



# Effect of temperature on the physico-mechanical and mineralogical properties of Homra pozzolanic cement pastes

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## Abstract

The effect of temperature on the phase composition and physico-mechanical properties of cement pastes is vital for fire resistance. Addition of fine, divided materials, such as dehydrated aluminum silicate (fired clay), natural hydrated aluminum silicate (clay), chromite, sintered magnesite, slag, silica, fly ash, diatomaceous earth, and Homra (crushed clay bricks), to Portland cement is known to increase heat resistance by combining with lime. Homra is a pozzolanic material that can react with lime liberated from the hydration of ordinary Portland cement (OPC). This reaction improves the microstructure of cement pastes. In this study, OPC was partially substituted by Homra in the ratios of 10, 20, and 30 wt.%. The cement pastes were fired for 3 h without any load at increasing temperatures from 100°C to 600°C by increment of 100°C. The results show that the replacement of OPC by 20 wt.% Homra improves the compressive strength by about 25.0%, but replacement by 10 and 30 wt.%, the strength increases by 4.0% and 8.5% at 600°C. This result is also due to the pozzolanic reaction of Homra with liberated lime to produce additional amounts of calcium silicate hydrates. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Heat treatment; Homra pozzolanic cement; Compressive strength; Phase composition; Microstructure

## 1. Introduction

When the building materials are exposed to fire, some deterioration takes place. This deterioration can often reach a level at which the structure may have to be thoroughly renovated or completely replaced.

The decay of the encapsulated radioactive nuclides may cause elevation of the temperature in the waste forms. Cement has been used for the immobilization of low and intermediate level radioactive wastes. Compared to other materials, which are used to immobilization of radioactive wastes, cement is not a very expensive raw material. Heat resistance materials are usually used for structural purposes. The need for such building materials is particularly important in the chemical and metallurgical industries, and for the thermal shielding of nuclear power plants.

The unstable component of concrete is the Portland cement pastes. Hydrated Portland cement pastes contain a large amount of  $\text{Ca}(\text{OH})_2$ , which dehydrated to CaO between 500°C and 600°C. On cooling and exposure to

moist air or wetting, the CaO is rehydrated to  $\text{Ca}(\text{OH})_2$  with a volume expansion of 97% and with the formation of cracks [1]. The pozzolanic materials can react with liberated lime from ordinary Portland cement (OPC) forming additional amounts of calcium silicate hydrates. The replacement of OPC by 10-wt.% silica fume improves the physico-mechanical properties as well as the microstructure of concrete when exposed to elevated temperatures [2,3]. The Portland cement containing 20–30 wt.% fly ash thus possesses good fire resistance and dimensional stability when exposed to high temperature and then high humidity or wetting [4]. The replacement of OPC by 20 wt.% of thermally activated kaolinite in cement paste increases its thermal stability against temperature up to 600°C [5].

Homra (crushed clay bricks) is a solid waste material, which is constituted mainly of silica quartz, aluminosilicate, anhydrite, and hematite. Therefore, it acts as a pozzolanic material [6]. The effect of Homra on the main hydration characteristics of Portland cement at early ages by means of electrical conductivity measurements as well as the physico-chemical and mechanical characteristics up to 90 days was studied [7,8].

This work is aimed at investigating the effects of elevated temperatures on the physico-mechanical and mineralogical

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Table 1  
Chemical composition of starting materials (wt.%)

Component	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>	L. O. I.
OPC	20.50	5.05	2.89	62.00	2.07	2.40	3.10
Homra	74.80	14.03	5.04	1.25	1.30	0.80	–

properties as well as the microstructure of thermally treated cement pastes containing Homra.

## 2. Experimental work

The pozzolanic cement used in this investigation was prepared from OPC that has been partially replaced by Homra at ratios of 10, 20, and 30 wt.%. The surface area of both Homra and OPC is  $\approx 3000 \text{ cm}^2/\text{g}$ , and the chemical composition is shown in Table 1.

The cement pastes were prepared using the amount of water required to obtain normal consistency [9]. The values of the water of Portland cement and pozzolanic cement pastes containing 10%, 20%, and 30% Homra are 23.0%, 24.0%, 25.0%, and 25.5%, respectively. The cement pastes were mixed and molded into 1-in. cubes. The moulds were vibrated for 1 min to remove any air bubbles and voids. Immediately after molding, the specimens were cured in a humidity chamber at  $23 \pm 1^\circ\text{C}$  for 24 h, then demolded and cured under water until the desired curing time. After 28 days of curing under water, the hardened cement pastes were dried at  $105^\circ\text{C}$  for 24 h. The pastes were kept for 3 h at each investigated temperature in the range of 200–600°C at intervals of 100°C, then cooled to room temperature. The compressive strength, ignition loss, total porosity, and apparent density were determined. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used for identification of the changes occurring in the microstructure of the formed or decomposed phases.

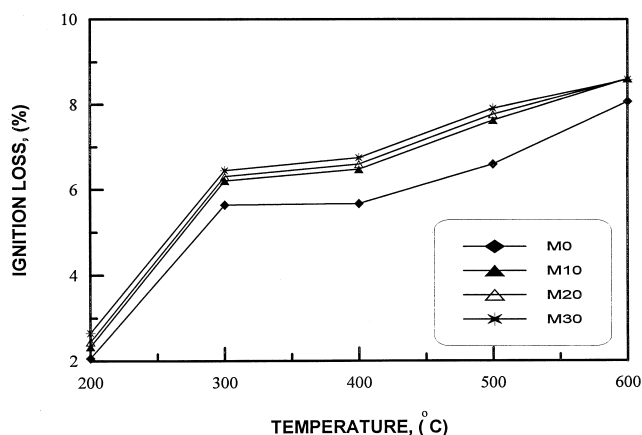


Fig. 1. Ignition loss of cement pastes as a function of temperature.

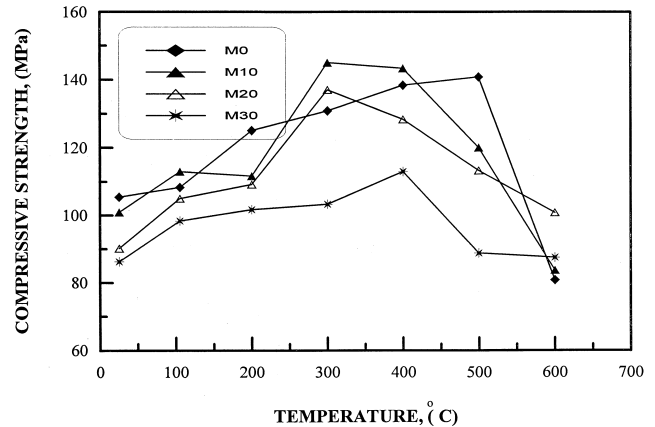


Fig. 2. Variations of compressive strength of cement pastes with temperature.

## 3. Results and discussion

### 3.1. Ignition loss

The relation between the ignition loss of cement pastes and temperature of thermal treatment was shown in Fig. 1. The ignition loss increases with the treatment temperature. This is due to the chemical processes stimulated by temperature in the different phases of cement pastes. The moisture was removed at  $105^\circ\text{C}$ , a partial decomposition of calcium silicate and sulfoaluminate hydrates occurred around  $200^\circ\text{C}$ . The decomposition of gehlenite hydrate ( $\text{C}_2\text{ASH}_8$ ) above  $200^\circ\text{C}$  and the dehydration of calcium hydroxide at temperatures above  $450^\circ\text{C}$  also occurred. Addition of Homra increases the ignition loss. This is due to the relatively high water consistency of the pastes containing Homra.

The ignition loss takes place in three steps. The first is up to  $300^\circ\text{C}$ , which is due to the decomposition of calcium sulfoaluminate hydrates (C-S-H) and calcium aluminosilicate hydrates. The second step at  $400^\circ\text{C}$  shows a slight increase due to the decomposition of

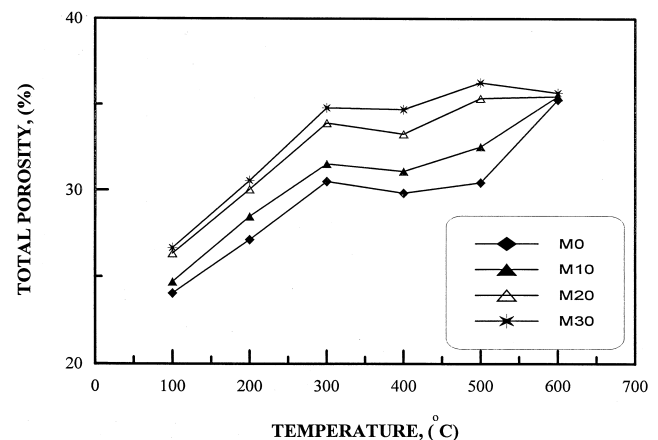


Fig. 3. Total porosity of cement pastes as a function of temperature.

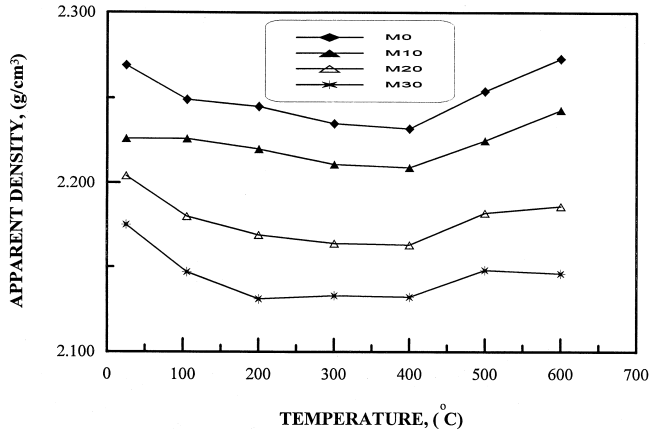


Fig. 4. Changes of apparent density of cement pastes with temperature.

some gehlenite hydrate. The third step is the decomposition of  $\text{Ca}(\text{OH})_2$  in the temperature range from 400°C to 600°C.

### 3.2. Compressive strength

Fig. 2 illustrates the variations of the compressive strength of the different thermally treated pozzolanic cement pastes. The compressive strength of OPC increases up to 500°C. The increase of temperature from 500°C to 600°C results in a decrease in the compressive strength by 47.0%. The temperature range between 100°C and 300°C leads to additional hydration products from the anhydrate cement grains. The compressive strength increases with the addition of Homra up to 400°C then decreases. The higher compressive strength of pozzolanic cement pastes containing 10 and 20 wt.% Homra than OPC cement pastes at 300°C is due to the pozzolanic reaction of Homra with the liberated lime to produce additional amounts of calcium silicate and aluminosilicate hydrates. These hydrates deposit within the pore system as shown later from SEM micrographs (Figs. 8 and

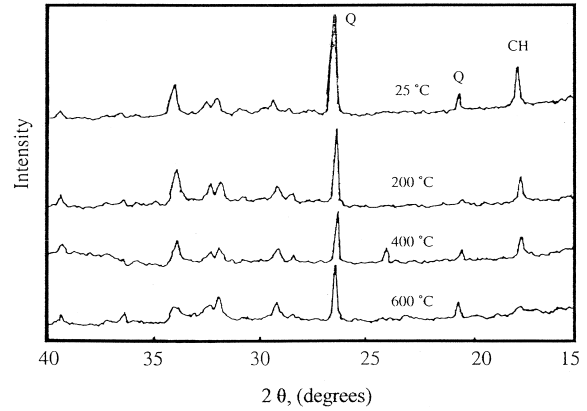


Fig. 6. XRD patterns of thermally treated pozzolanic cement pastes containing 20% Homra at different temperatures.

9). The decrease of the compressive strength of mix M-30 (30-wt.% Homra) is due to the decrease of the clinker content. The cement paste containing 10 wt.% Homra shows a decrease in compressive strength at 200°C; this may be due to the decomposition of C-S-H and tobermorite gel, which are decomposed between 110°C and 150°C [10]. The cement pastes made with pozzolanic materials as a partial replacement of Portland cement are more sensitive when exposed to fire. The lower strength of cement pastes made with pozzolanic materials was found especially at a temperature of 500°C when they were compared with the conventional Portland cement paste. Homra content of 20 wt.% improves the compressive strength by 25% more than that of OPC paste at 600°C; but in the case of partially substituted OPC by 10 and 30 wt.% Homra, the compressive strength rises only by 4% and 8.5%, respectively, at the same temperature. As the temperature increases from 25°C to 600°C, the compressive strength of neat OPC and OPC with 10 wt.% Homra decreases by 23.4% and 17.0%; whereas, the compressive strength increases by 11.80% and 1.43% from the pastes containing 20 and 30 wt.%

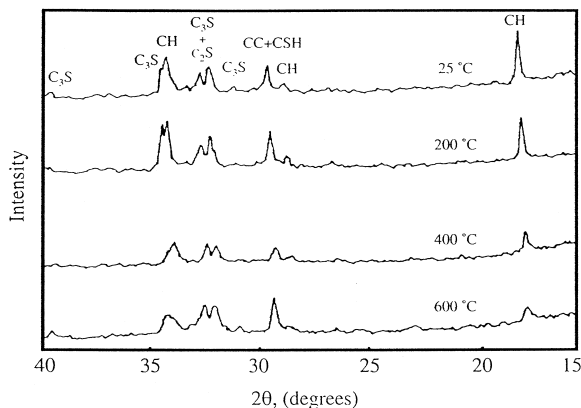


Fig. 5. XRD patterns of thermally treated OPC paste at different temperatures.

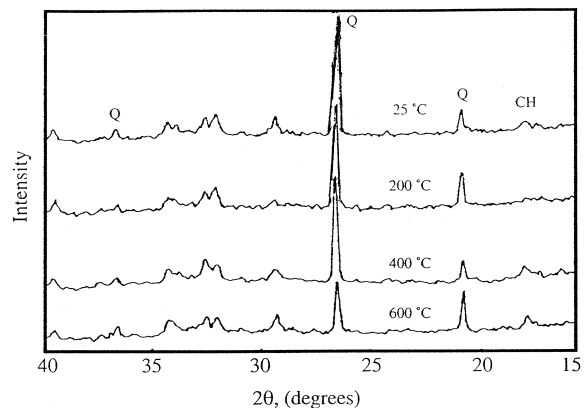


Fig. 7. XRD patterns of thermally treated pozzolanic cement pastes containing 30% Homra at different temperatures.

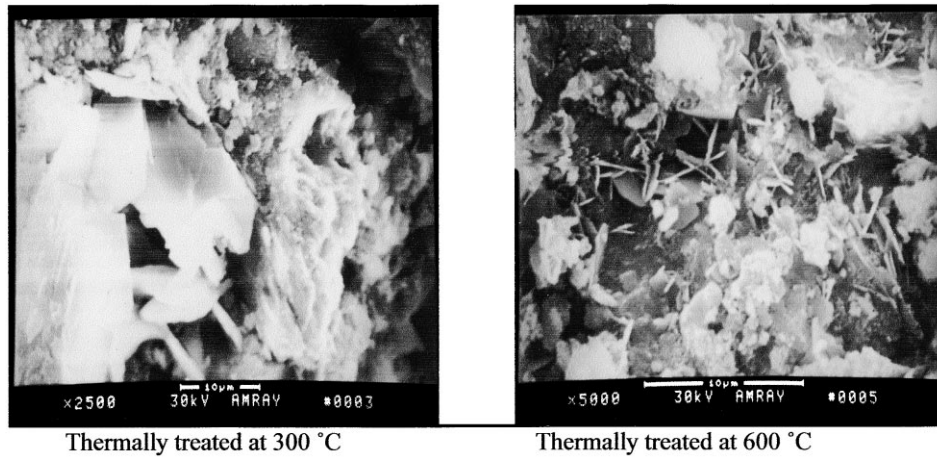


Fig. 8. SEM micrographs of thermally treated OPC paste.

Homra, respectively. Therefore, the blended cement pastes made with 20% Homra represents the most suitable fire resistant cements up to 600°C.

### 3.3. Porosity

Fig. 3 shows the change of total porosity of pozzolanic cement pastes as a function of temperature. The porosity of cement pastes increases with increasing Homra content. This is due to the initial water/cement ratio. The values of the water consistency of Portland cement and pozzolanic cements containing 10%, 20%, and 30% Homra are 23.0%, 24.0%, 25.0%, and 25.5%, respectively. The increase of porosity with temperature of thermal treatment is due to the formation and enlargement of microcracks and/or increase of degree of crystallinity of the formed hydrates leading to a sort of opening of the pore system of cement pastes [3].

### 3.4. Apparent density

The change of apparent density of different cement pastes with temperature of thermal treatment was illustrated in Fig. 4. Generally, the apparent density of the cement pastes decreases with increasing Homra content of the paste, a result that is mainly associated with the relatively low density of Homra in comparison to Portland cement. On the other hand, the change of apparent density with temperature takes place in three steps. During the first step, the density decreases from room temperature up to 300°C due to the removal of free water as well as combined water of C-S-H and CASH hydrates; therefore, the porosity increases and the apparent density decreases. From 300°C up to 400°C, the density has almost the same value; during this step, there is no further evaporation of water or destruction of minerals. The third step (from 400°C to 600°C) is accompanied by an increase in the density for all cement pastes. This is mainly

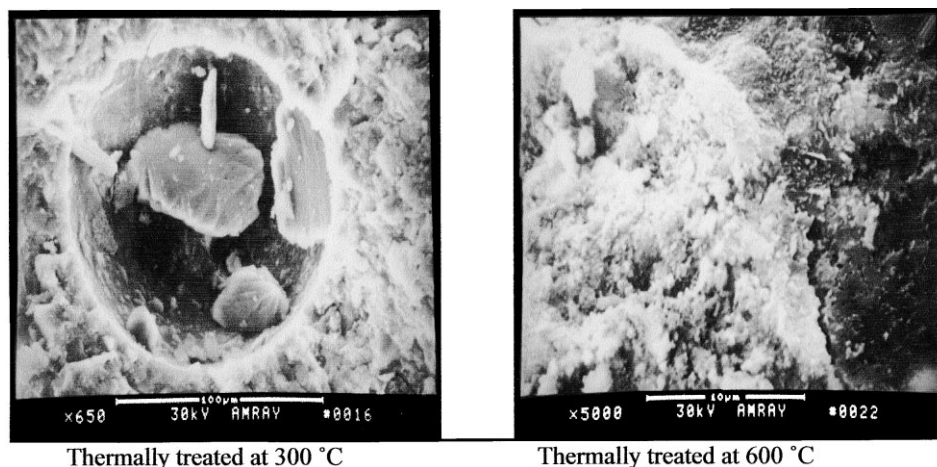


Fig. 9. SEM micrographs of thermally treated pozzolanic cement paste containing 20% Homra.

attributed to the decomposition of  $\text{Ca(OH)}_2$ , and the associated shrinkage leading to a denser structure has occurred. Evidently, the changes in the porosity are in good agreement with those of apparent density.

### 3.5. Phase composition

Figs. 5–7 show the XRD patterns of cement pastes fired up to  $600^\circ\text{C}$ . The XRD patterns of OPC pastes are shown in Fig. 5. The results of Fig. 5 indicated that the intensity of C-S-H peak increases at  $200^\circ\text{C}$ , then decreases at  $400^\circ\text{C}$  and  $600^\circ\text{C}$ . The increase of peak intensity of C-S-H at  $200^\circ\text{C}$  is accompanied by a decrease in  $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$  peak intensities. The decrease of  $\text{Ca(OH)}_2$  peak in the temperature range between  $200^\circ\text{C}$  and  $600^\circ\text{C}$  is due to the partial conversion of  $\text{Ca(OH)}_2$  to  $\text{CaCO}_3$  as well as decomposition of  $\text{Ca(OH)}_2$  to quick lime  $\text{CaO}$ .

The peak area of  $\text{Ca(OH)}_2$  decreases with increasing additions of Homra, which leads to the consumption of free lime obtained during the hydration of OPC. Figs. 6 and 7 show the XRD patterns of the pastes containing 20 and 30 wt.% Homra. Evidently, the pozzolanic reaction of Homra (active pozzolana) with lime, leading to the formation of calcium silicate or aluminosilicate hydrates, is associated with a consumption of free  $\text{Ca(OH)}_2$ . The peak intensity of calcium carbonate increases as the temperature of thermal treatment increases. This result is due to physico-chemical processes connected with the liberation of water from cement pastes in the temperature range  $200\text{--}500^\circ\text{C}$ , which are accompanied by a partial carbonation of calcium hydroxide [5]. This was also proved by the decrease of the peak intensities of  $\text{Ca(OH)}_2$  with increasing temperature.

### 3.6. Microstructure

High-resolution SEM provides a useful information on the morphology of the hydration products. Fig. 8 shows a mixture of hydration products having a massive structure of well crystalline C-S-H and sheets of  $\text{Ca(OH)}_2$  representing the microstructure of thermally treated OPC pastes at  $300^\circ\text{C}$ ; the sheets of  $\text{Ca(OH)}_2$  are stacked as parallel layers. The space between fibers becomes filled with an apparently amorphous material composed of calcium silicate hydrates and/or calcium hydroxide. The micrograph of thermally treated OPC paste at  $600^\circ\text{C}$  shows the formation of several microcracks leading to a destruction of binding forces as represented by the low compressive strength and high porosity of OPC at  $600^\circ\text{C}$ .

Fig. 9 shows the SEM micrographs of pozzolanic cement paste made with 20-wt.% Homra. Evidently, the pore spaces are available for the deposition of hydration products. The micrograph obtained at  $300^\circ\text{C}$  shows the formation of C-S-

H, which is produced as result of consumption of hydrated lime by Homra. The C-S-H phases are deposited within the pore system, which can accommodate larger amounts of hydration products leading to relatively high compressive strength values as compared with those of OPC paste. The microstructure obtained at higher temperature ( $600^\circ\text{C}$ ) displayed the formation of dense masses of hydration products having micro- and narrow pores.

## 4. Conclusions

From the above findings, it can be concluded that:

1. 20 wt.% Homra is the suitable amount, which improves the compressive strength of OPC paste by 25%.
2. The pastes of mixes containing Homra are thermally stable at temperature between  $100^\circ\text{C}$  and  $400^\circ\text{C}$ .
3. C-S-H phases are deposited in the pore system leading to relatively high compressive strength values of pozzolanic cement paste at  $300^\circ\text{C}$ .

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