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Building materials from siliceous clay and low grade dolomite rocks

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Abstract

New building bricks could be prepared from appropriate mixtures of local low melting clay and low grade dolomite rocks after firing at a relatively low firing temperature of ≃750°C. Results showed that the thermal interaction between the constituents of clay and dolomite at 750°C ensures better and relatively high mechanical strength for the resulting products. The XRD and DTA analyses indicated that the produced articles are composed mainly of carbonates and new formations of calcium silicates, calcium aluminates and MgO in amorphous or fine crystalline state. The fired products after hydraulic hardening at a dried environment recorded the highest mechanical properties. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: B. X-ray methods; C. Strength; D. Clays; D. Silicate

1. Introduction

It is well known that dolomite rock is composed mainly of dolomite mineral as [Mg, Ca $(CO_3)_2$], in addition to some SiO_2, Al_2O_3 and Fe_2O_3 as impurities associating with the carbonates. Firing of dolomite at different firing temperatures, materials of various compositions can be obtained for use in a variety of applications [1–4].

On sintering of pure dolomite at ≃1500°C, the resulting product contains mainly crystalline inactive MgO and CaO. Firing of dolomite at 1000°C, the complete dissociation of dolomite minerals can take place and the end products are essentially active MgO and CaO. On its firing at 800–850°C, the resulting articles include MgO, CaO and Ca CO_3. By firing dolomite up to 750°C, a product of great chemical reactivity could be obtained consisting of MgO, $MgCO_3$ and $CaCO_3$. Such products when mixed with water, complete hydration of MgO occurs within three days. When dolomite rock contains appropriate amounts of SiO_2, Fe_2O_3 and Al_2O_3, or mixtures of dolomite and clay are fired, other phases are formed such as calcium silicates and calcium aluminates in addition to the previously mentioned phases [5]. As SiO_2 and Fe_2O_3 ratios increase in the dolomitic raw material, a considerable amount of liquid phase is expected to form in such grains leading to their densification at a relatively lower temperature [4]. Therefore, the objective of this paper is to study the physicomechanical properties and phase composition of a new building material prepared from appropriate mixtures of local low melting clay and low grade dolomite raw materials.

2. Experimental procedure

2.1. Raw materials

The raw materials used in the present study are low melting clay and low grade dolomite obtained from Assuit and Abo-Rawash, respectively, Egypt. Very huge deposits of these raw materials are available, and could be obtained by simple mining methods. The clay sample was first dried at 105°C for 24 h. The raw materials were ground separately using a ball mill to pass through 16 mesh sieve.

2.2. Constitution of raw materials

The chemical composition of clay and dolomite was carried out on the laboratory using standard wet method [6] as well as X-ray fluorescence techniques. Table 1 shows the chemical composition of clay and dolomite. The grain size distribution is given in Table 2 which was carried out by normal sieve techniques. The mineralogical constitution of clay and dolomite was employed by X-ray diffraction patterns (XRD) and differential thermal analysis (DTA) as shown in Fig. 1. The XRD analysis was carried out using a Philips X-ray

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Table 1
Chemical analysis of raw materials (wt.%)

Raw materials	Oxides							
	L.O.I.[a]	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	R_2O
Clay	6.51	64.62	13.94	5.06	2.86	0.52	0.52	4.20
Dolomite	40.71	6.27	2.53	3.84	30.49	13.73	–	2.43

[a] Loss of ignition.

Table 2
Particle size distribution of raw materials (μ)

Raw materials	< 250	< 125	< 63	< 32	< 16	< 8	< 4	< 2
Clay	2.9	8.7	5.6	12.4	8.8	3.2	2.8	55.6
Dolomite	1.6	3.8	8.3	4.2	12.3	5.6	6.4	57.8

Diffractometer, Model 1390 with Ni-filtered, Cu-K_α radiation. The DTA analysis was performed using Perkin-Elmer 7-Series Thermal Analysis System at a heating rate 10°C/min up to 1200°C with finely powdered alumina as a reference material. It is clear that clay sample is composed mainly of kaolinite, illite and quartz as major elements as well as calcite and feldspar as minor components. The endothermic peaks in the temperature ranges 100–200 and 400–750°C are mainly due to the dewatering and decarboxylation of clay minerals, while the endothermic peak at the temperature range of 570–580°C is principally due to α-β-quartz transformation. The dolomite sample is composed essentially of dolomite minerals ($CaCO_3$, $MgCO_3$). The two sharp endothermic peaks in the temperature ranges 800–830 and 850–900°C are essentially due to the decarbonation of dolomite and calcite, respectively.

The XRD analysis further indicated the presence of calcite mineral in addition to the dolomite mineral.

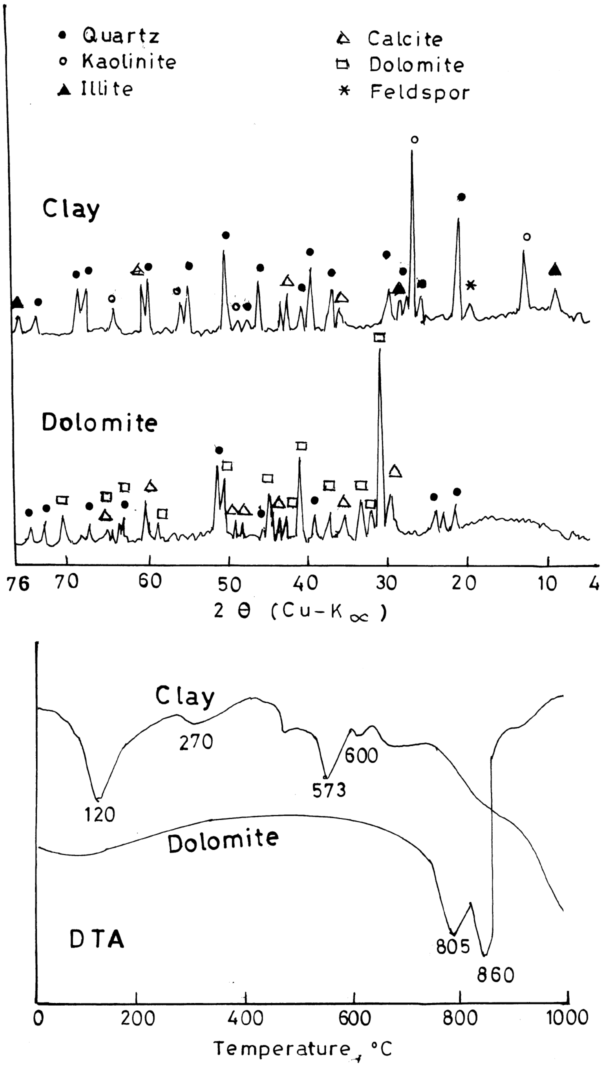

Fig. 1. X-ray diffraction patterns and differential thermal analysis thermograms of clay and dolomite.

Table 3
Mix compositions of the prepared batches (wt.%)

Raw materials	No.								
	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8	M_9
Clay	90	80	70	60	50	40	30	20	10
Dolomite	10	20	30	40	50	60	70	80	90

2.3. Preparation of sample briquettes

Table 3 illustrates the initial composition of the various batches containing clay and dolomite. The mixing process of the batches was carried out on the basis of dry weights in a porcelain ball mill using two balls for 1 h in order to keep the fineness of all batches nearly the same. Specimens were prepared using water as a binder, and then moulded under a high shaping pressure of 40 KN to form cylinders of 2 cm diameter and 3 cm height. Specimens were let to dry in room temperature for 24 h, in a dryer for another 24 h, and then fired at 750°C for 2 h soaking. Some of the fired specimens were kept in a dryer at 60°C for 24 h and some others were exposed to a wet environment for 24 h. All specimens of the three groups (after firing, after hydraulic hardening in a dried state and in a wet environment) were subjected to ASTM standards of crushing strength [7]. The test of crushing strength was carried out using the most recently machine "Instron Universal Testing Instrument", Model 1128. Three samples were measured for each test, and the mean value was considered. The free CaO content of the fired samples was determined by the extraction method of Lerch and Bogue [8]. The optimum body batch was then selected. The crushing strength of the optimum fired batch according to the time of hydraulic hardening, moisture content and soaking time was further investigated. The chemically bound water content of the optimum fired batch after hydration was also measured on the basis of ignition loss. The phase composition of the optimum batch (powder and fired) was identified by XRD and DTA analyses.

3. Results and discussion

The data of Table 1 show that the deposit from which clay was taken contains a considerable amount of Al_2O_3 (13.94%) and Fe_2O_3 (5.06%). This means the suitability of this clay for building bricks production. Also, the amount of CaO (2.86%) and Fe_2O_3 (5.06%) is sufficient to give the end product a suitable colour and good appearance [9–11]. Moreover, the presence of large amounts of fluxes in both clay and dolomite such as R_2O (4.20 and 2.43%) as well as Fe_2O_3 (5.06 and 3.84%), respectively increases the chance to form a considerable amount of liquid phase at a relatively lower firing temperature when mixed together [4].

Fig. 2 shows the crushing strength and free lime content of clay/dolomite ceramic articles fired at 750°C depending on the dolomite content. It is clear that the free CaO content of the fired samples increases gradually with the increase of dolomite content, while the crushing strength decreases continuously. This is primarily attributed to the continual defficiency of the essential binding properties provided by the clay minerals which give the good compaction and bonding strength to the article [10,12]. Also, the gradual increase of the free CaO content, resulting from the partial decomposition of $CaCO_3$ present in dolomite during firing process, affects adversely on the crushing strength of the fired articles [10]. Moreover, the partial decomposition of dolomite during firing often accompanies by the evolution of CO_2 outside the structure of the fired articles.

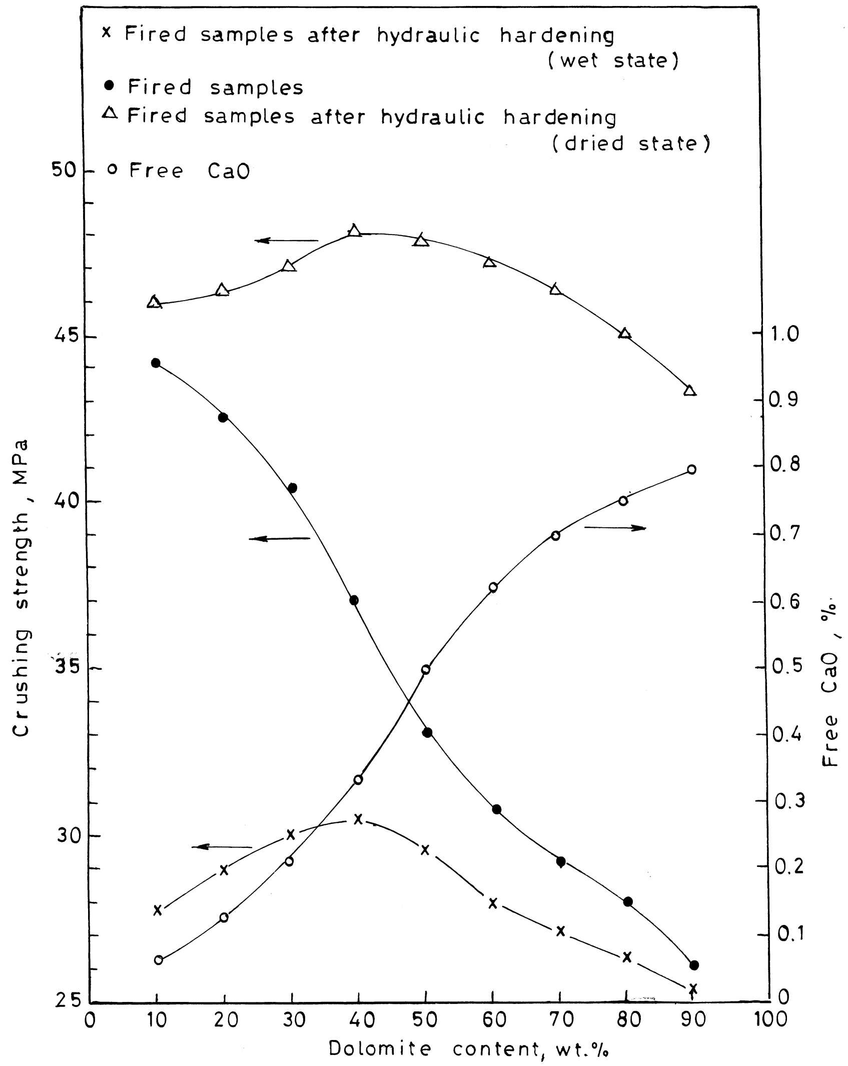

Fig. 2. Crushing strength and free CaO content of various clay/dolomite batches depending on the dolomite content for different experimental conditions.

This tends to create a more porous structure. Hence, the permeability of the produced bodies are accordingly enhanced [10]. This behaviour often increases with increasing dolomite content. This is essentially due to the fact that as the dolomite content increases, the rate of decomposition increases which followed by the migration of more CO_2 outside the fired bodies. This often causes stress and creates more voids inside the bodies which reflected adversely on the crushing strength and other specific properties of the fired products [5,12]. Though the crushing strength of the fired articles decreases continuously with the increase of dolomite content, the values of crushing strength are however yet sufficiently high. This is mainly due to the higher fineness of raw materials which gives the good compaction of samples during moulding, particularly when using a high shaping pressure. This in turn has a positive and strong influence on the mechanical strength of fired samples [8].

The crushing strength of the fired samples after hydraulic hardening in a wet environment is lower than that of the directly fired ones nearly with all dolomite contents. This is mainly attributed to the presence of excess mechanical water inside the intermolecular spaces which ensures lower strength due to the lowering effect on the compactness of the tested samples [13]. Furthermore, the crushing strength of the fired samples after hydraulic hardening in a dried atmosphere is much higher than those of the other two groups, particularly those containing larger amounts of dolomite. This is principally due to that after drying at 60°C, the mechanical water was driven off. As a result, the fine particles are partially combined with the neighbooring grains of clay to form a more compact structure. This tends to promote the formation of more bond strength between the various ingredients [13]. Also, some chemical and thermal reactions may occur during both firing and hydraulic hardening processes either through decomposition or recombination changes [5,10]. These changes depend mainly on the shape and size of the pore system of the tested specimens as well as the type of hydraulic hardening, especially in presence of fluxing elements. Hence, the mechanical properties of the tested samples are evidently improved [4,5]. Consequently, the optimum batch was then selected which containing 60% clay and 40% dolomite fired at 750°C after hydraulic hardening in a dried state which achieved the highest crushing strength.

The influence of time of hydraulic hardening on the crushing strength of the optimum clay/dolomite batch = 6/4 fired directly at 750°C and fired after hydraulic hardening is shown in Fig. 3. The crushing strength of the fired samples at different ages of hydraulic hardening up to 28 days seems to be nearly the same. This may be due to their amorphous or fine crystalline state which did not easily affect by the process of hydraulic hardening [5], i.e. the chemical composition and bonding strength are still unchanged whatever the time of hydraulic hardening. Therefore, no changes on the mechanical strength were observed.

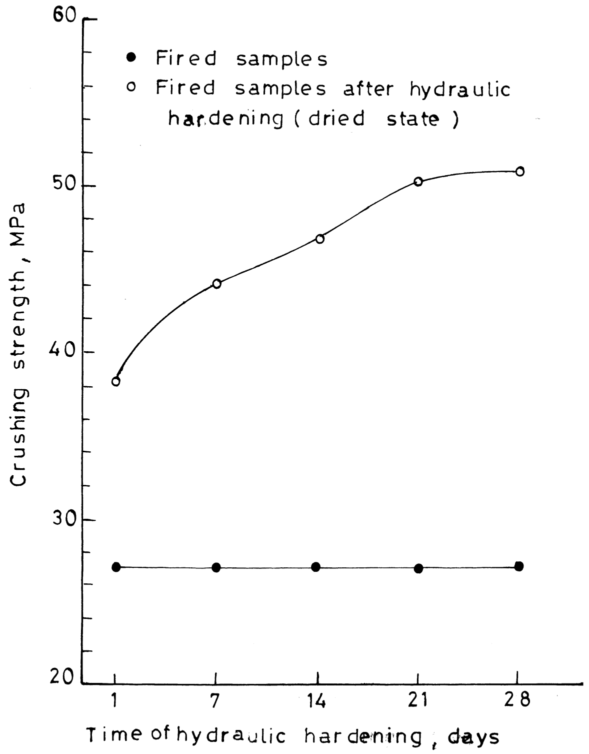

Fig. 3. Crushing strength of clay/dolomite batch fired at 750°C according to the time of hydraulic hardening.

On the other side, the crushing strength of the fired samples after hydraulic hardening increases gradually with the time of hydraulic hardening up to 21 days, and then increases slowly up to 28 days. This is essentially attributed to the fact that as the time of hydraulic hardening proceeds, some changes in the chemical composition and bonding strength may take place, which improve physically the compaction of the tested samples [4,5]. This evidently enhances and modifies the mechanical strength.

Fig. 4 shows the effect of moisture and bound water contents as well as duration of firing on the crushing strength of the optimum clay and dolomite batch = 6/4 fired at 750°C. The crushing strength of the tested samples increases slightly as the moisture content increases up to 9%. This is mainly attributed to the gradual modification and improvement in the compaction of sample grains due to the continual hydration of MgO and other phases of the fired samples [5,8]. This is evidently confirmed by the gradual increase of chemically bound water content of the same samples as the moisture content increases as clearly shown in Fig. 4. With moisture content >9%, the crushing strength tends to be nearly stable. This may be due to that excess moisture content has a negative action on the compactness of sample grains [3]. Hence, the crushing strength unchanged. So, the optimum moisture content was up to 9%. On the other hand, the crushing strength of the same sample decreases sharply if the soaking time of firing is > 2 h. This is principally due to that as the duration of firing increases, the rate of decomposition increases. Hence, the total porosity increases gradually due to the evolution of more CO_2 outside the structure. Therefore, the crushing strength diminishes [4,10]. The relatively high mechanical properties of all clay/dolomitic ceramic products are essentially due to their specific structure which is mainly composed of carbonates and new formations of calcium silicates and aluminates as well as MgO in amorphous or fine crystalline state [5].

Fig. 5 illustrates the XRD patterns of raw and fired clay/dolomite batch = 6/4. It is clear that kaolinite, illite, calcite and quartz are detected in the raw batch. In the fired sample, new phases are identified as MgO, calcium

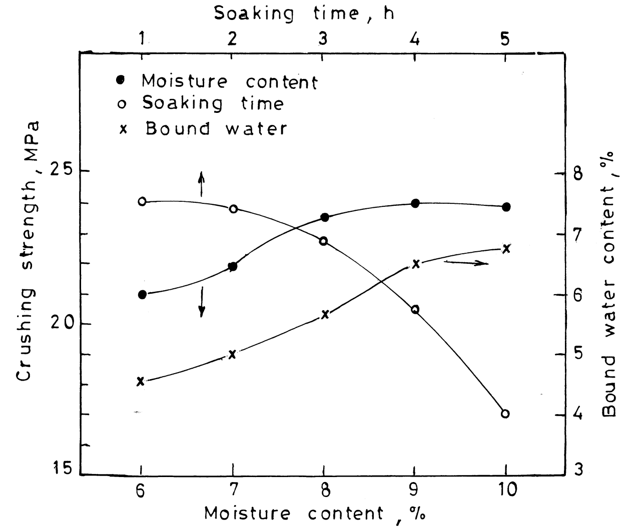

Fig. 4. Crushing strength as well as bound water content of the fired clay/dolomite batch = 6/4 as a function of moisture content and soaking time.

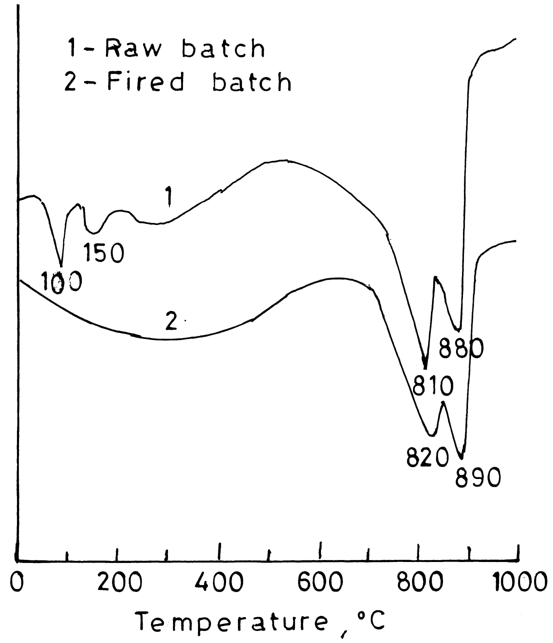

Fig. 6. Differential thermal analysis-thermograms of raw and fired clay/dolomite batch = 6/4.

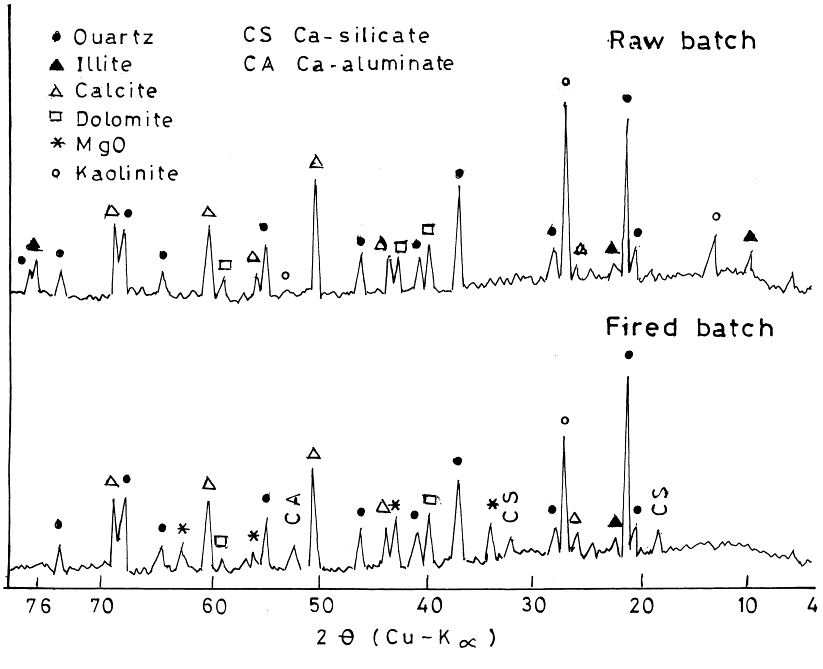

Fig. 5. X-ray diffraction patterns of raw and fired clay/dolomite batch = 6/4.

silicates and aluminates, in addition to residual quartz and calcite. The DTA thermograms of the same samples are shown in Fig. 6. The endothermic peaks at the temperature range of 100–300°C are mainly due to the dehydration of clay minerals. The two sharp endothermic peaks at the temperature ranges of 800–830 and 850–900°C are principally related to the decarbonation of dolomite and calcite, respectively.

4. Conclusions

New building material could be prepared from a mixture of 60% clay and 40% dolomite after firing at $\simeq$750°C. The fired bodies after hydraulic hardening at a dried environment possess the highest values of mechanical strength. The resulting products have specific structure composed of carbonates and new formations of MgO, calcium silicates and aluminates as fine crystals or amorphous phases. The new structure of clay/dolomitic ceramics possess semihydraulic properties.

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