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# Physicochemical characteristics of fired clay-limestone mixes

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## Abstract

The effect of calcination temperature on Belbeis clay and Sammlout limestone as well as hydration characteristics of calcined products were investigated. Three mixes 50/50, 60/40, 70/30 wt.% clay-limestone were calcined at 700, 800, 900, and 1,000°C for 2 h, then hydrated for up to 90 days. The degree of calcination was investigated from the free lime content and the ignition loss for each mixture. Also, the mineralogical composition of the fired mixes was investigated with the aid of X-ray diffractometry. The results revealed that the free lime of each mix increased up to 800°C then decreased gradually up to 1,000°C. Mix 60/40 clay-limestone fired at 800°C shows the presence of $Ca(OH)_2$ with quartz. As the firing temperature increased gehlenite appeared and increased up to 1,000°C with the disappearance of lime. Mix 50/50 gave the highest hydration kinetics as measured from determination of free lime and combined water contents. As the limestone decreased, the rate of hydration decreased. The suitable firing temperature of the clay-limestone mixes was 800°C for 2 h.

*Keywords:* Clays; Limestone; Calcination; Hydration kinetics; Calcium aluminosilicate hydrate

## 1. Introduction

Clays are the main raw materials for all ceramics and cement industries. They contain both clay minerals and variable amounts of nonclay materials, such as quartz, mica, gypsum, iron compounds, and feldspars, in addition to some organic materials.

Sayanam et al. [1] studied the calcination of clay at various temperatures. Thermodynamic calcination and X-ray diffraction data were used to determine the phase transformations in clays during firing at 700 to 1,100°C. Forsterite, wollastonite, $2CaO \cdot SiO_2$, mullite, anorthite, and diopside formed at 627 to 727°C. Firing at 1,027 to 1,127°C resulted in the formation of diopside, forsterite, wollastonite, mullite, anorthite, and monocalcium aluminate.

The phase changes of some clays fired at $>$900°C were studied elsewhere [2]. The phase assemblage depended on the type of clay structure and Fe, which substituted cations in the structure. Lattice Fe played a dominant part in the growth of crystal phases during the thermal reactions. The reaction temperature was diminished with the fineness of the clay particles.

Ghosh [3] claimed that the calcination of limestone ($CaCO_3$) at temperatures between 700 and 1,000°C depends on its composition. The phase changes occurring during firing clay-lime mixture were studied. It was concluded that the clay minerals dissociated between 500 to 700°C into an amorphous aluminosilicate mixture, whereas calcium carbonate decomposed into CaO between 600 to 800°C. Above 800°C, the CaO content decreased and disappeared almost completely at 950°C due to the formation of meta-stable phases: wollastonite ($CaO \cdot SiO_2$) (CS), anorthite ($CaO \cdot Al_2O_3 \cdot$ -$2SiO_2$) ($CAS_2$), and gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) ($C_2AS$). The formation of these phases began at 850°C and their amounts increased with temperature up to 1,050°C. The rate of formation of gehlenite ($C_2AS$) was higher than that of wollastonite (CS) and anorthite ($CAS_2$).

The hydration products formed during mixing calcium hydroxide with water metakaolinite obtained by fixed-bed calcination of a commercial kaolinite at 730°C were essentially $C_2ASH_8$ and CSH with small quantities of $C_4AH_{13}$ [4]. DTA exhibited the characteristic endothermic peaks of these three hydrates. Characterization of hydrates by X-ray diffraction (XRD) is very easy for hydrated gehlenite but is difficult for the two other hydrates because of the overlap of some lines. Tobermorite gel cannot be detected with accuracy on the XRD pattern.

The hydration products of metakaolin-lime mixes were investigated previously [5] by XRD, DTA, and TG techniques. Each mix was activated for 2 h at 800°C and then hydrated at room temperature for up to 28 days. The results showed that the gehlenite hydrate ($C_2ASH_8$) is the main hy-

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dration product and increases with curing time as well as lime content. Hydrogarnet is also formed at the early ages of hydration in the mixes of lower lime content and increases with curing time.

The hydraulic reactivity of some artificial pozzolanas made from burnt clays using lime as an activator was studied previously [6]. These pozzolanas were made by firing of montmorillonite, montmorillonite-illite mixed layer, and kaolinite clays at 600, 700, and 800°C. Pozzolana-lime pastes with water/solid ratio of 0.40 were hydrated at room temperature for various time intervals. The hydration and microstructural characteristics of the hardened pastes were studied.

The hydration of calcined clays with $Ca(OH)_2$ produces calcium silicate as well as calcium aluminosilicate hydrates as cementing materials. Therefore, this work aims to study the calcination conditions of locally available materials such as Belbes clays with limestone from El-Menya, Egypt, preheated at various temperatures up to 1,000°C. This study includes the hydration characteristics of the calcined mixes up to 90 days.

## 2. Materials and experimental techniques

The raw materials used in this work were Belbeis clay in El-Sharkia Governorate, Egypt, and limestone high purity >99% provided from Sammalout, El-Menya Governorate, Egypt. The chemical composition of clay was: $SiO_2$ = 59.54, $Al_2O_3$ = 22.24, $Fe_2O_3$ = 9.47, CaO = 0.56, MgO = 2.21, $K_2O$ = 1.29, $SO_3$ = 0.19, $Cl^-$ = 0.63, and ignition loss = 10.50%. Limestone composition was: $SiO_2$ = 0.20, $Al_2O_3$ = 0.10, $Fe_2O_3$ = 0.93, CaO = 51.89, MgO = 2.02, $K_2O$ = 0.02, and ignition loss = 34.44%.

The crushed materials were wet ground separately in a porcelain ball mill to pass through 90-μm sieve and dried at 105°C until completely dry. Clay was mixed with limestone in the mass ratio of 50:50, 60:40, and 70:30 clay/limestone, and denoted as M I, M II, and M III, respectively. The mixes were mechanically mixed in a porcelain ball mill using few balls for 1 h to ensure complete homogeneity, and were calcined in a porcelain dish at 700, 800, 900, and 1000°C for 2 h at heating rate 10°C/min. Each mix was hydrated with distilled water in suspension using water/solid ratio 10:1 and introduced in polyethylene quick-fit bottles and filtered at 1, 3, 7, 28, and 90 days. After a predetermined curing time, the hydration of the suspended materials as stopped using the technique described elsewhere [7,8]. The hydration characteristics were examined by determining the combined water ($W_n$) by the ignition loss of the hydrated samples after firing at 1,000°C and free lime contents [9].

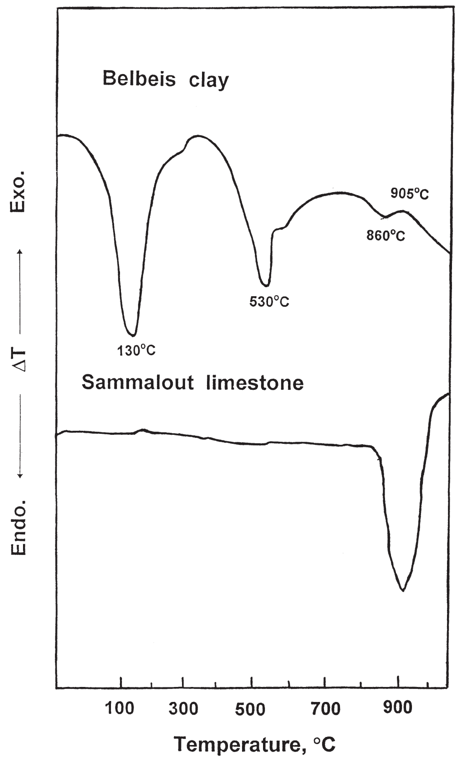

Fig. 1. DTA runs for raw materials.

DTA curves of Belbeis clay and Sammalout limestone are shown in Fig. 1. The clay material shows three endothermic peaks at 130, 530, and 860°C and one exothermic peak at 905°C. The first endothermic peak represents the removal of free water from the interlayer montmorillonite and illite structure. The second peak, which extends between 500 and 680°C, is indicative for complete dehydroxylation of kaolinite, illite, and montmorillonite clay minerals [10]. The endothermic peak at 860°C and the exothermic one at 905°C might characterize the formation of new crystalline phases at the expense of the destructed montmorillonite and illite structures.

The DTA curve of limestone exhibits only one strong endothermic peak at temperatures between 800 and 900°C, which is related to the dissociation of $CaCO_3$.

## 3. Results and discussion

### 3.1. Calcination of clay-limestone mixes

The effect of firing temperature of the three mixes was studied by determining the ignition loss and free lime contents of each mix fired at 700, 800, 900, and 1,000°C. For calcination above 850°C, a slow recrystallization of aluminosilicate into mullite, spinel, and amorphous silica occurred, which greatly diminished the reactivity of the solid with calcium hydroxide [11]. The degree of calcination can be measured by the ignition loss and free lime contents of the fired mixes, as well as the phases by XRD techniques.

### 3.1.1. Free lime content

The free lime contents of the mixes 50/50, 60/40, and 70/30 clay/limestone fired up to 1,000°C are graphically repre-

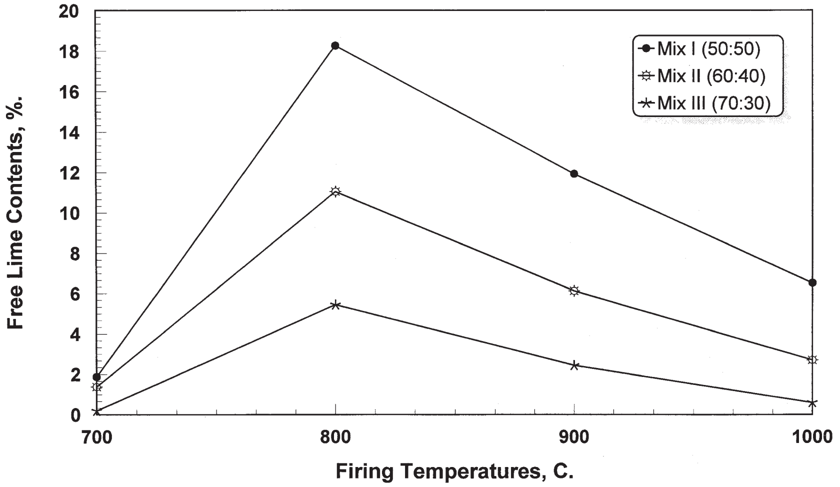

Fig. 2. Free lime content of fired clay/limestone mixes as a function of firing temperatures.

sented as a function of firing temperature in Fig. 2. The free lime for all mixes increased continuously with firing temperature up to 800°C and then decreased up to 1,000°C. Also, it was found that mix I (50/50) has higher free lime contents than those of mix II (60/40) and mix III (70/30). This is attributed to the fact that mix I had a greater amount of limestone than mix II and mix III. This increase was attributed to the increase of the amount of dissociated limestone into calcium oxide at lower calcination temperatures (700–800°C).

Calcination at higher temperatures (900 and 1,000°C) showed that the free lime content decreased with firing temperature. Firing at 1,000°C gave lower values than firing at 900°C for all mixes. This decrease was mainly attributed to the solid state reaction between the CaO, formed by calcination of limestone and the active $SiO_2$ and $Al_2O_3$, as well as $Fe_2O_3$-bearing minerals with the partial formation of calcium silicates and aluminates (spinel formation). These minerals were formed as a result of the reaction of the dissociated CaO from the limestone and calcined clay.

### *3.1.2. Ignition loss*

The ignition loss of each mix fired at temperatures from 500 up to 1,000°C is graphically plotted as a function of firing temperature in Fig. 3. It can be seen that the ignition loss for each mix increased with calcination temperature due to the decomposition of $CaCO_3$ into CaO and the evolution of $CO_2$. In the range 500 to 700°C, as the clay content in-

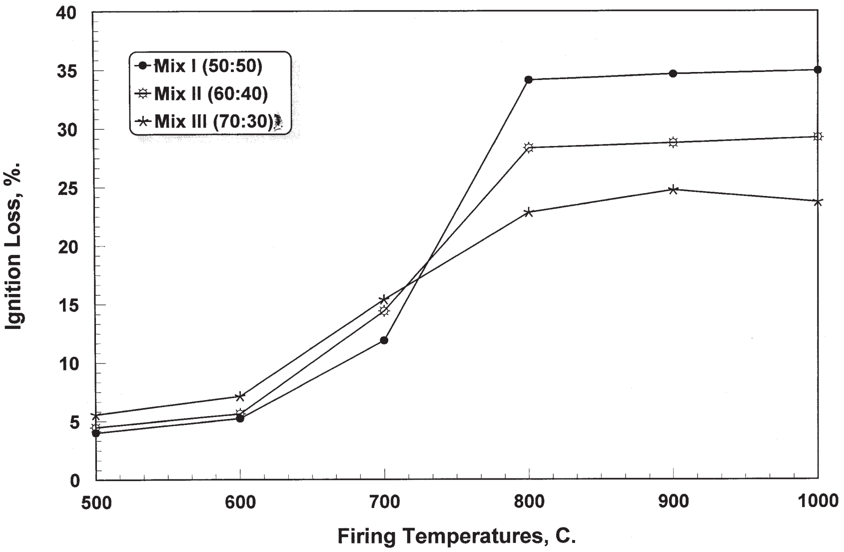

Fig. 3. Ignition loss of clay/limestone mixes as a function of firing temperatures.

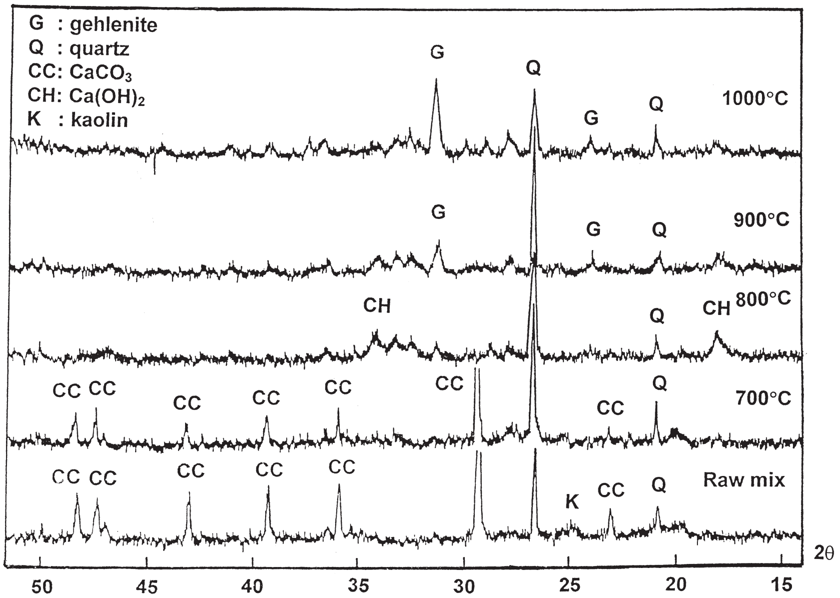

Fig. 4. XRD patterns of mix II (60:40) clay/limestone calcined at different temperatures for 2 h.

creased, the ignition loss increased. This was mainly due to the dehydration of clay minerals: mix III (70/30 clay/limestone) showed higher values. On the other hand, in the range 800 to 1,000°C, as the limestone increased, the ignition loss increased due to the effective decomposition of $CaCO_3$. Mix 50/50 gave higher values than 60/40 and 70/30 clay/limestone, respectively.

### *3.1.3. Mineralogical composition*

Fig. 4 shows the XRD patterns of mix II fired at 700, 800, 900, and 1,000°C. It is clear that the raw mix shows the existence of $CaCO_3$, quartz, and a weak peak of kaolin. The mix fired at 700°C shows the diffraction lines of free quartz and $CaCO_3$. Therefore, this temperature is insufficient for the dissociation of $CaCO_3$. At 800°C, the $CaCO_3$ completely disappeared, indicating a complete dissociation of $CaCO_3$. Also, some lines of $Ca(OH)_2$ appeared. At 900°C, the diffraction pattern shows the appearance of some lines of gehlenite ($C_2AS$), which formed due to the solid-state reaction between CaO and the amorphous aluminosilicate material. Finally, at 1,000°C all the diffraction lines of well-crystallized gehlenite together with some free quartz were detected. The degree of crystallinity of gehlenite increased with firing temperature from 900 to 1,000°C.

## *3.2. Hydration of calcined clay-lime mixes*

The effect of firing temperature can be studied on the hydration characteristics of aluminosilicate-lime. Three mixes

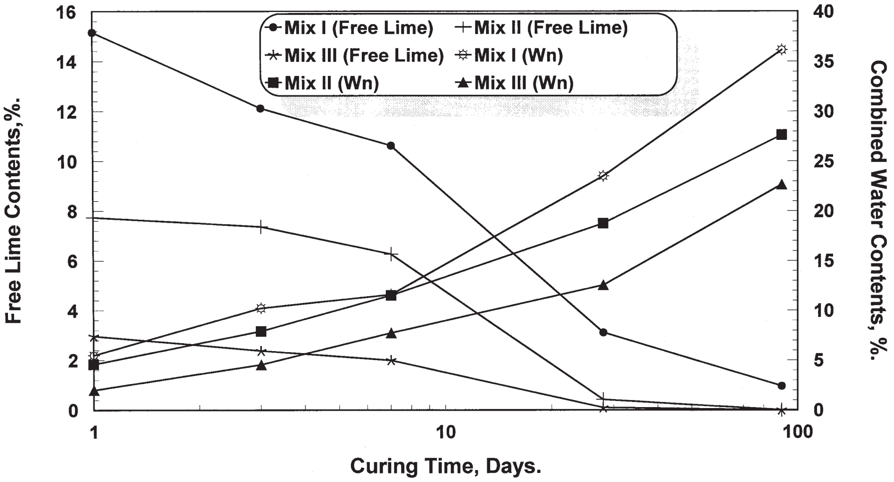

Fig. 5. Hydration kinetics of clay:lime mixes fired at 800°C for 2 h with curing time.

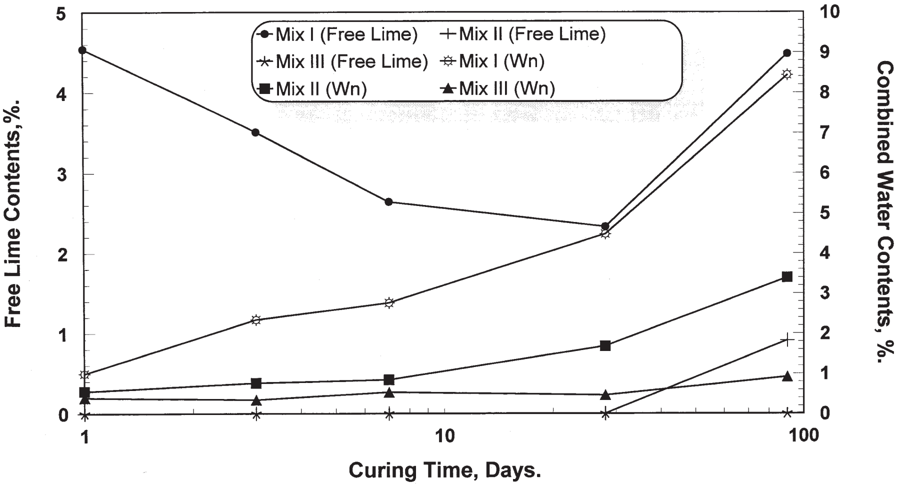

Fig. 6. Hydration kinetics of clay:lime mixes fired at 1,000°C for 2 h as a function of curing time.

were calcined at different temperatures from 700 up to 1,000°C. The free lime and combined aluminosilicate-lime suspension.

The free lime and combined water contents of the suspended hydrated materials of the mixes fired at 800 and 1,000°C as a function of curing time are graphically plotted in Figs. 5 and 6. At 800°C the free lime content decreased for all mixes. Mix I had higher free lime contents than those of mix II and mix III, respectively, at 800 and 1,000°C at all ages of hydration. 800°C was the firing temperature that gave the optimum values of free lime at all ages of hydration. Firing at this temperature tended to dissociate the limestone and clay minerals, with little chemical reaction between clay minerals and lime. Therefore, the hydrated materials showed free lime contents higher than those fired at 1,000°C. At 800°C, the free lime content decreased slowly for all mixes up to 7 days and then decreased sharply up to 90 days. The sample fired at 1,000°C shows that mix III had no free lime at any age of hydration; also, for mix II no free lime was observed up to 28 days but at 90 days some amounts of free lime appeared, possibly due to the release from these hydration products. But for mix I, the free lime decreased up to 28 days then increased at 90 days. This decrease was mainly attributed to the solid-state reaction between the CaO and the active $Al_2O_3$- and $SiO_2$-bearing minerals with partial formation of calcium aluminosilicates as gehlenite ($C_2AS$) and anorthite ($CAS_2$), which have poorly hydraulic properties. The increase after 28 days may be due to the liberation from the hydrated rich calcium aluminosilicate.

Generally, the combined water contents increased with curing time and decreased with calcination temperature from 800 to 1,000°C for all mixes. Samples fired at 800°C gave the maximum combined water contents at all ages of hydration. This was due to the high content of free lime, which activated the hydration of amorphous aluminosilicate. The hydration products increased and therefore the combined water content also increased. Samples fired at a higher temperature (1,000°C) showed lower values of combined water contents. This was due to the formation of calcium aluminosilicate phases such as gehlenite and anorthite, which have poor hydraulic properties.

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