

## Physicochemical, Microstructural and Thermal Characteristics of Some Artificial Pozzolanic Cement Pastes Containing Burnt Clay with and without Silica Fume

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### ABSTRACT

Pozzolanic cement blends were prepared by the partial substitution of ordinary Portland cement (OPC) with different percentages of burnt clay (B.C.), Libyan clay fired at 700°C, of 10, 20 and 30%. The pastes were made using an initial water/solid ratio of 0.30 by weight and hydrated for 1, 3, 7, 28 and 90 days. The pozzolanic OPC-B.C. blend containing 30% B.C. was also admixed with 2.5 and 5% silica fume (SF) to improve the physicochemical characteristics. The hardened pozzolanic cement pastes were subjected to compressive strength and hydration kinetics tests. The results of compressive strength indicated slightly higher values for the paste made of OPC-B.C. blend containing 10% B.C. The results of DSC and XRD studies indicated the formation and later stabilization of calcium silicates hydrates (CSH) and calcium aluminosilicate hydrates (C<sub>3</sub>ASH<sub>4</sub> and C<sub>2</sub>ASH<sub>8</sub>) as the main hydration products in addition to free calcium hydroxide (CH). Scanning electron microscopic (SEM) examination of the pozzolanic cement pastes made of OPC-B.C. mixes possesses a much denser structure than that of the neat OPC paste. Furthermore, the addition of silica fume resulted in a further densification of the microstructure of the hardened OPC-B.C.-SF pastes; this is reflected on the observed improvement in the compressive strength values at all ages of hydration.

### Introduction

The object of producing pozzolanic cements has been of considerable scientific and technological interest because such addition increases the chemical resistance to sulphate attack, interpermeability, lowering heat of hydration and thermal expansion<sup>1</sup>. Recently, the use of pozzolanic cement is increasing world-wide because it needs less energy for production.

Early hydration reactions of Portland cement-silica fume blends were studied and revealed that silica fume accelerated both C<sub>3</sub>S and C<sub>3</sub>A hydration in the first few hours<sup>2</sup>. In addition the compressive strengths of silica fume cement paste and mortar were evaluated at various water-cementitious ratios; the results showed that the increase in compressive strength of mortar containing silica fume, as a partial replacement for cement, greatly contributes to strengthening the bond between the cement paste and aggregate<sup>3</sup>.

The reaction of pozzolana with the lime liberated during the hydration process of Portland cement modifies some properties of cement and resulting concrete. The change occurring in the phase composition and microstructure of pozzolanic cement pastes containing activated kaolinite clay was investigated<sup>4</sup>. The artificial pozzolana (burnt kaolinite clay) was thermally activated by firing at 850°C for two hours. The hydration and pozzolanic reactions of cement pastes made with different levels of metakaolin replacement were investigated using differential scanning calorimetry (DSC)<sup>5</sup>. It was found that the DSC technique could follow the hydration process quantitatively by measuring the peak temperature and enthalpy corresponding to decomposition of hydration products.

The kinetics and mechanism of hydration interaction between lime and silica fume were studied on the basis of the phase composition and the physical state of the formed hydration products<sup>6</sup>. The developed strength could be related to the lime content of the lime-silica

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mixture and the formed hydrates. Silica fume (SF) and dealuminated kaolin (DK) from Egyptian sources have been characterized chemically and mineralogically, and a comparative study of their reactivities toward lime were conducted using isothermal conduction calorimetry and an accelerated chemical method<sup>7</sup>.

The role of silica fume in the reaction kinetics and mechanisms of the early stage hydration of Portland-slag cement-silica fume pastes (W/S= 0.5 at 20°C) has been studied<sup>8</sup>. The reaction stages have been analysed and explained by kinetic terms. The delay in CH formed during hydration between 8 and 10 h from the beginning of hydration has been noticed and a mechanism has also been discussed. The results of this study have revealed evidence of the accelerator effect of silica fume during the first 8 h of hydration when it still exists as chemically inert filler.

The utilization of calcined clay as a pozzolanic material for mortar and concrete has received considerable attention in recent years<sup>9</sup>. This interest is a part of the widely spread attention directed towards the utilization of wastes and industrial by-products in order to minimize Portland cement consumption. Another reason is that mortar and concrete, which contain pozzolanic materials, exhibit considerable enhancement in durability properties. High-calcium fly ash (HCFA) and silica fume (SF) were used as mineral admixtures. The effect of these admixtures on the microstructure of cement paste was investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The reaction of HCFA and SF with portlandite, which occurs in Portland cement (PC), forms a new calcium-silicate-hydrate (C-S-H) gel<sup>10</sup>.

There are two main models of alkali-activated cements, one is the case of the activation of slag (Si+Ca) and the other is the activation of metakaolin (Si+Al). Li et al reviewed knowledge about the comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements, including the general properties of slag and metakaolin, hydration products reaction mechanisms, and the role of Ca and Al<sup>11</sup>.

Pozzolanic activity of clinoptilolite, the most common natural zeolite mineral, was studied by Uzal et al in comparison to silica fume, fly ash and a non-zeolitic natural pozzolan<sup>12</sup>. Chemical, mineralogical and physical characterizations of the materials were considered in comparative evaluations. Pozzolanic activity of the natural zeolite was evaluated with various test methods including electrical conductivity of lime-pozzolana suspensions, free lime content, compressive strength and pore size distribution of hardened lime-pozzolana pastes. The results showed that the clinoptilolite possessed a high lime-pozzolana reactivity that was comparable to silica fume and was higher than fly ash and a non-zeolitic natural pozzolana. The high reactivity of the clinoptilolite is attributable to its specific surface area and reactive SiO<sub>2</sub> content.

The object of this paper is to study the physicochemical and mechanical properties of the hardened pozzolanic

cement pastes made of OPC-burnt clay blends and the results were compared with those of the neat OPC paste.

## Materials and Experimental

### Materials

Ordinary Portland cement (OPC) was supplied from Egyptian Tourah Portland Cement Company with a Blaine surface area of 2945 cm<sup>2</sup>/g; its chemical oxide composition is given in Table 1. The clay used in this study was supplied from United Arabic Company (UAC), Libya; its chemical composition is also shown in Table 1.

The clay was first ground and passed completely through 90 µm B.S. sieve. Artificial pozzolana was prepared by burning of clay at 700°C for a soaking period of four hours and designated as burnt clay (B.C.). Condensed silica fume is a by-product of silicon or ferrosilicon alloys industries. It is obtained from Ferro-Silicon Company, Kom-Ombo, Egypt. Silica fume particles are spherical and have an average diameter of about 0.1 µm. It consists of ~ 99 % amorphous silica with a specific surface area of 20000 m<sup>2</sup>/kg. These characteristics account for the substantial pozzolanic activity of silica fume in terms of both its capacity of binding lime and rate of hydration reaction.

### Experimental

Different pozzolanic cement pastes were prepared from different OPC-burnt clay dry mixes made without and with silica fume. Table 2 shows the percentage composition of the different mixes and their designations. Each dry cement blend was mechanically mixed in a porcelain ball mill for 12 hours to ascertain complete homogeneity of the mix. Each paste was prepared by mixing the dry mix with the required amount of water, using the same water/solid (W/S) ratio of 0.30, for about three minutes continuously. After complete mixing, the resultant fresh paste was molded into cubic specimens by using one inch cube moulds. The moulds, containing the pastes, were cured at 100% relative humidity for 24 hours in order to attain the final setting, and then the cubic specimens were removed from the moulds and cured under water at room temperature for time intervals of 3, 7, 28 and 90 days.

At each time interval, compressive strength tests were performed on the hardened pozzolanic cement pastes using three cubic specimens at each hydration time and the average value was recorded as kg/cm<sup>2</sup>. This was performed using a Ton-industrial machine (West Germany) for maximum load of 60 tons. The resulting crushed specimens of the hardened cement pastes were ground and the hydration reaction was stopped using the method described in an earlier publication<sup>13</sup>. The samples were then dried at 90°C for three hours in CO<sub>2</sub>-free atmosphere and maintained in a desiccator containing soda lime and CaCl<sub>2</sub> until the time of testing was reached.

Kinetics of the hydration reaction was studied by the determination of chemically combined water and free lime contents at the different ages of hydration using the

Table 1: Chemical oxide composition of OPC and clay, wt %.

| Material | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | MgO  | SO <sub>3</sub> | Na <sub>2</sub> O | k <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | Loss of ignition |
|----------|------------------|--------------------------------|--------------------------------|-------|------|-----------------|-------------------|------------------|------------------|-------------------------------|------------------|
| OPC      | 20.89            | 4.68                           | 3.43                           | 63.33 | 2.18 | 2.95            | 0.44              | 0.25             | -                | -                             | 0.4              |
| Clay     | 49.23            | 17.18                          | 5.25                           | 7.56  | 3.40 | 1.17            | 0.58              | 2.30             | 0.82             | 0.21                          | 12.1             |

Table 2. The percentage composition of the different mixes and their designations.

| Mix        | Composition                     | Water/Solid (W/S) ratio |
|------------|---------------------------------|-------------------------|
| Blank      | 100% OPC                        | 0.30                    |
| Mix I      | 90% OPC+10% B.C."700°C"         | 0.30                    |
| Mix II     | 80% OPC+20% B.C."700°C"         | 0.30                    |
| Mix III    | 70% OPC+30% B.C."700°C"         | 0.30                    |
| Mix III-S1 | 70% OPC+30% B.C.(700°C)+2.5% SF | 0.30                    |
| Mix III-S2 | 70% OPC+30% B.C.(700°C)+5% SF   | 0.30                    |

ground dried samples. The chemically combined water content, W<sub>n</sub> (%), was determined as follows; exactly about a weight of one gram of the dried cement sample was charged to a silica crucible and ignited in a muffle furnace for one hour at 1000°C (20°C/min). The crucible containing the sample was cooled in a desiccator then weighed at room temperature. Duplicate measurements were carried out for each sample and the mean value was recorded.

$$W_n (\%) = [(W_o - W_i) / W_i] \times 100$$

Where W<sub>o</sub>= dried sample weight and W<sub>i</sub>= ignited sample weight.

The free lime content, CaO (%), was determined by using the glycerol/ethanol extraction method and the mean value of the two independent determinations was recorded<sup>14</sup>.

The phase composition and microstructure of the formed hydrates were investigated by means of X-ray diffraction (XRD) and differential scanning calorimetry (DSC). XRD was studied using cobalt target (λ = 0.17889 nm) and nickel filter under working conditions of 40 kV and 40 mA. The morphology and microstructure of hydrated phases were identified using JSM-5410 scanning electron microscope (SEM).

## Results and Discussion

### Compressive strength

The results of compressive strength of the hardened pozzolanic cement pastes made of Portland cement-burnt clay (OPC-B.C) blends without and with silica fume are graphically represented as a function of hydration age in Fig. 1.

Evidently, the compressive strength increases with increasing age of hydration as a result of formation and

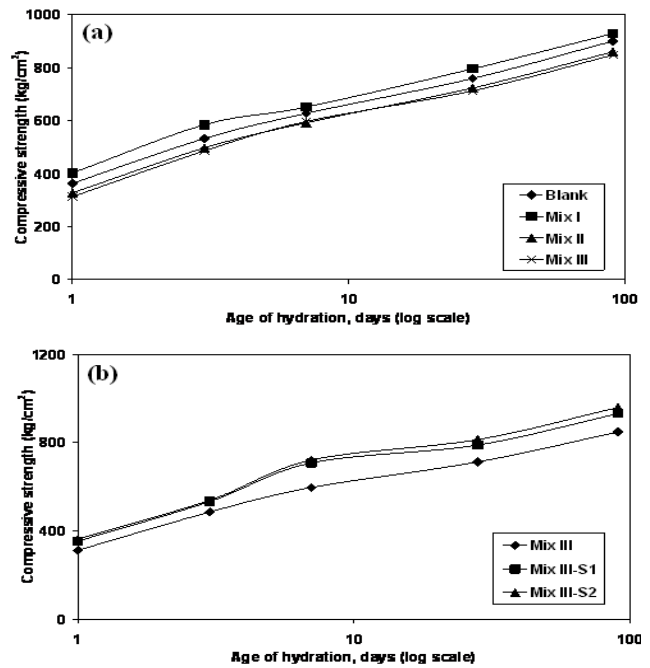


Fig. 1: Compressive strength versus age of hydration for the pastes made of: (a) Blank (100% OPC), Mix I, Mix II and Mix III and (b) Mix III, Mix III-S1 and Mix III-S2.

later accumulation of hydration products which act as binding centers between the remaining unhydrated parts of cement grains, (Fig. 1-a). The hydration products of both OPC and OPC-B.C blends, mainly as calcium silicate hydrates, represent the main binding centers between the remaining unhydrated parts of OPC and B.C (artificial pozzolana) grains. On the other hand the pastes made of Mix I (90% OPC+10% B.C) possess the highest strength values at all hydration ages as compared to other pastes containing 0, 20 and 30% burnt clay.

The highest strength values of the hardened pastes made of Mix I can be attributed to the pozzolanic reaction between the free calcium hydroxide, liberated from Portland cement hydration, with burnt clay (B.C) to form excessive amounts of hydration products, mainly as CSH gel as well as crystalline hydrates, that serve as micro-fills which leads to a reduction in the total porosity as well as an increase in the total contents of binding centers in the specimens; consequently an increase in compressive strength values was obtained<sup>15</sup>. This was clear at the early ages of hydration. This increase in strength of the paste made of 90% OPC-10% B.C blend (Mix I) may be attributed to the following mechanism. When water is added to the OPC-burnt clay mixture, then lime concentration is high, the silica and alumina go into solution quickly and react to form secondary hydration products, mainly as calcium silicate hydrate (CSH) together with formation of hexagonal calcium aluminate hydrate, mainly as  $C_4AH_{13}$  which are precipitated as soon as saturation is approached. It is also clear from the results of Fig. 1-a that the blended pozzolanic cement pastes containing 20 and 30% burnt clay (corresponding to Mixes II and III, respectively) possess lower strength values. In conclusion, the burnt clay (as an artificial pozzolana) can be used up to 10% as a replacement to ordinary Portland cement in the pozzolanic OPC-B.C blends without any reduction in strength which agrees with the results of Singh and Grag<sup>16</sup>. The decrease in strength of the hardened pastes made of mixes having higher percentages of burnt clay, namely 20 and 30%, may be attributed to the presence of large amount of lime (CaO) which appears from calcination of clay at 700°C. Lime first hydrates to give calcium hydroxide of weakly hydraulic property and it consumes water that is no longer available for correct OPC hydration<sup>17</sup>. However, the slight reduction in the strength values of the pozzolanic cement blend of Mix III (containing 30% B.C) leads to the conclusion that Mix III, for economic reasons, can be considered as the reasonable composition which produces acceptable compressive strength results and was used for further investigations using silica fume in the pozzolanic cement blends.

The results of compressive strength of the hardened pozzolanic cement pastes made of OPC-B.C. blend of Mix III with different ratios of silica fume (SF), namely; 2.5 % (Mix III-S1) and 5% (Mix III-S2), are graphically represented as a function of hydration age in Fig. 1-b. Obviously, in this case burnt clay and silica fume act as active pozzolana in the OPC-B.C.-SF cement blends. The addition of SF to Mix III (70% OPC-30% B.C.) leads to a marked increase in the compressive strength values of the hardened OPC-B.C. pozzolanic cement pastes containing 2.5 and 5% SF (Mixes III-S1 and III-S2); this is mainly due to the large consumption of portlandite, as a result of pozzolanic interaction with burnt clay and the significant amounts of active  $SiO_2$  in SF leading to the production of larger amounts of amorphous CSH gel. Therefore, the physical action of pozzolanas (B.C. and SF) provides more denser, homo-

genous and uniform pastes having stronger hydraulic and strength-producing characters. Again, an additional pozzolanic reaction occurs between the active silica fume particles and portlandite (CH) produced from OPC hydration leading to an increase in the compressive strength values of the hardened OPC-B.C.-SF (Mixes III-S1 and III-S2) as compared to those of the OPC-B.C. paste (Mix III). These findings are in agreement with the results of Mitchell et al<sup>18</sup>. The values of compressive strength of the hardened paste made of Mix III-S2 (containing 5% SF) are slightly higher than those of Mix III-S1. In conclusion, SF seemed to be an efficient pozzolanic material, it activates the constituents of cement towards hydration and the air content has been reduced due to its microfilling effect which leads to an increase in the compressive strength of the hardened cement pastes containing SF<sup>19</sup>.

### Hydration kinetics

Kinetics of hydration was studied by the determination of free lime and chemically combined water contents at the different ages of hydration. Fig. 2 represents the variation of free lime content (CaO, %) versus age of hydration for the various cement pastes made of all dry mixtures; these are: OPC (blank), Mix I (90% OPC-10% B.C.), Mix II (80% OPC-20% B.C.), Mix III (70% OPC-30% B.C.), Mix III-S1 (Mix III+2.5% SF) and Mix III-S2 (Mix III+5% SF).

In Fig. 2-a the free lime (CaO, %) content increases continuously with increasing age of hydration for the neat OPC pastes indicating the continuous liberation of free portlandite (CH) from the hydration of OPC. On the other hand the observed free lime contents for all OPC-B.C. pozzolanic cement pastes is the result of a combined effect of cement hydration (which generates CH) and the pozzolanic reaction (which consumes CH). The results of Fig. 2-a indicate that the free lime contents obtained for all admixed OPC-B.C. pastes are lower than those of the neat OPC paste. As hydration proceeds with age of hydration, the free lime content decreases for all of the pozzolanic cement pastes made of Mixes I, II, III as a result of the pozzolanic interaction between B.C. and free lime. In addition, as the percentage of burnt clay replacement increases the free lime content decreases as a result of the consumption by the pozzolanic reaction. Obviously, the pozzolanic cement paste having the highest B.C. content (Mix III) has the lowest free lime contents at all ages of hydration; this is due to the marked consumption of free lime by burnt clay as a result of the pozzolanic reaction. These results are in agreement with the results reported in earlier publications<sup>15</sup> as well as the results of compressive strength obtained in this study.

Fig. 2-b represents the free lime content (CaO, %) obtained for the hardened pastes made of Mixes III, III-S1 and III-S2 containing 0, 2.5 and 5% silica fume, respectively, at all ages of hydration. Evidently, the pastes containing silica fume (Mixes III-S1 and III-S2) possess lower values of free lime contents as compared to those of the pozzolanic OPC -B.C. paste made without SF (Mix III); this phenomenon is attributed to

the additional pozzolanic reaction of SF with the free CH liberated from OPC hydration. Furthermore, the admixed pastes containing 5% silica fume (Mix III-S2) possess the lowest values of free lime contents indicating that the higher SF addition the higher the pozzolanic action and the lower the values of free lime contents.

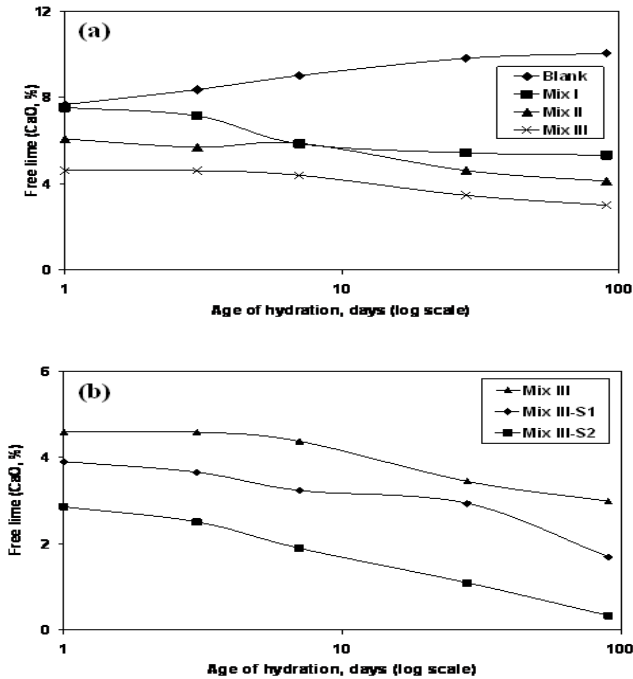


Fig. 2: Free lime content versus age of hydration for the pastes made of: (a) Blank (100% OPC), Mix I, Mix II and Mix III and (b) Mix III, Mix III-S1 and Mix III-S2.

The results of chemically combined water content ( $W_n$ , %) versus ages of hydration for all of investigated pastes are graphically represented in Fig. 3.

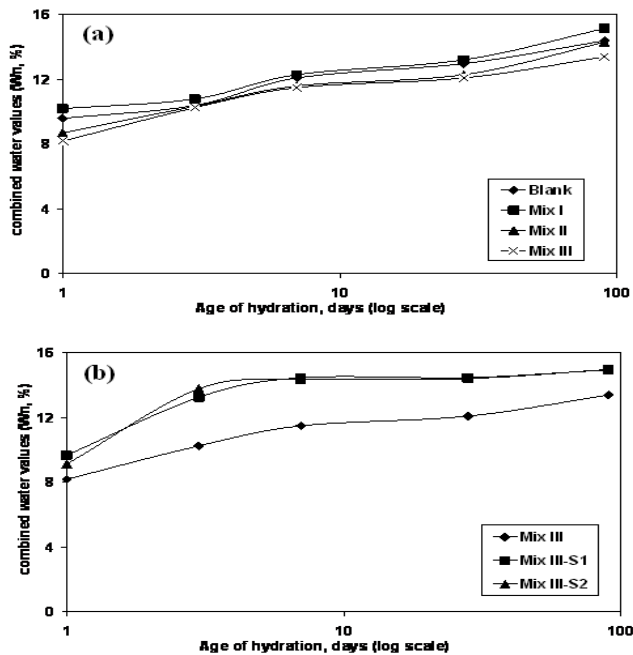


Fig. 3: Chemically combined water content versus age of hydration for the pastes made of: (a) Blank (100% OPC), Mix I, Mix II and Mix III and (b) Mix III, Mix III-S1 and Mix III-S2.

It is clear from the results of Fig. 3 that the combined water content increases with increasing age of hydration for all of the hardened pozzolanic cement pastes. The results of chemically combined water content ( $W_n$ , %) indicate that a fast hydration reaction takes place from the time of mixing up to one day of hydration. After that the initially formed hydration products shield the cement grains leading to a slower rate of hydration reaction; this is followed by a gradual increase in the rate of hydration up to the final stages of hydration (90 days). Obviously, it is clear from the results of Fig. 3-a that the chemically combined water contents of the hardened pozzolanic cement paste of Mix I (90% OPC-10% B.C.) are slightly higher than those of the neat OPC paste especially at the earlier ages of hydration. This increase is attributed to the additional amounts of CSH produced from the pozzolanic reaction of B.C. with the free lime released from OPC hydration. However, the pastes made of Mixes II and III, containing 20 and 30% B.C., possess relatively lower water contents and the  $W_n$ -values decrease with decreasing the proportion of the Portland cement in the OPC-B.C. mixes. This indicates that for these mixes (Mixes II and III), containing larger fractions of B.C., the main hydration products formed, especially, during early ages of hydration are those of OPC and not of the artificial pozzolana (burnt clay). The results of chemically combined water content of the pozzolanic cement pastes containing silica fume (Mixes III-S1 and III-S2) are graphically represented in Fig. 3-b. The data of the graph show that the combined water content ( $W_n$ , %) increases with increasing age of hydration which is attributed to the increase of the amount of the main hydration product, mainly as CSH, as hydration proceeds. The pastes made of Mixes III-S1 and III-S2 (containing 2.5 and 5% SF) possess higher combined water contents as compared to those of Mix III (without silica fume) indicating the higher pozzolanic reaction of silica fume leading to excessive amounts of CSH with higher water content. Obviously, the variations of  $W_n$ -values with age of hydration show the same trends observed for the changes in values of compressive strength.

### Phase composition and microstructure.

#### Differential scanning calorimetry (DSC).

The DSC thermograms of specimens made of Mixes blank, I and III corresponding to 0, 10 and 30% replacement of B.C., respectively, at 1, 7 and 90 days of hydration are shown in Figs. (4-6).

All thermograms indicate six endothermic peaks at 90-120, 170-200, 380-410, 490-510, 700-740 and 750-810°C. Only one exothermic peak could also be distinguished at 870-940°C. This exothermic peak is very obvious for the admixed OPC paste made of Mix III (70% OPC+30% B.C.). The identification of these peaks is the same as those mentioned in the earlier publications<sup>20-22</sup>. The first endothermic peak located at about 90-120°C characterizes the decomposition of the



nearly amorphous calcium silicate hydrates, mainly as CSH-I and CSH-II, as well as calcium sulphoaluminate hydrates (ettringite and monosulphate hydrates). The second endothermic peak observed at about 170-200°C represents the decomposition of calcium aluminate hydrate, mainly as  $C_4AH_{13}$ , and/or the decomposition of microcrystalline CSH. The third endothermic peak located at about 380-410°C represents the decomposition of hydrogarnet, mainly as  $C_3ASH_4$  and  $C_2ASH_8$ . The fourth endothermic peak observed at about 490-510°C is characteristic to the decomposition of CH. The last two endothermic peaks appeared at 750°C and 810°C represent the decomposition of amorphous  $CaCO_3$  and its crystalline form, respectively. From thermograms of Fig. 4, obtained for the hardened OPC paste (blank), the areas and intensities of the peaks characteristic for CSH,  $C_4AH_{13}$  and CH which represent the main hydration products increase with increasing age of hydration. The endothermic peak characteristic for calcium silicate hydrates (CSH) becomes more distinguishable at the longer age of hydration (90 days). In addition, the two endotherms characteristic for  $CaCO_3$  are reduced to one endotherm located at 780°C after 90 days of hydration. The effect of replacement of OPC by 10 and 30% burnt clay (B.C.) can be observed from thermograms shown in Figs. 5 and 6 for the pastes made of OPC-B.C. Mixes I and III, respectively.

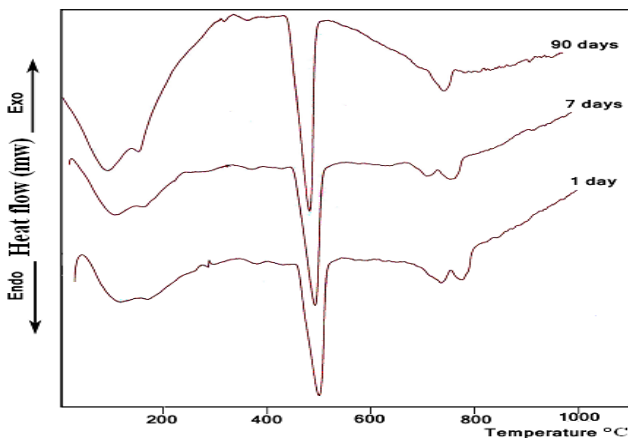


Fig. 4: DSC-Thermograms of hardened neat OPC paste (Blank, 100% OPC) after 1, 7 and 90 days of hydration.

The main features of these thermograms are the decrease in the peak area of CH as compared to that of the thermogram of the neat OPC paste (blank). In fact this decrease is due to the consumption of CH in the pozzolanic reaction between CH, produced from OPC hydration, and burnt clay (B.C.). This decrease in the intensity of the endotherm characterizing CH becomes more obvious in the hardened paste of Mix III (70% OPC+30% B.C.). These results are in agreement with the data obtained for the free lime content shown in Fig. 2. We conclude that the addition of blending materials such as pozzolana can effectively reduce the CH content of the hardened OPC paste.

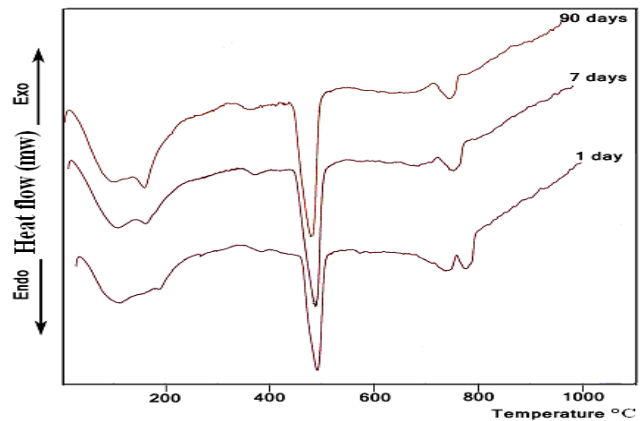


Fig. 5: DSC- Thermograms of hardened paste made of Mix I after 1, 7 and 90 days of hydration.

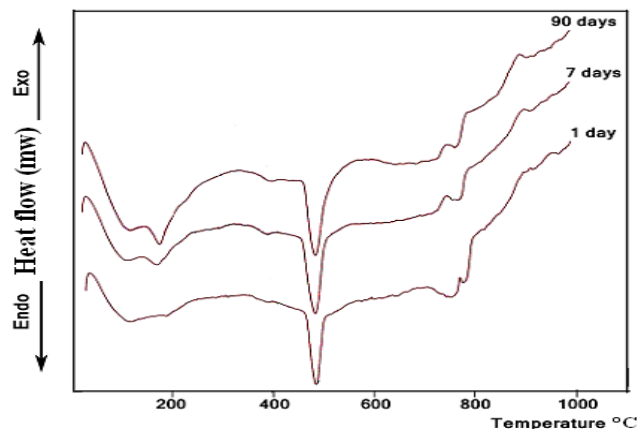


Fig. 6: DSC-Thermograms of the hardened paste made of Mix III after 1, 7 and 90 days of hydration.

On the other hand the peak area of CSH in thermograms of Mixes I and III (10 and 30% B.C., respectively) increases as the amount of burnt clay increases up to 30%. Evidently, addition of burnt clay, as an artificial pozzolana, results in an acceleration of the rate of hydrolysis of clinker silicates in addition to the aluminates present in burnt clay<sup>4</sup>. The peak areas of calcium carbonate phase decreases as the artificial pozzolana (burnt clay) content increases up to 30%. Therefore, pozzolana addition increases the resistance of the hardened cement pastes towards carbon dioxide attack. Only one exothermic peak located at about 900°C is obtained for the hardened paste of Mix III (70% OPC+30% B.C.) which is attributed to the crystallization of the pseudo-wollastonite phase (mono calcium silicate, CS) (Fig. 6); this exothermic peak is characteristic for the decomposition of the hydrated calcium silicate hydrate. Obviously, the endothermic peaks characteristic for the crystalline calcium silicate hydrates (CSH) and  $C_4AH_{13}$  phase become more distinguishable for the paste of Mix III, containing 30% B.C., especially at the longer ages of hydration; this is also reflected on the clear appearance of the exothermic peak characteristic for the pseudo-wollastonite (CS) phase.

The results of DSC thermograms obtained for the hardened pozzolanic cement pastes made of Mixes III-S1 and III-S2, having the constitutions of Mix III + 2.5% SF and Mix III + 5% SF, after 1, 7 and 90 days of hydration are shown in Figs. 7 and 8, respectively. These thermograms are characterized by the presence six endotherms at 90-120, 170-200, 380-410, 490-510, 700-740 and 750-810°C in addition to one exothermic peak located at 870-940°C. The main features of the thermograms shown in Figs. 7 and 8 are the decrease in the peak area of CH for the pozzolanic cement pastes containing SF (Mixes III-S1 and III-S2) as compared to the thermograms obtained for the pozzolanic cement paste of Mix III made without SF (Fig. 6). It is clear from this decrease in the peak area of CH that SF acts as a new active pozzolanic blend in addition to B.C. which consume excessive amounts of the free CH required for the pozzolanic reaction.

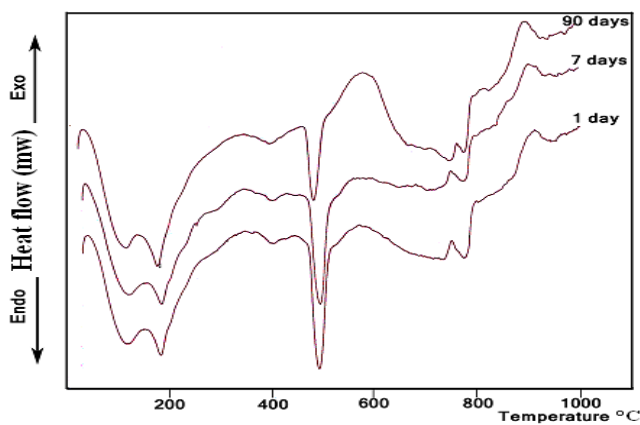


Fig. 7: DSC-Thermograms of the hardened paste made of Mix III-S1 after 1, 7 and 90 days of hydration.

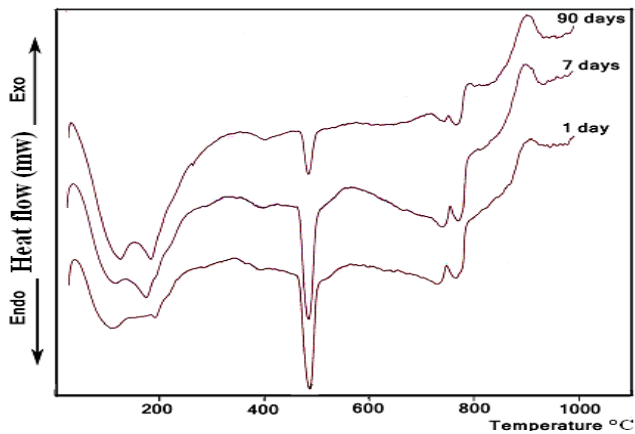


Fig. 8: DSC-Thermograms of the hardened paste made of Mix III-S2 after 1, 7 and 90 days of hydration.

This larger consumption of CH is also confirmed from the results of lime content which is strongly reduced at the later ages of hydration (Fig. 2-b). Also the exothermic peak located at 870-900°C which is attributed to the crystallization of the pseudo-wollastonite phase (mono calcium silicate, CS), becomes more distinguishable. This exothermic peak is characteristic for the decomposition of the hydrated calcium silicate hydrates. Obviously, the endothermic peaks characteristic for the crystalline calcium silicate

hydrates (CSH) become more obvious for the paste made of Mix III-S2 (Mix III + 5% SF). In conclusion, it is clear that SF plays an additional effective role in the pozzolanic reaction beside B.C. with CH produced from OPC hydration. This could be clearly distinguished from the increase in the peak areas of the endotherms characteristic for the crystalline calcium silicate hydrates (CSH); this confirms the formation of additional amounts of CSH as a result of the pozzolanic reaction of SF and B.C. with the free CH liberated from OPC hydration.

#### X-ray diffraction (XRD) analysis

The X-ray diffractograms obtained for the hardened pozzolanic cement pastes made of Mix III (70% OPC + 30% B.C.) and III-S2 (Mix III + 5% SF) are shown in Figs. 9 and 10, respectively.

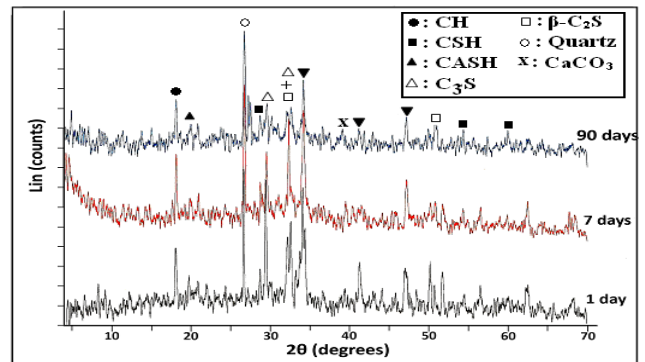


Fig. 9: XRD patterns of the hardened paste made of Mix III after 1, 7 and 90 days of hydration.

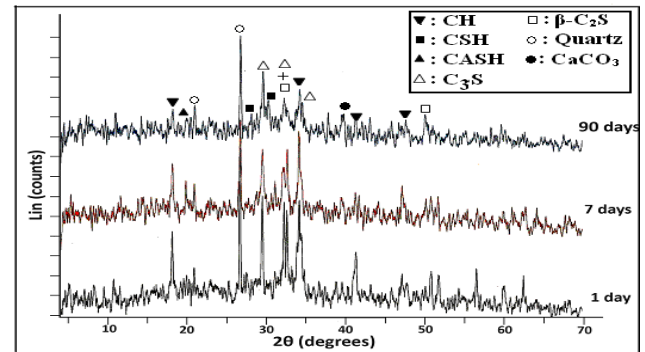


Fig. 10: XRD patterns of the hardened paste made of Mix III-S2 after 1, 7 and 90 days of hydration.

The results of Fig. 9 indicate that the main hydration products of the hardened paste made of Mix III, are the nearly amorphous and microcrystalline calcium silicate hydrates (CSH), calcium hydroxide (CH) and calcium aluminosilicate hydrates (CASH); the peaks characteristic for the unhydrated parts of C<sub>3</sub>S and β-C<sub>2</sub>S grains could also be distinguished as well as quartz (Q) and calcium carbonate.

Obviously, the results of Fig. 9 show that the intensities of the peaks characterizing C<sub>3</sub>S and β-C<sub>2</sub>S (the anhydrous constituents of Portland cement clinker) decrease with increasing age of hydration; meanwhile, the intensities of the peaks characterizing the hydration products, namely calcium silicate hydrates (CSH) and calcium aluminosilicate hydrates (CASH) increase with increasing age of hydration. However, the intensities of

the peaks characteristic for the free calcium hydroxide decrease with increasing age of hydration; this is due to its consumption by the pozzolanic reaction of burnt clay with the formation of additional amounts of CSH and CASH products.

The results of Fig. 10 indicate the formation of CSH, CASH and CH phases as the main hydration products of the hardened paste made of Mix III-S2; the peaks characterizing the anhydrous cement constituents ( $C_3S$  and  $\beta-C_2S$ ), quartz (Q) and calcium carbonate appeared also in the XRD-diffractograms.

The features of X-ray diffractograms shown in Fig. 10 are almost similar to those of Fig. 9 with two main basic differences, namely: (i) the marked decrease in the intensities of the peaks characterizing the portlandite (CH) phase with increasing age of hydration and (ii) the noticeable increase in the intensities of the peaks characteristic for calcium silicate hydrates (CSH). These two findings are mainly due to the enhanced rate of pozzolanic interaction between the free lime released from Portland cement and the active silica fume leading to a marked consumption in the free lime content with increasing age of hydration.

#### Morphology and microstructure

The microstructure of the neat OPC paste after 1, 7 and 90 days of hydration is shown in Fig. 11.

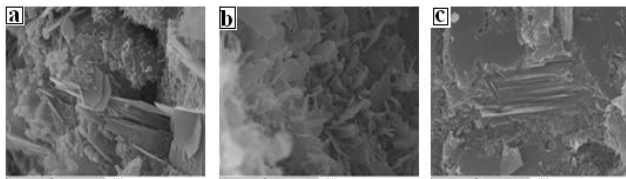


Fig. 11: SEM micrographs of the hardened paste made of Blank (100% OPC) after a) 1, b) 7 and c) 90 days of hydration..

The initial hydration products obtained after 1 day of hydration were the more acicular ettringite crystals, the hexagonal crystals of monosulphate hydrate and the microcrystalline fibers of calcium silicate hydrates (CSH) which changes on drying to give honeycombs or reticular networks around the remaining unhydrated parts of cement grains (Fig. 11-a); massive crystals of calcium hydroxide (CH) appeared also in the structure. After 7 days of hydration, the SEM micrograph indicated the formation of crumpled fibrous particles of tobermorite-like CSH phases as the dominant hydration products among the other hydrated phases deposited in the originally water-filled space (Fig. 11-b). At the later age of hydration (90 days), the microstructure displayed a more dense structure of CSH with a massive tabular structure showing parallel cleavage of CH (Fig. 11-c). Obviously, the larger amounts of CH form massive crystals in the pore system of the hardened OPC paste and the growing of crystals engulf some of the smaller cement grains.

The microstructure of the hardened pozzolanic cement paste made of Mix III, 70% OPC-30% B.C., displayed nearly amorphous hydration products with a more open porosity after 1 day of hydration (Fig. 12-a) which chan-

ges on prolonged hydration to denser structures after 7 and 90 days of hydration which mainly composed of microcrystalline hydration products (Fig. 12-b and -c). Evidently, the SEM micrographs obtained for the hardened paste of Mix III indicated the less crystalline character of the residual amounts of CH which appeared as small hexagonal crystals (Fig. 12).

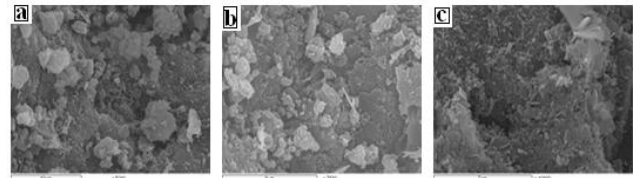


Fig. 12: SEM micrographs of the hardened paste made of Mix III after a) 1, b) 7 and c) 90 days of hydration.

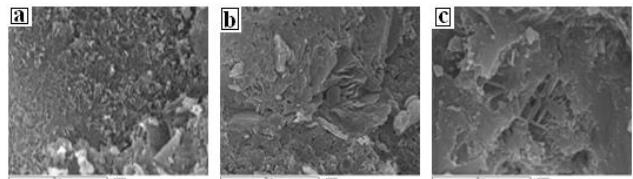


Fig. 13: SEM micrographs of the hardened paste made of Mix III-S2 after a) 1, b) 7 and c) 90 days of hydration.

The microstructure of the hardened pozzolanic cement paste made of Mix III-S2, 70% OPC+30% B.C.+5% SF, displayed crumpled particles of tobermorite-like CSH as the main hydration product formed during the initial stage of hydration after 1 day (Fig. 13-a); this kind of CSH product is mainly formed as a result of interaction of the active silica fume with the free CH liberated from OPC hydration. The SEM micrograph obtained after 7 days of hydration for the hardened OPC-B.C.-SF paste made of Mix III-S2 displayed a mixture of massive plates and amorphous films of hydration products and unhydrated grains of the pozzolanic cement constituents (Fig. 13-b). After 90 days of hydration, the hardened OPC-B.C.-SF paste had a dense microstructure in which plates had a straight and oriented appearance; the amorphous hydrates could also be distinguished (Fig. 13-c).

#### Conclusions

On the basis of the results obtained in this investigation, the following conclusions could be derived:

- Mix III, (70% OPC-30% B.C.), for economic reasons, can be considered as the reasonable composition which produces acceptable compressive strength results.
- The physical action of pozzolanas (B.C. and SF) provides more denser, homogenous and uniform pastes having stronger hydraulic and strength-producing characters.
- SF seemed to be an efficient pozzolanic material, it activates the constituents of cement towards hydration and the air content has been reduced due to its microfilling effect which leads to an increase in the compressive strength of the hardened cement pastes containing SF.
- The admixed pastes containing 5% SF (Mix III-S2) po-



assess the lowest values of free lime contents indicating that the higher SF addition the higher the pozzolanic action and the lower the values of free lime contents.

-The variations of Wn-values with age of hydration show the same trends observed for the changes in values of compressive strength.

-DSC thermograms and XRD analysis for the pastes indicate the formation of: nearly amorphous calcium silicate hydrates (mainly as CSH-I and CSH-II), calcium sulphoaluminate hydrates (ettringite and monosulphate hydrates), calcium aluminate hydrates (mainly as  $C_4AH_{13}$ ), hydrogarnet (mainly as  $C_3ASH_4$  and  $C_2ASH_8$ ), CH and  $CaCO_3$ .

-After 90 days of hydration, the hardened OPC-B.C.-SF paste possesses a more denser microstructure as compared to other investigated pastes.

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