate (mainly as C_4AH_{13}). © *1997 Elsevier Science Ltd*

Introduction

Clays have been used as pozzolanic materials for thousands of years. Calcination increases the pozzolanic activity of clays and so the compressive strength of the Portland cement-clay mortars (1). The addition of thermally or chemically activated clay on the hydration of Portland cement; increases the rate of the early hydration of cement due to adsorption and ion-exchange processes occurring on the surface (2). Pozzolanic addition reduces the heat of hydration and improved the durability of cements. It caused some increasing in mortar shrinkage and decreasing the workability of mortars and concretes (3). The pozzolanic material (silica fume) showed an improving of the microstructure of cement paste in concrete by densifying the cement paste matrix and the porous paste-aggregate interfacial zone (4–6). The addition of silica fume to ordinary concrete leads to the consumption of $Ca(OH)_2$ obtained during cement hydration as a result of interaction with active silica fume to form the CSH phases (7,8).

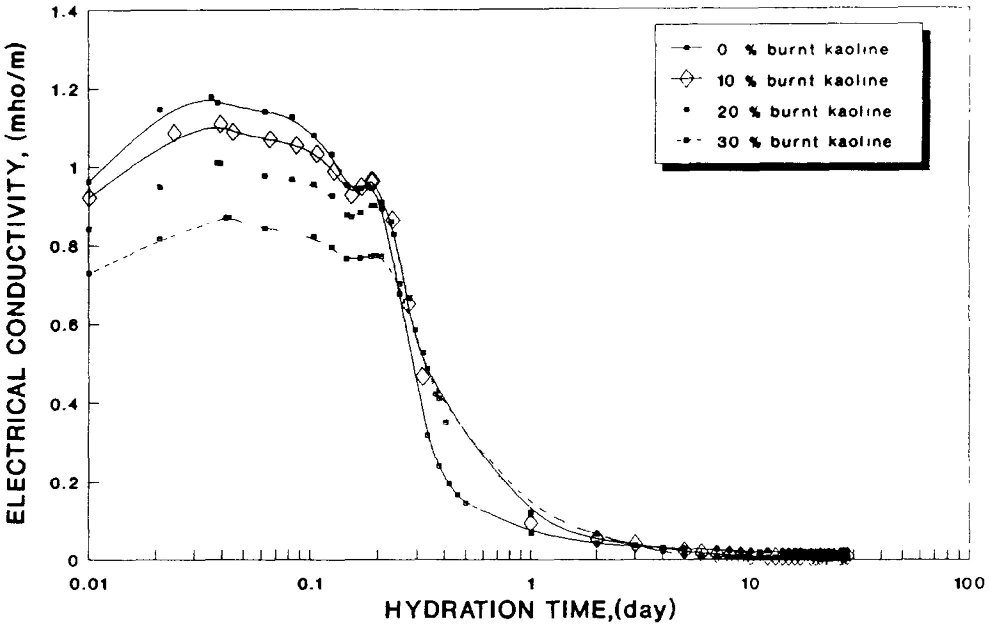

FIG. 1.
Electrical conductivity of cement pastes containing thermally activated kaolinite clay.

Experimental Work

The ordinary Portland cement has been partially substituted by thermally activated kaolinite clay (burnt at 850°C for 2 hours) with ratios of 0, 10, 20 and 30% by weight. The pastes were prepared using the standard water of consistency with water/solid ratios 0.255, 0.263, 0.275 and 0.287 for 0, 10, 20 and 30% burnt kaolinite, respectively. The pastes were molded in 2 cm. cubes for porosity, differential thermal analysis and microstructure tests. The moulds were vibrated for one minute to remove any air bubbles and voids. The sample was left in moulds at 100% relative humidity for 24 hours, then removed from the moulds and immersed in water for 28 days to curing. The total porosity is determined by following the method reported in BS 812 (9). In electrical conductivity measurements, the test cell was of the co-axial type (10) and included concentric inner and outer electrodes mounted on insulated base plate; the electrodes were polished before the experiment. The cement pastes were placed in the space between the electrodes and the cell was kept in a desiccator at 100% relative hymidity during the test period. The measurement began exactly, three minutes after the first contact with water; this is the zero time of test. The electrodes were hooked to LCR meters, model SR 720; 1000 Hz for resistance measurements between the electrodes over the hydration stages of setting and hardening.

Results and Discussion

Figure (1) shows the effect of addition of thermally activated kaolinite clay on the electrical conductivity of neat cement pastes. It is clear that, the electrical conductivity of pastes

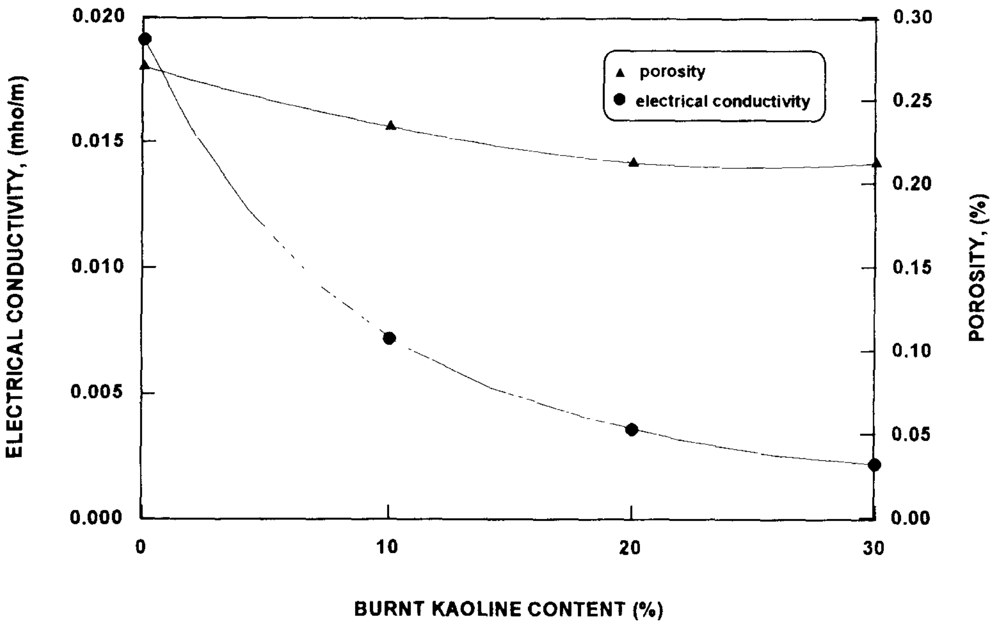

FIG. 2.

Relationship between electrical conductivity or porosity of cement pastes containing thermally activated kaolinite clay.

increases shortly after mixing with water, followed by an initial decrease. The increase of electrical conductivity in the initial stage of hydration is due to the increase of ionic concentrations and mobility of ions (Ca^{++}, OH^-, SO_4^{--}, Na^+ and K^+). These ions are, however, readily absorbed by the formation of a thin layer of hydration products, which form an envelope around the unhydrated cement grains. These envelope consists of electrical double layers of adsorbed calcium ions and counter ions which leads to a decrease in both of the number and mobility of ions, and consequently the conductivity after the first peak. The second peak in the conductivity-time curve is actually due to the ettringite transformation into the monosulphate hydrate and to the osmotic pressure development around cement grains (10). At the later stage of hydration, the formation and later accumulation of the various kinds of cement hydrates resulted in a marked consumption of the number of ions leading to a sharp decrease in the conductivity of the hardened pastes. The partial replacement of OPC by activated kaolinite clay of ratios 10, 20 and 30%; prolonged both the first setting time from 52 to 61 minutes and the second setting time from 261 to 282 minutes. Therefore, the partial substitution of OPC by burnt kaolinite leads to a decrease in the rate of initial hydrolysis of cement with the release of ions at a lower rate; this leads to lower conductivity values during the initial stage of hydration as compared with neat OPC pastes.

Figure (2) illustrates the relationship between electrical conductivity as well as the porosity of cement pastes with the burnt kaolinite content. It is clear that, the electrical conductivity of hydrated cement after 28 days, decreases as the activated kaolinite clay ratio increases. This result is mainly associated with the consumption of the number of ions with the formation of larger amounts of cement gel with increasing content of kaolinite clay. It is also evident that, the porosity decreases as pozzolana (burnt kaolinite) ratio increases. This result

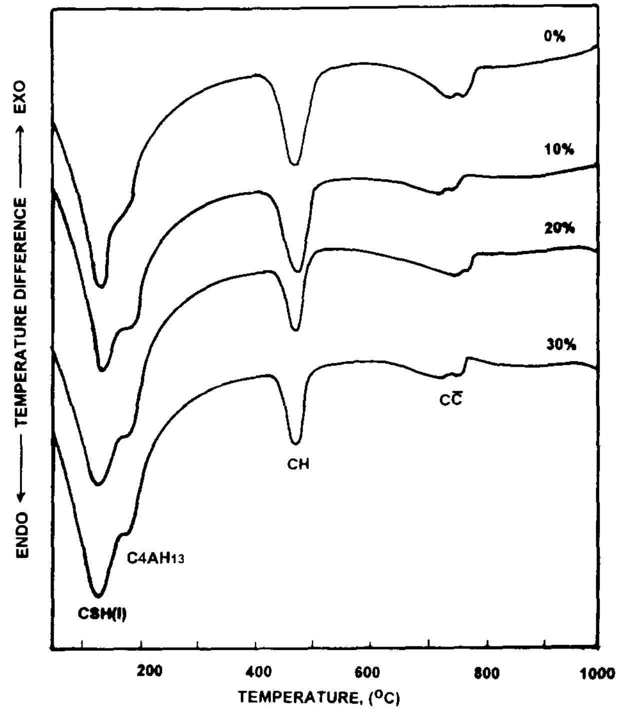

FIG. 3.
DTA Thermograms of cement pastes containing thermally activated kaolinite clay.

is due to the filler effect of artificial pozzolana in the porosity of the coarser particles as well as its pozzolanic reaction with $Ca(OH)_2$ to produce larger amounts of hydrates which deposit in the pore system. The electrical conductivity of hardened burnt kaolinite-cement paste water cured for 28 days, can be correlated by the following equation:

$$\sigma = 0.019 - 0.0018\, x + 7.18E\text{-}5\, x^2 - 1.012E\text{-}6\, x^3$$

and the porosity can be correlated by the following equation:

$$P = 0.269 - 0.0039\, x + 3.12E\text{-}5\, x^2 + 1.28E\text{-}6\, x^3$$

where x is the burnt kaolinite content by weight of cement.

Figure (3) shows the DTA thermograms of hardened cement pastes containing 0, 10, 20 and 30% burnt kaolinite clay. It is clear that, the existence of four endothermic peaks. The first peak located at about 135°C which is mainly due to the decomposition of calcium silicate hydrates, mainly as CSH-(I). The second endothermic peak observed at about 175°C represents the decomposition of the hexagonal calcium aluminate hydrate, mainly as C_4AH_{13}. The third endothermic peak is located at about 480°C represents the decomposition of calcium hydroxide (CH). In addition, two other endotherms appeared at 740 and 765°C which represent the decomposation of amorphous and crystalline calcium carbonate ($CaCO_3$), respectively. It is clear that, the peak areas of CSH(I) and C_4AH_{13} phases increase as the amount of thermally activated kaolinite clay increases up to 30%. Evidently addition of burnt

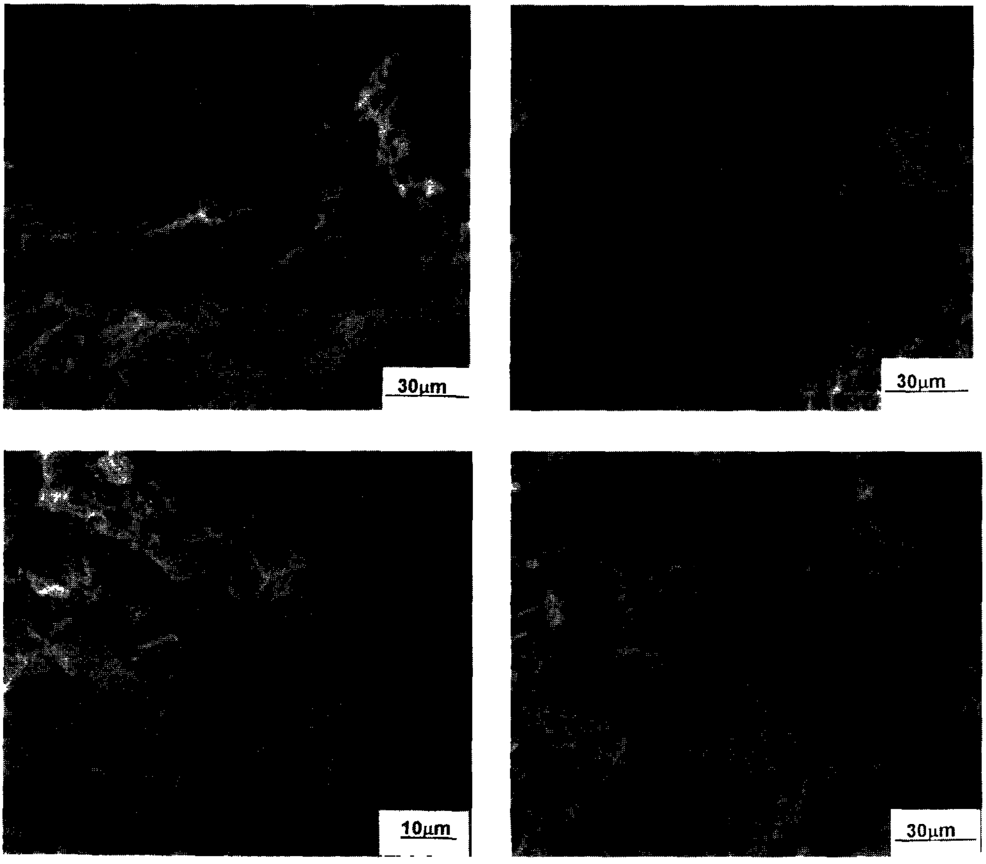

FIG. 4.
SEM micrograph of cement pastes containing thermally activated kaolinite clay.

kaolinite, as an artificial pozzolana, results in an acceleration of the rate of hydrolysis of clinker silicates in addition to the aluminates present in burnt kaolinite (11). Thermograms also show that, the peak area of $Ca(OH)_2$ decreases with increasing content of burnt kaolinite. This result is mainly attributed to the further hydration pozzolanic reaction between the thermally activated kaolinite clay and the calcium hydroxide. The peak area of calcium carbonate phase decreases as the artificial pozzolana (burnt kaolinite) content increases from 0 to 30%. Therefore, pozzolana additions increase the resistance of the hardened cement pastes towards carbon dioxide attack.

Figure (4) demonstrates the SEM micrographs of cement pastes containing 0, 10, 20 and 30% burnt kaolinite as an artificial pozzolana. The SEM micrographs indicated that the microstructure of the neat hardened cement paste consists mainly of ill-crystallized and fibrous particles of calcium silicate hydrates; which appeared as a clear binders between cement grains; these hydrates (mainly as CSH-(I)) were engulfed with small hexagonal particles of calcium hydroxide. The SEM micrographs of pastes containing 10, 20 and 30% pozzolana clay indicate that, the microstructure displayed mainly ill-crystallized and well-crystallized hydration products; these are a massive structure of calcium silicate hydrates and appreciable amounts of calcium aluminate hydrates (C_4AH_{13}). Short ettringite crystals are also appeared in the microstructure of the hardened pozzolana cement pastes. Therefore, the addition of pozzolana accelerates the hydration of C_3A of Portland cement since its grains offer the precipitation sites of the formed ettringite in presence of gypsum (12). Apparently, the micrographs obtained for pozzolanic cement pastes show a more dense structure than those of the neat Portland cement pastes. This dense structure accounts for the structure stability of pozzolanic cement pastes towards carbonation and aggressive ions.

Conclusions

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

1. The replacement of OPC by thermally activated kaolinite clay in cement paste prolonged the initial and the final setting time.
2. The electrical conductivity of kaolinite clay cement paste moist cured for 28 days decreases, as the kaolinite clay ratio increases.
3. The porosity of kaolinite clay cement paste decreases, as the kaolinite clay ratio increases.
4. The microstructure of hardened kaolinite clay cement paste show that the hydration products were mainly ill-crystallized, will-crystallized calcium silicate hydrate and calcium aluminate hydrates.
5. The dense structure of hydrated burnt kaolinite cement pastes leads to the structure stability towards carbonation and aggressive ions.

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