

Improvement of Engineering Properties of Fired Clay Bricks Through the Addition of Calcite

by

J F MARTIRENA¹, R L DAY², D BETANCOURT¹ and Y DIAZ¹

¹ Universidad Central de Las Villas, Santa Clara, Cuba

² Schulich School of Engineering, University of Calgary, Canada

ABSTRACT

Calcium carbonate as a source of calcite has been used as an admixture in fired clay bricks. The research aims at decreasing the firing temperature and dwell-time for production of clay bricks. The presence of small amounts of calcium carbonate improves the compressive strength of the bricks at firing temperatures around 900°C, apparently because of the fluxing effect associated with the presence of calcite, which basically enables the sintering reaction to take place at lower temperature in clays rich in kaolin. The tests were performed on cylindrical specimens and on practical-size bricks, and include SEM observation and EDS/EDX mapping, XRD, porosimetry and compressive strength measurement. Bricks having between 2% and 5% calcium carbonate showed the best performance when fired at 900°C for 2-3 hours; these bricks show a 40% increase in compressive strength. The resulting bricks are denser and stronger. The slight increase in porosity observed is apparently related to the presence of cracks produced by the release of CO₂ during the decomposition of the calcite. The specimens made with calcite performed well under wet/dry cycles and salt crystallization tests when compared to normal bricks made without calcium carbonate.

1. INTRODUCTION

Ceramics made from fired clay is one of the most popular building materials of all times. Most ancient civilizations are identified with this material for building temples, houses and cities. Through the years the technology has evolved to allow higher productivity, and lower energy consumption, mainly through the improvement of the firing kilns, the use of better insulating materials in kiln construction and the automation of the process. Further energy improvements will be restricted to temperature and time factors required to fire the clay body.

The brick acquires mechanical strength through sintering during the thermal treatment of the clay used to shape it; the contact points between adjacent clay grains melt in a vitreous phase and bind the grain together. The process known as liquid phase sintering starts at temperatures close to 800°C, and continues to temperatures close to 1200°C, where the materials fuse and a re-crystallization takes place [1].

Encouraging results were reported through the introduction of a grog, which acts as a flux and gives fired clay brick the strength necessary for structural purposes; it also lowers the fusing point. In one study, recycled ground glass was used as a grog, and fly ash was used to replace clay. An ash/glass ratio of 60:40 produced the most promising results from both an economic and engineering viewpoint. A firing temperature of 900°C for a duration of three hours was found sufficient to initiate the mineralogical changes to convert the glassy material of unfired ash to a system of predominantly crystalline components. Both temperature level and firing duration were much better than those generally used for firing clay brick, which are about 1100°C for a minimum of 18 hours [2].

The use of carbonates as fluxing agents is also reported as a good practice to reduce the energy input of brick firing [3-7]. The presence of dolomite and calcite during firing is associated with a reduction of the sintering temperature, basically because these minerals influence the transformations taking place in the clay minerals during thermal treatment, and allow the formation of more vitreous phases at lower temperatures compared to materials having no carbonates. During firing, two main processes take place: a) the dehydroxylation of kaolinite (500-600°C), and b) the decarbonation of the carbonates (700-850°C). A large amount of amorphous, low-ordered material is created through these processes, which favours the formation of new phases [1,3,4].

TRAORE AND BLANCHART [3-4], define two stages in the phase transformation process. In the first phase, the metakaolinite reacts with calcium oxide to form gehlenite (Ca₂Al₂SiO₂), and a second phase, in which gehlenite is combined with alumina and silica from metakaolinite and the remaining fine grained quartz to crystallize the anorthite phase (2CaAl₂Si₂O₈). The microstructure of the material formed at low temperatures (below 1100°C) shows dense zones apparently formed by anorthite, which are partially interconnected and embedded in a porous matrix. It is supposed that this grid of dense zones favours the mechanical reinforcement of this low-temperature-sintered material [4].

The influence of calcite and sintering time on the reactions of aluminosilicates in solid state was studied by MAYORAL et al. [5], for which a procedure was developed to monitor the mineral transformation that occurs in aluminosilicates fired at high temperatures by using Dynamic Scanning Calorimetry (DSC). It was shown that sintering could start at temperatures as low as 850°C, and sintering time could eventually be shortened through the use of calcite to as little as 30 min; the best results were accomplished for a 33% calcite proportion.

CULTRONE et al. [6-7] also studied the performance of hand-made fired clay bricks with various additives, among them calcium carbonate. The addition of 10% calcium carbonate is reported to increase vitrification at temperatures between 800-900°C, however, an increase of the porosity and the capacity of absorbing water of the resulting bricks is reported, due to the presence of small cracks. These cracks are probably caused by the sudden expansion of CaO in the presence of moisture; the newly formed portlandite exerts a notable crystallization pressure in the confined spaces of the brick previously occupied by CaO, thereby producing radial fractures around the carbonate grains. This process is very much dependent on the size of the carbonate grains.

The current paper aims at assessing whether adding smaller amounts of calcium carbonate to the clay used to manufacture fired clay bricks contributes to reducing the firing temperature and sintering time, and how this influences the mechanical properties and durability of the bricks.

2. MATERIALS AND TESTING PROCEDURES

Test cylinders were made of clay consisting mainly of a mixture of montmorillonite and kaolinite. Analytical grade calcium carbonate was used as the source of calcite. The oxide compositions of the clay and calcium carbonate are given in Table 1. For durability studies full-size bricks were prepared and fired under realistic firing conditions.

The clay and calcium carbonate were mixed with 8-10% water. Different proportions between clay and calcium carbonate were tested. The material was made homogeneous and then pressed into cylindrical moulds having 3.5cm diameter and a height between 4 and 5cm. The moulding pressure was 7MPa. A control series was prepared with no CC where recycled glass was used a grog, as recommended by DAY [2].

The fresh cylinders were allowed to dry for 3-5 days and then fired in an electric oven. The firing process was divided in two phases: a) removing all combined water up to 500°C, and b) high temperature firing. The specimens were all held 2 hr in phase a). Three different firing temperatures (900, 950 and 1000°C) were used in phase b); the specimens were burnt for times varying from 2-3 hours. Figure 1 shows the cylinders and the mould used to prepare them.

The experimental program aimed at evaluating some of the engineering and chemical/morphological properties of the resulting bricks. Brick cylinders were first tested for water absorption and then for compressive strength. Microstructural examination of samples that underwent engineering testing consisted of: measurement of the porosity of the bricks with a Mercury Intrusion Porosimeter (MIP), observation of fracture surfaces of the bricks with the Scanning Electronic Microscope (SEM), mineralogical analysis of powdered samples of the fired cylinders by X-ray diffraction (XRD), observation of polished surfaces of the bricks with Petrographic and Scanning Electronic Microscopy. EDX mapping and Differential Thermal Analysis (DTA) performed on the clay used in brick firing, which was

mixed with calcium carbonate. Full-size bricks were also subjected to durability evaluation consisting of wet-dry cycling and salt scaling tests; more details of these tests are described in the appropriate section below.

3. TEST RESULTS AND DISCUSSION

3.1 Influence of the amount of calcium carbonate and firing temperature

The first set of tests was done with a calcium carbonate percentage varying from 0-20% by mass of clay (Figure 2). The highest compressive strength was achieved at 950°C with 5% CC. For CC content above 10% a drop in compressive strength was observed. This is consistent with Cultrone's results [6-7]. The compressive strength of the cylinders made with 5% CC was of the same range of those made with 40% recycled glass as a grog [2] – denoted “glass” on Figure 2.

A second test series was performed, this time with CC content under 5%, with firing at 900°C for 2 and 3 hours and at 1000°C for 2 hours. The results of the compressive strength tests are presented in Figure 3. For the cylinders burnt at 900°C the addition of 2% CC produced a significant increase in the compressive strength compared to both 0 and 5%. The increase of firing time from 2 to 3 hours does not appear to have any influence on the mechanical performance of the cylinders. The test results shown on both Figures 2 and 3 suggest that if firing is at 1000°C the use of any amount of calcium carbonate results in a reduction in strength.

The changes in the physico-mechanical properties in the cylinders are probably associated with modification of their mineralogical composition caused by the calcite present in calcium carbonate, and also the occurrence of physical changes in the microstructure resulting from the new reactions that take place. Calcite favours the strength development in samples burnt at 900°C, and seems to hinder it in samples burnt at 1000°C.

Table 1
Chemical composition of the materials used in the experiment

Description	Clay	CC
SiO ₂	49.56	0.99
Al ₂ O ₃	10.41	2.38
Fe ₂ O ₃	10.73	0.90
TiO ₂	0.88	<0.02
CaO	3.82	52.72
MgO	12.32	1.89
Na ₂ O	1.39	<0.10
K ₂ O	0.22	<0.10
P ₂ O ₅	0.07	0.05
MnO	0.16	0.02
SO ₃	<0.10	<0.10
LOI	9.04	40.08



Figure 1 Test brick-cylinders and mould

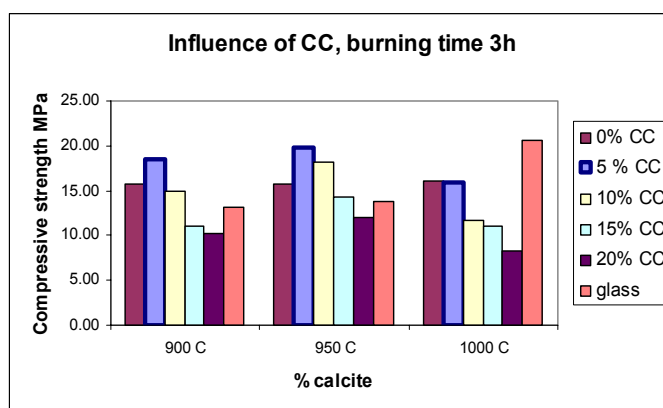


Figure 2 Compressive strength of cylinder with CC between 0-20%

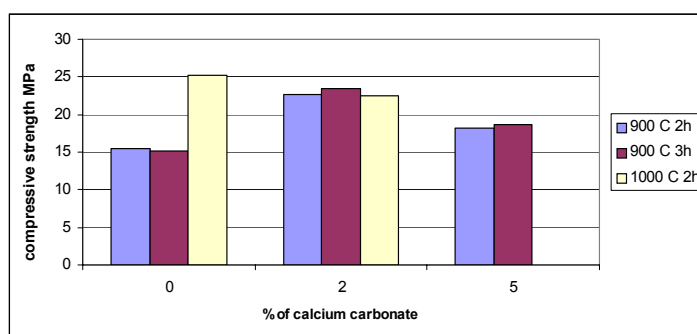


Figure 3 Results of compress

3.2 Mineralogical and structural changes due to calcium carbonate addition

Adding calcium carbonate modifies the porosity and the pore size distribution in the fired clay bricks. Figure 4 presents the results of the MIP tests performed on pieces of the fired cylinders. The control series fired at 900°C shows a typical pore size distribution with a peak around 1µm equivalent radius, this agrees with results of CULTRONE et al [6]. The amount of smaller pores with radius under 1µm increases in samples with calcium carbonate fired at 900°C. It is thought this occurs for two reasons: a) the transformation of calcite to CaO favours a system with very small pores, and b) the microcracks produced during hydration of CaO [6]. SEM observation of a fracture surface of this brick, presented in Figure 5, clearly indicate the presence of small pores and also some small cracks.

The cylinders made with calcium carbonate and fired at 1000°C show a typical displacement of the pore radius peak towards larger pores, pores having radius larger than 1µm is consistent with the increase in pore size associated with the rise of firing temperature described in the literature [6]. The amount of smaller pores is decreased in comparison with that of the sample made with 2% calcium carbonate and fired at 900°C, which could indicate that some vitrification takes place to close some pores. This is confirmed by the presence of a glass melt in Figure 6a, apparently produced through the fluxing action of calcite. The remaining small pores are probably caused by the microcracks produced during hydration of CaO during water absorption testing, as presented in Figure 6b. The cracks are bigger and more frequent in comparison to the bricks fired at 900°C.

The improvement of the mechanical properties of the bricks, and the changes in the pore structure of the resulting matrix can be explained through the mineralogical changes that take place when calcium carbonate is added. This becomes more obvious in bricks fired at 900°C, which show the best results.

It is important to assess whether the added calcium carbonate undergoes a transformation into CaO or combines with the clay mineral to form other phases. DTA tests performed on clay with and without calcium carbonate do not indicate that CaO has formed as a result of the thermal treatment. It could also happen that the calcite combines with the clay minerals to form other phases, as referred in the literature [3-6].

The fact that there are differences in grain size between the clay and calcium carbonate used to manufacture the bricks and the ones used in the DTA testing could help clarifying the observations. A larger calcium carbonate grain with less specific surface – the one that would probably slip through in brick manufacture- would not combine with clay minerals and instead would undergo decarbonation, resulting in CaO formation. This could then subsequently lead to volume instability and microcracking in the solid matrix when water is absorbed into the pore structure. DTA sample preparation demands intensive grinding of the material in an agate mortar, and the possibility to have larger calcium carbonate grains is very low. A smaller calcium carbonate grain, with higher specific surface would likely combine with clay minerals to form other phases instead of decarbonating.

Anorthite ($2\text{CaAl}_2\text{Si}_2\text{O}_8$) is one of the main phases expected to be present in the fired bricks, according to the chemical and mineralogical composition of the materials mixed. Powdered samples from the bricks were subjected to XRD tests in order to assess the existing crystalline phases. Figure 7 presents the XRD diagrams. Sample M3, burnt at 1000°C, showed a new peak at 2-theta 22 degrees that matches very well with anorthite. This peak is not identified in sample M2, burnt at 900°C. There are also other broad bands in all samples where anorthite should exist, but probably as an existing phase in the clay originally burnt (feldspar), or as newly formed anorthite.

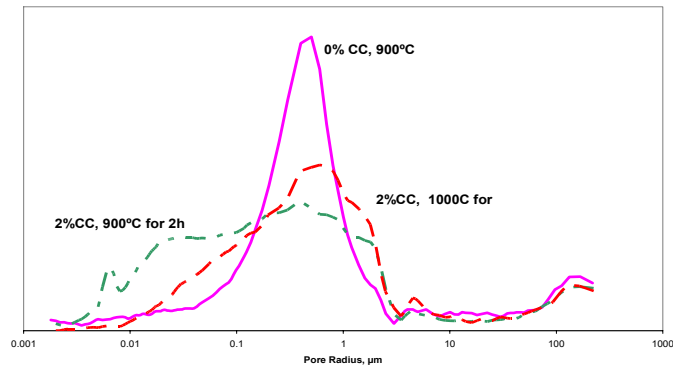


Figure 4 Results of MIP tests performed in samples M1, M2 and M7

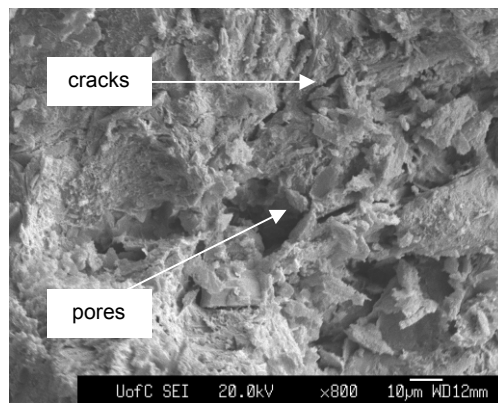


Figure 5 SEM picture of a of a cylinder made with 2%CC and fired at 900°C

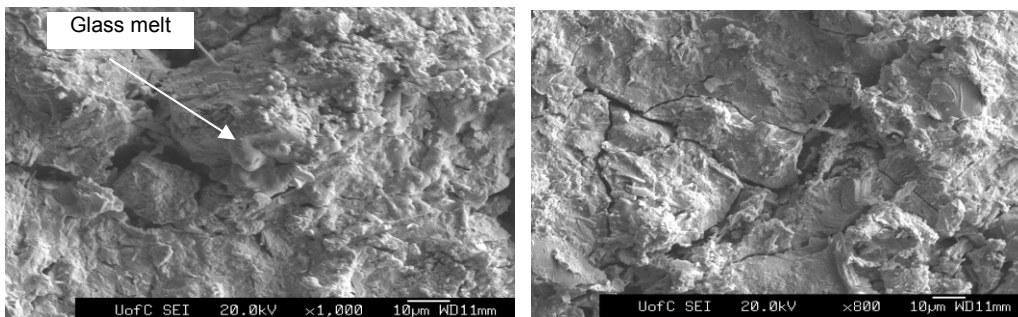


Figure 6 a) Presence of a glass melt in bricks made with 2% CC and fired at 1000°C
b) Micro cracks in the same brick

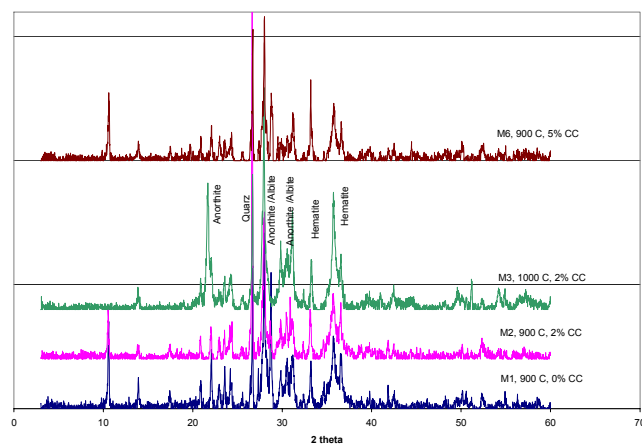


Figure 7 XRD of powder from fired bricks

3.3 Influence of calcium carbonate addition on brick durability

Figure 8 presents the results of water absorption tests performed on the cylinders made with calcium carbonate less than 5%. Contrary to what was expected, the difference between the results in all tested specimens was very low. The lowest results are obtained for cylinders burnt at 1000°C. In all cases neither the addition of calcium carbonate nor the firing time appears to have a significant influence on water absorption. All the bricks fulfill the water absorption requirements of the Spanish standard UNE 67-019.

In order to make an in-depth study of durability, full-size bricks were prepared and fired, all with calcium carbonate less than 5%. A control series with no calcium carbonate was also prepared for reference. The bricks were subjected to wet & dry cycles in three phases: immersion in water for 16 hours at room temperature (20°C), forced desiccation in an oven at 100°C for 6 hours and cooling to room temperature (20°C) for 2 hours. The bricks were also subjected to crystallization tests in three phases: immersion

in sodium sulphate (14%) (20°C) for 4 hours, oven drying at 100°C for 16 hours, and cooling at room temperature (20°C) for 4 hours.

Figure 9 shows the bricks fired at 900°C for 3 hours that were subjected to wet & dry tests. The control series is on the right side, and the 5% calcium carbonate bricks are on the left side. No major differences in weight or size were observed after 10 cycles. The bricks made with calcium carbonate did not show cracks or delamination, potentially caused by slaking of calcium oxide.

Figure 10 gives an overview of the bricks subjected to salt crystallization tests. The control specimen is labeled as MP-1, and the remaining bricks were manufactured with 5% calcium carbonate. The rate of weight loss and deterioration due to salt crystallization appears to be the same in both the control and bricks made with 5% calcium carbonate. These initial tests indicate that adding calcium carbonate does not weaken the matrix against internal volume changes due to salt crystallization. However, more extensive durability investigations are required before definitive conclusions can be made.

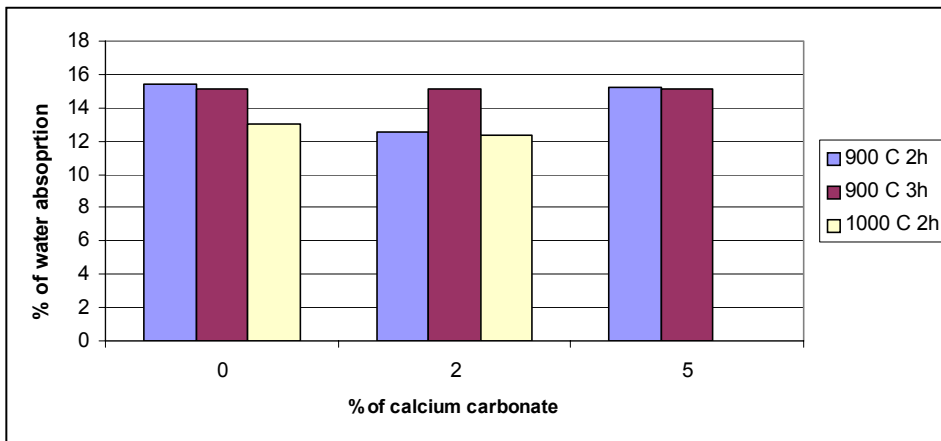


Figure 8 Results of water absorption tests



Figure 9 Results of wet & dry tests performed on real bricks



Figure10 Results of salt crystallization tests performed on real bricks

4. CONCLUSIONS

Based upon the tests outlined in this paper, the following conclusions are made:

1. The addition of small amounts of calcium carbonate (under 5%) to the clay used to manufacture fired clay bricks increases their compressive strength in the range of 40-50% when the bricks are fired at 900°C. The best results are obtained for a 2% (mass) proportion of calcite:clay. Firing time does not seem to have a great influence. Raising the temperature to 1000°C results in a decrease in compressive strength in bricks made with calcium carbonate, apparently caused by the decarbonation of the calcite to form CaO, whose subsequent hydration can cause rapid expansion and microcracking.
2. Adding calcium carbonate brings about an increase of the amount of small pores (pores having radius under 1µm) in all bricks where calcium carbonate is added. These pores result from the formation of CaO, and the microcracks produced during the expansion caused by the hydration of CaO. Cracking is more intense in bricks fired at 1000°C. The differences in micro-porosity do not seem to have a significant influence on the water absorption.
3. Calcium carbonate addition is more effective when the bricks are fired at 900°C because at this temperature decomposition of the calcium carbonate will occur more slowly than at higher temperatures. There appears to be two potential reactions during decomposition of calcium carbonate that influence subsequent performance: (a) rapid decarbonation of the larger calcium carbonate grains, and (b) reactions of calcite with clay minerals to form new phases that predominate when smaller calcium carbonate grains are present.
4. The main new phase formed as a result of firing is anorthite, which is a larger component in bricks fired at 1000°C, but also exists in bricks fired at 900°C. Anorthite occurs in well distributed dense areas, thus contributing to improving the mechanical properties of the matrix.
5. The durability tests performed on real bricks made with calcium carbonate proportion less than 5% appear to indicate that adding calcium carbonate does not contribute to weakening of the brick matrix during exposure to the elements. No major differences in performance were found in comparison with the control series, made with no CC.

ACKNOWLEDGEMENTS

The authors wish to thank the German Academic Exchange Service (DAAD), Alexander von Humboldt Foundation, Germany and the International Fellowships programme of the University of Calgary for financial support of this work.

REFERENCES

1. HATZL, T, D-München; Peer-L. Gehlken, D-Ebergötzen Mineralische Rohstoffe in der Ziegelindustrie – Wichtige Parameter in der täglichen Praxis des Geowissenschaftlers (Mineral raw materials in the brick industry- important parameters for the geologists) (Part 1 and 2). Journal Ziegelindustrie International ZI – 11 and 12/2001).
2. HUIZER, A and DAY, R L. A Fly-Ash Masonry Unit, Alberta Municipal Affairs Report ISBN: 0-88654-425-4, February, 1994, pp. 47.
3. TRAORE, K, KABRE T S and BLANCHART, P. Gehlenite and anorthite crystallization from kaolinite and calcite mix. Ceramics International 29 (2003) 377-383.
4. TRAORE, K and BLANCHART, P. Structural transformation of a kaolinite and calcite mixture to gehlenite and anorthite. Journal of Material Research, Vol. 18, February 2003.
5. MAYORAL, M C, IZQUIERDO, M T, ANDRES J M and RUBIO, B. Aluminosilicates transformations in combustion followed by DSC. Thermochemica Acta 373 (2001) 173-180.
6. CULTRONE, G, SEBASTIÁN, E, ELERT, K, de la TORRE, M J, CAZALLA, O and RODRÍGUEZ-NAVARRO, C. Influence of mineralogy and firing temperature on the porosity of bricks. Journal of the European Ceramic Society 24 (2004) 547-564.
7. CULTRONE, G, de la TORRE, M J, SEBASTIÁN, E, CAZALLA, O and RODRÍGUEZ-NAVARRO, C. Behaviour of bricks simples in aggressive environments. Water, Air and Soil Pollution 119: 191-207, 2000.