EFFECT OF CARBONATES ON FIRING SHRINKAGE AND ON MOISTURE EXPANSION OF POROUS CERAMIC TILES

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ABSTRACT

The effects of calcium carbonate and magnesium carbonate on firing shrinkage and on moisture expansion were investigated, as a function of chemical composition and firing temperature of ceramic bodies. The mineralogical composition of the specimens was examined by X-ray diffraction. The results showed that additions of calcium carbonate improved the resistance of ceramic bodies to moisture expansion and reduced the firing shrinkage. On the other hand, additions of magnesium carbonate increased the moisture expansion of ceramic bodies. The firing shrinkage was slightly increased by adding magnesium carbonate, particularly in bodies fired at high temperatures.

INTRODUCTION

Moisture expansion and firing shrinkage are characteristics that affect the product quality and they must be controlled mainly, in porous ceramic tiles produced through fast single firing.

In contact with moisture, the constituent phases of ceramic bodies can adsorb water, resulting in an overall increase of the body dimensions. This moisture expansion may cause crazing in glazed ceramics and the failure of ceramic tiles[1]. Moisture expansion is

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[1]. Enrique, J.; Beltran, V.; Negre, P.; Feliú, C.; *Técnica Cerámica*, 183, p. 282-297, 1990.

related to mineralogical constitution of the fired body and the surface energy of the constituent's phases is pointed out as the driving force of the phenomenon[2, 3]. This implies that amorphous silicates due to their high surface energies are the main responsible for water adsorption. Otherwise, crystalline phases are least susceptible to moisture expansion because they usually have low specific surface area and then, relatively low surface energies. Glassy phases, when leached, can expose surfaces like those of amorphous silica and then contribute to moisture expansion[4].

Calcite ($CaCO_3$) is usually introduced in the composition of ceramic tiles to control the firing shrinkage and then, enables a perfect fit between the body and the glaze. On the other hand, the carbonate decomposition ($CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$) occurs in a temperature range of 750°C to 950°C, corresponding to the melting zone of traditional glazes. The release of CO_2 in this temperature range causes the bloating of the glazed surface[5]. Magnesite ($MgCO_3$) have a lower decomposition temperature ($\approx$700°C) that allows the use of glazes having lower softening temperatures. These glazes require less expensive raw materials. Nevertheless, a substitution of calcite is only possible if the effects of magnesium carbonate on tiles characteristics, such as firing shrinkage and moisture expansion, are comparable with those obtained by using calcium carbonate. These effects were investigated in the present study.

EXPERIMENTAL PROCEDURE

Specimens were formed from the following raw materials: kaolin, quartz and controlled additions of calcite ($CaCO_3$) and magnesite ($MgCO_3$). The bodies were pressed in a hydraulic press at 24,5 MPa, with dimensions of 55 x 126.mm^2. Then, they were fired at three different temperatures: 1050, 1125 and 1200°C, with a heating rate of 40°C/min.

The specimens lengths were measured before firing and after firing for the determination of firing shrinkage. In order to determine moisture expansion the specimens were reheated at 550°C, to remove the expansion that has occurred after they left the kiln. Then, the bodies were placed in a steam autoclave and submitted to 500 kPa for 4 hours. The measurement was made at an apparatus for linear measurement to the nearest 0,01 mm. For the determination of the mineralogical phases, the specimens were milled and submitted to x-ray diffraction (Cu-Kα).

RESULTS AND DISCUSSION

Figure 1(a) shows the firing shrinkage as a function of firing temperature for bodies with additions of $CaCO_3$. Higher shrinkage was obtained for specimens fired at higher temperatures. As the $CaCO_3$ content increases from 5 to 15%, the firing shrinkage gradually decreases.

The effect of calcium carbonate on moisture expansion is shown on figure 1(b). The

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[2]. SMITH, A. N.; *Trans. Brit. Ceram. Soc.*, 54 (5), p. 300-318, 1955.

[3]. LIRA, C.; *"Efeito de Carbonatos de Ca, Mg e Li e do Ciclo de Queima na Expansão por Umidade de Materiais Cerâmicos Porosos para Revestimento"*; Dissertação de Mestrado, Universidade Federal de Santa Catarina, 1997.

[4]. YOUNG, J. E.; BROWNELL, W. E.; *Journal of the American Ceramic Society"*; 42 (12), p. 571-581, 1959.

[5]. FABBRI, B.; *Ceramic Industries International*, p. 12-15, august, 1993.

autoclave expansion is related to $CaCO_3$ content for three firing temperatures. The addition of calcium carbonate causes a decrease in moisture expansion. This effect was more accentuated for specimens fired at 1200°C than for specimens fired at lower temperatures.

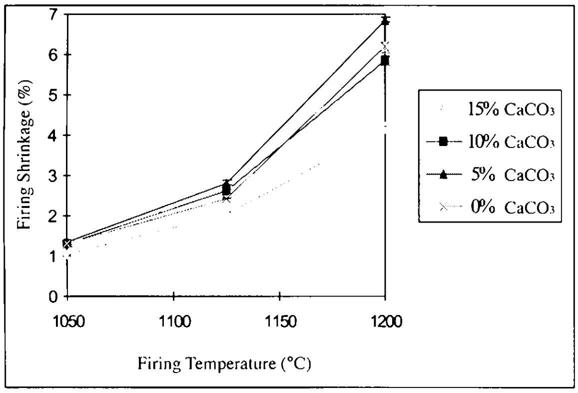

Figure 1: a) Linear shrinkage as a function of firing temperature for different $CaCO_3$ contents.

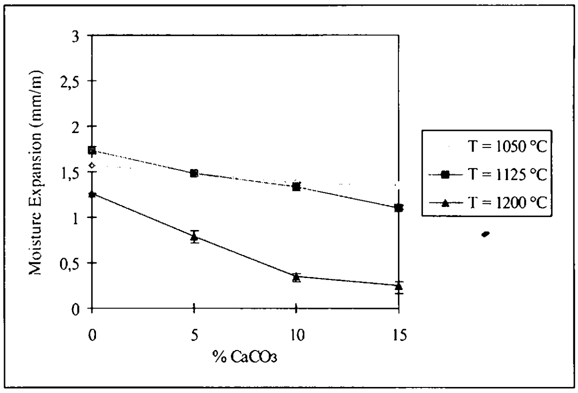

Figure 1: b) Effect of $CaCO_3$ on moisture expansion of ceramic bodies (T = firing temperature).

The influence of calcium carbonate on moisture expansion and firing shrinkage can be related to mineralogical constitution of the body. Figure 2(a) shows the mineralogical analysis of specimens with 15% of calcium carbonate after firing. After sintering at 1050°C, the crystalline phases gehlenite ($2CaO.Al_2O_3.SiO_2$), anorthite ($CaO.Al_2O_3.SiO_2$) and some mullite ($3Al_2O_3.2SiO_2$) have formed. At higher firing temperatures anorthite and mullite were better developed and gehlenite was reduced. Gehlenite and anorthite are calcium aluminosilicates and have resulted from reaction between calcium oxide and the product of decomposition of clay minerals during firing. In this reaction, calcium oxide consumed amorphous phases, which could hydrate, to form crystalline phases, which are resistant to moisture expansion. In this manner, the presence of calcium carbonate favored a smaller moisture expansion of specimens. At higher temperatures more crystalline phases are favored and, therefore, specimens fired at 1200°C presented lower moisture expansion.

The behavior of the firing shrinkage curves on Figure 1(a) can also be explained by the formation of crystalline phases in firing of bodies. From dehydration of kaolinite results an amorphous product named metakaolinite. Around 980°C metakaolinite decomposes to form mullite and releases amorphous silica[6]. This silica, at higher temperatures, start to dissolve forming a liquid phase. However, if the reaction of calcium oxide and metakaolinite occurs, the silica is consumed for the formation of aluminosilicates and will not be available to form liquid phase. Thus, the formation of calcium aluminosilicates seems to involve a smaller amount of liquid phase during sintering, thereby resulting in a smaller firing shrinkage.

Figure 2(b) shows the mineralogical analysis of specimens with 15% of magnesium carbonate. After firing at 1050°C, the crystalline phases present were quartz and periclase (MgO). At higher temperatures mullite appears and, at 1200°C, it can be observed some presence of sapphirine ($4MgO.5Al_2O_3.2SiO_2$). These results demonstrated that magnesium oxide practically did not react with the other constituents to form crystalline phases.

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[6]. KINGERY, W. D.; BOWEN, H. K.; UHLMANN, D. R.; *John Wiley & Sons Inc.*, 2nd ed., New York, 1976.

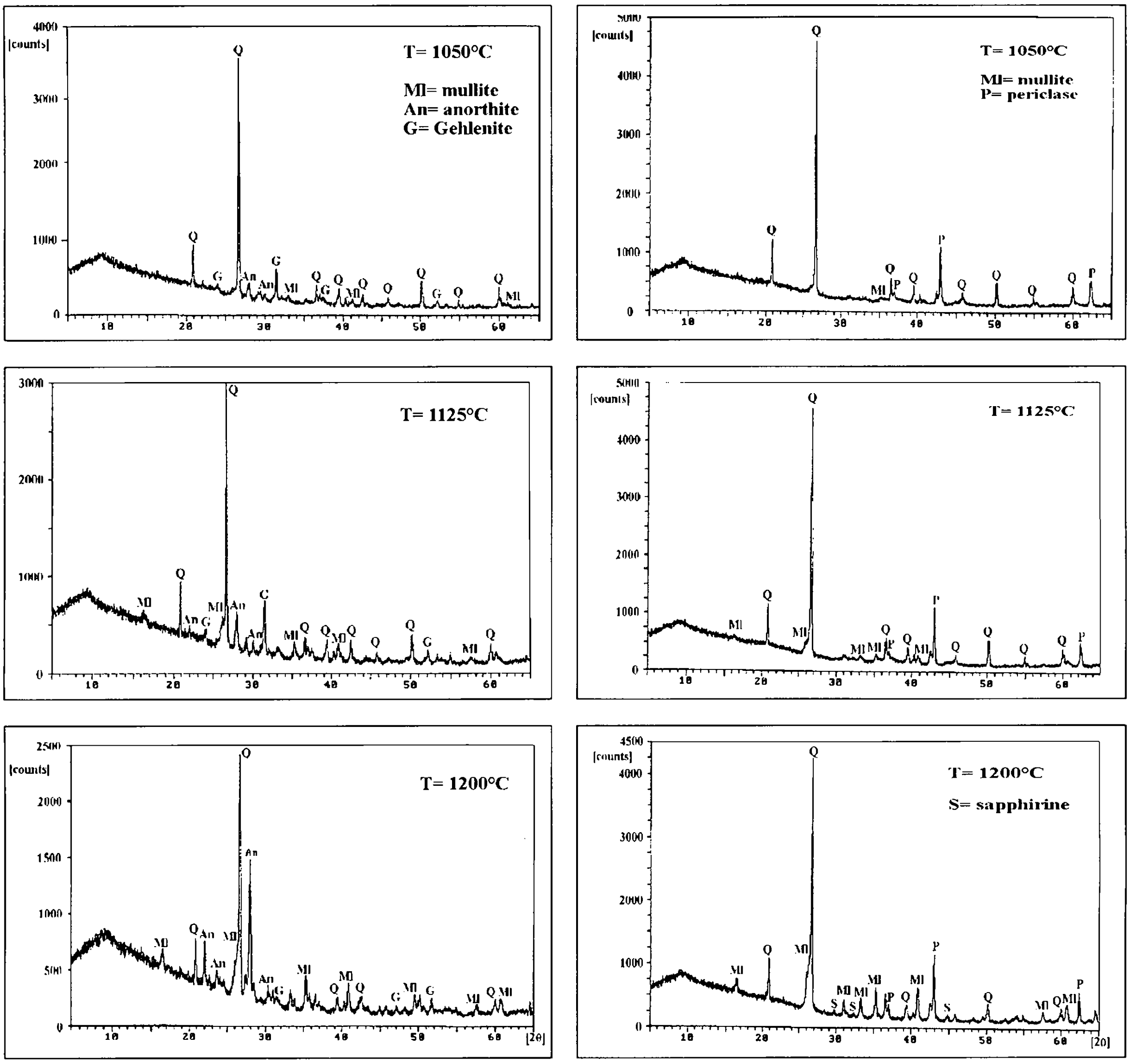

Figure 2. Mineralogical analysis of specimens with addition of: a) 15% de $CaCO_3$ and b) 15% de $MgCO_3$.

Firing shrinkage curves for specimens with additions of magnesium carbonate are shown on figure 3(a). At lower temperatures the $MgCO_3$ content does not affect significantly the linear shrinkage. In the other hand, at 1200°C, an increase in magnesium carbonate content causes a notable increase (≈ 6% to 9%) in the firing shrinkage. Since magnesium oxide did not react to form aluminosilicates, amorphous silica was free to form liquid phase. At 1200°C, the MgO possibly form eutectics favoring liquid phase formation and therefore increasing linear shrinkage.

On figure 3(b), it can be observed an increase in moisture expansion with increasing $MgCO_3$ content, for specimens fired at 1050 and 1125°C. In the case of the 1200°C firing, the curve showed a distinct behavior: the addition of magnesium carbonate caused a decrease in moisture expansion.

Figure 4 shows the mineralogical analysis of specimens with 15% of magnesium fired at 1200°C, after autoclave treatment. The presence of magnesium hydroxide ($Mg(OH)_2$ - brucite) denotes that magnesium oxide have hydrated on autoclave treatment. For this reason, additions of $MgCO_3$ cause moisture expansion to be high. The decrease of moisture expansion with increasing amounts of $MgCO_3$

for specimens fired at 1200°C (Figure 3.b) can be related to firing shrinkage results. Firing at this temperature causes a drastic increase in linear shrinkage (Figure 3.a), denoting a pronounced reduction in porosity of specimens. In reduction of porosity, penetration of water inside the body becomes difficult and moisture expansion results smaller.

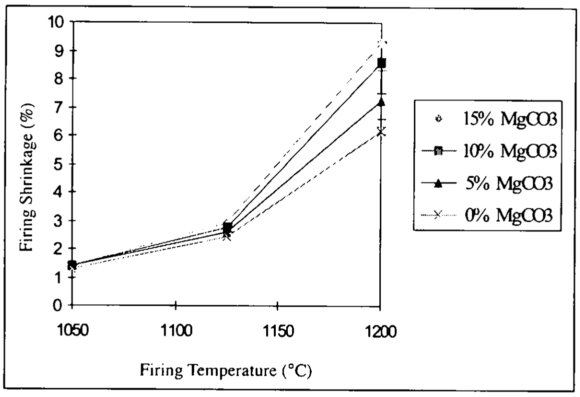

***Figure 3: a)** Linear shrinkage as a function of firing temperature, for different $MgCO_3$ contents.*

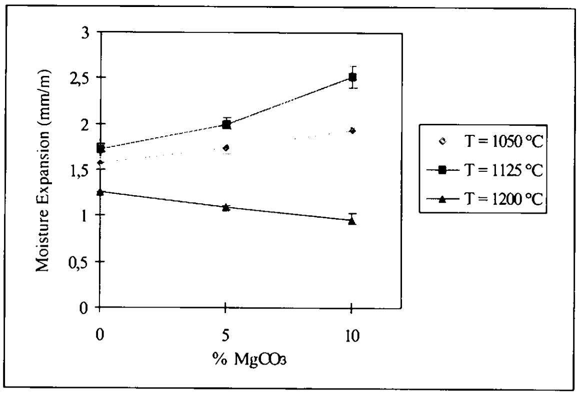

***Figure 3: b)** Effect of $MgCO_3$ on moisture expansion of ceramic bodies (T = firing temperature).*

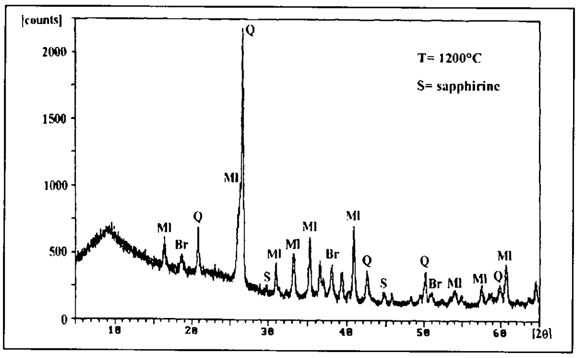

***Figure 4.** Mineralogical analysis of specimens with addition of 15% de $MgCO_3$, after autoclave treatment.*

CONCLUSIONS

- Increasing amounts of calcium carbonate (5, 10 e 15%) in ceramic bodies composition reduces their moisture expansion as well as their firing shrinkage. This effect is related to the reaction of calcium oxide with the other mineralogical constituents to form crystalline calcium aluminosilicates.

- Additions of magnesium carbonate (5 e 10%) tends to increase moisture expansion, since magnesium oxide remains unreacted on firing and so susceptible to hydration. Increasing amounts of magnesium carbonate induce firing shrinkage to increase. It seems that magnesium oxide favor liquid formation on sintering reducing the porosity of the body. If reduction in porosity is accentuated, the moisture expansion can be reduced.

- Firing at higher temperatures (1200°C) improves crystallinity, and reduces moisture expansion for both carbonates additions.

It can be conclude that the effects of magnesium carbonate on moisture expansion and firing shrinkage do not favor its introduction on tiles composition, while calcium carbonate confirmed good characteristics with respect to firing shrinkage and also to moisture expansion control in ceramic bodies.

AKNOWLEDGMENT

The authors extend their grateful thanks to Mr. Ângelo A. Bianchi, Edison L. Honorato from Centro de Pesquisas Eliane and to CTC - Centro de Tecnologia Cerâmica, Criciúma - Brazil, for their helpful discussions and experimental assistance.