

The Effect of CaO Addition on Mechanical Properties of Ceramic Tiles

Lucie Vodova, Radomir Sokolar, Jitka Hroudova

Abstract—Stoneware clay, fired clay (as a grog), calcite waste and class C fly ash in various mixing ratios were the basic raw materials for the mixture for production of dry pressed ceramic tiles. Mechanical properties (water absorption, bulk density, apparent porosity, flexural strength) as well as mineralogical composition were studied on samples with different source of calcium oxide after firing at 900, 1000, 1100 and 1200°C. It was found that samples with addition of calcite waste contain dmisteinbergit and anorthite. This minerals help to improve the strength of the body and reduce porosity fired at lower temperatures. Class C fly ash has not significantly influence on properties of the fired body as calcite waste.

Keywords—Ceramic tiles, class C fly ash, calcite waste, calcium oxide, anorthite.

I. INTRODUCTION

IN the past decades there has been continuing effort to use various kinds of waste in the ceramic industry. For example, fly ash has been used in the manufacturing of ceramic wall and floor tiles [1], [3], [5]. It is also possible to use fly ash in brick industry [4]. There are similarities between chemical and mineralogical composition of fly ash and ceramic raw materials (clay or brick soil).

Fly ash is a mixture of SiO₂, Al₂O₃, Na₂O, Fe₂O₃, CaO etc. According to ASTM C618 we can find two types of fly ash. Class F is classical high temperature fly ash where burning temperature is up to 1450°C. Class C fly ash (or fluidized fly ash) is generated during burning a fine grain mixture of coals powder and limestone or dolomite at lower temperatures (usually up to 900°C). The basic difference between C and F class ash consist in the mineralogical composition. Class F contain up to 80 % glassy phase and up to 20% mullite. Class C ashes are characterized by their higher SO₃ content (in the form of anhydrite CaSO₄), free calcium oxide and calcite. Therefore, it is possible to use class C fly ash as a source of calcium oxide.

An advantage of calcite (calcium oxide) addition is a small irreversible contraction of the fired body during after firing. That is caused by the presence of anorthite and gehlenite.

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Creation of gehlenite and anorthite is accompanied with an increase in the fired body's volume [1], [2].

The objective of this paper is an experimental investigation of mechanical properties of samples with a different source of calcium oxide depending on firing temperature.

II. MATERIALS AND METHODS

Kaolinic clay B1 was applied as the plastic component in the raw material mixture, as it belongs in the group of refractory clays with a good binding power and sinterability (sintering temperature max. 1250°C) It contains 85% of grain below 2µm (sedimentation analysis). Mineralogical composition of used clay is kaolinite, illite, hydromuskovite and quartz.

As grog we used clay B1 fired at 1000°C with a soaking time 90 min at the maximum temperature.

Calcite waste came from crushing of the limestone.

Class C fly ash from Hodonin thermal power plant was used. Chemical composition of raw materials is shown in Table I.

TABLE I
CHEMICAL COMPOSITION OF RAW MATERIALS

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO	SO ₃	LOI
Clay	48.6	33.8	2.6	0.28	0.1	1.98	0.36	0	11.3
Calcite waste	0.01	0.08	0.09	54.55	-	0.02	0.6	0.87	43.77
Fly ash	28.6	16.4	6.9	32.7	0.9	0.6	4.3	4	5.1

TABLE II
MIXING PROPORTION

	Clay	Grog	Calcite waste	Fly ash
I	60	40	-	-
II	60	30	10	-
III	60	20	20	-
IV	60	20	-	20

Grog was ground and sieved and then mixed with clay, milled calcite waste/fly ash. Dry mixture was homogenized in laboratory homogenizer for 2 hours. Raw materials were moistened to obtain a plastic mass (water content 30%). Test samples of size 100x50x20mm were prepared by hand churning of a plastic mass into metal mold according to ČSN 72 1565-4. Samples were dried at 110°C.

Green bodies were fired in electric laboratory furnace at 900, 1000, 1100 and 1200°C with heating rate 4°C/min and 30min soaking time at the maximum temperature. The subsequent cooling proceeded spontaneously following the natural cooling rate of the furnace.

After firing, the body properties were defined according to

the official testing standard EN ISO 10 545 (water absorption E, bulk density B, apparent porosity P, apparent density T). The flexural strength σ_f was measured using the three point bending method and was calculated from formula

$$\sigma_f = \frac{3.F.l}{2.a^2} [\%],$$

where F is the maximum loading force at the moment of rupture, l is the span between supports and a is the dimension of the square cross-section.

Firing shrinkage FS was calculated according to the following formula:

$$FS = \frac{(l_f - l_d) \times 100}{l_d} [\%]$$

where l_d is length of dried test samples (mm) and l_f is the length of fired test samples (mm).

The XRD analysis was performed with the diffractometer Phillips PW 1170 (with $\lambda = 0.15406$ nm).

III. RESULTS OF EXPERIMENTS

At the lower firing temperatures (900 and 1000°C) calcite waste works as a flux (samples II and III), porosity of fired body is significantly decreased (Fig. 1). It leads to improvement of flexural strength and increasing of firing shrinkage (Table III).

At the highest firing temperature (1200°C) is sample porous, water absorption exceeded 25% (Fig. 1). This can be explained by stopping sintering due to the crystallization of anorthite (Figs. 5, 6).

Addition of class C fly ash at the lowest firing temperature (900°C) slightly increases water absorption compared to the sample reference (signed as I), at higher firing temperatures water absorption decreases (Fig. 1). While flexural strength is higher in comparison with samples I without calcite waste (fly ash).

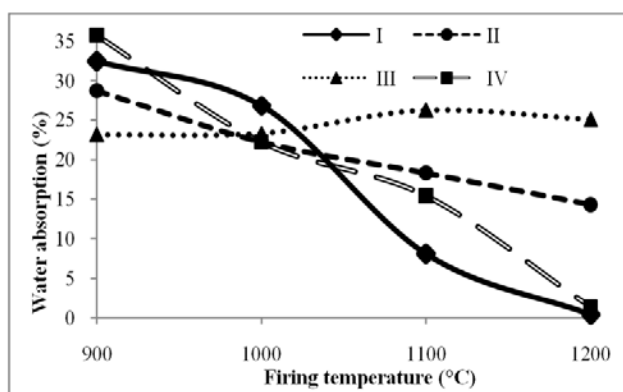


Fig. 1 Water absorption of fired samples

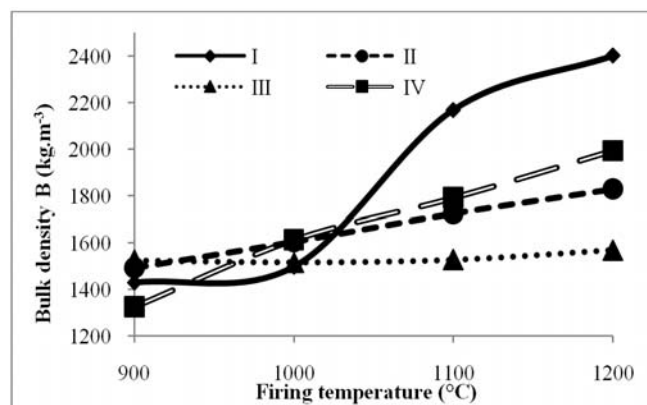


Fig. 2 Bulk density of fired samples

TABLE III
PROPERTIES AFTER FIRING

	FS (%)	P (%)	T (kg/m³)	σ_f (MPa)	
900°C	A	0.74	43.31	2717	10,5
	B	1.34	34.22	2629	15,8
	C	2.07	26.32	2333	19,5
	D	1.86	38.94	2539	14
1000°C	A	2.91	37.75	2533	16,2
	B	3.81	27.31	2514	28,5
	C	2.69	25.86	2334	25,9
	D	7.25	27.25	2516	24,8
1100°C	A	11.52	11.91	2606	22,5
	B	6.01	22.73	2625	34,4
	C	2.77	25.62	2474	30,5
	D	11.47	15.57	2471	35,5
1200°C	A	13.11	0.05	2490	75,4
	B	5.88	13.08	2584	38,9
	C	2.91	21.96	2574	32,2
	D	13.49	1.09	2068	45,3

The addition of calcite waste has a significant impact on reducing the length changes during firing; firing shrinkage ranges 2 to 3% at all firing temperatures.

Based on the results DKTA analysis can be seen that the addition of calcite waste (clear form Fig. 3) reduce firing shrinkage of samples. The more calcite is added, the lower shrinkage is. Formation of anorthite is evident from a temperature 950°C when in samples II and III almost stops firing shrinkage in comparison with a reference sample I which was significantly sintered.

The addition of fly ash reduces the length changes during firing, but the content of calcium oxide is much lower, so its effect is not as evident as the samples II or III.

Both admixtures can be described as a melting agent accelerating sintering of samples at lower firing temperatures.

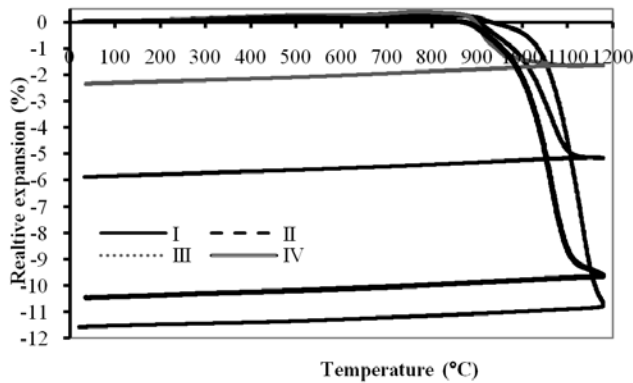


Fig. 3 Therm dilatometric curves of the samples

After firing at the lowest temperature of 900°C can be observed in all samples mica residues that disappears with higher temperatures.

For reference sample marked I is a typical formation of mullite observed from firing temperature of 1100°C with consequent increase of its content in the body and the formation of cristobalite (firing at 1200°C).

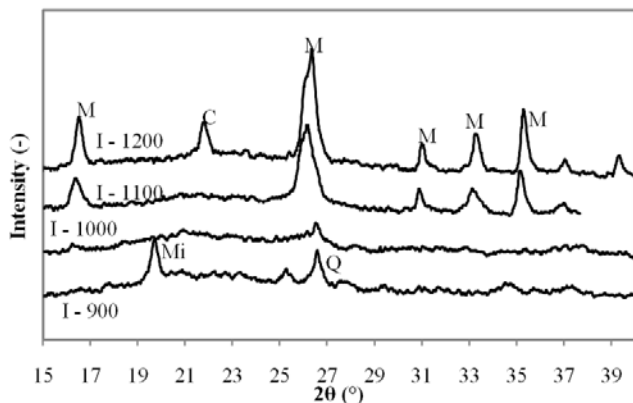


Fig. 4 Mineralogical composition of fired body I - M – mullite, C – cristobalite, Q – quartz, Mi - mica

CaO content in the mixture has a significant influence on the mineralogical composition of the fired body.

For samples containing calcite waste in the raw material mixture occurs at lower temperatures (900 and 1000°C) hexagonal dmisteinbergite which may be taken as an analogy primary anorthite (LAS) described in [2], which has the same composition as the triclinic anorthite. With increasing firing temperature decreases the amount of dmisteinbergite and increases the amount of anorthite. Mullite in samples II and II is almost not detected, only there are signs of its existence after firing at 1200°C.

At the firing temperature 900°C and 1000°C can be identified anorthite in the sample labeled IV (containing class C fly ash in the raw material mixture).

At higher temperature the anhydrite decomposes and formed CaO reacts to form anorthite. After firing at a temperature 1100°C can be found in sample IV mineralogical symbiosis of anorthite and mullite.

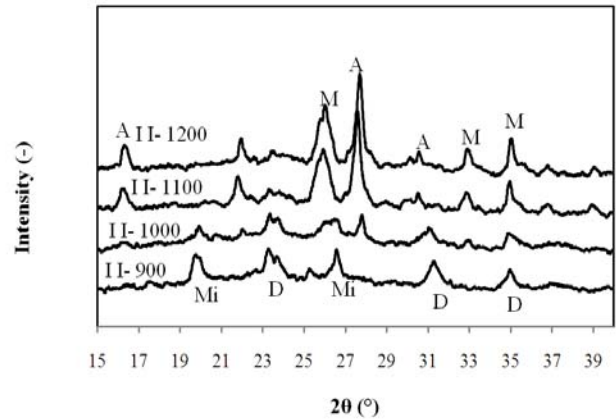


Fig. 5 Mineralogical composition of fired body II (10 % of calcite waste) – A- anorthite, D – dmisteinbergite, Mi - mica

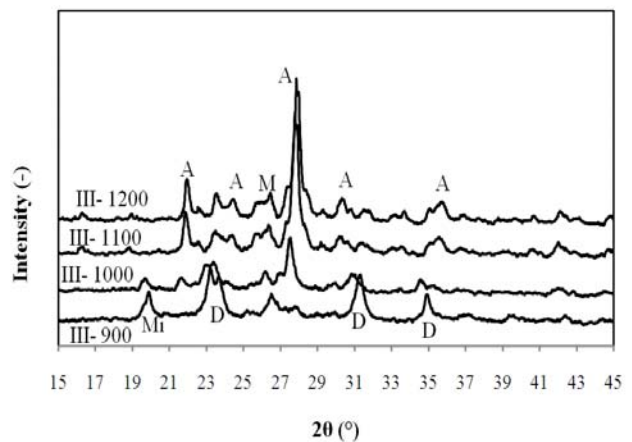


Fig. 6 Mineralogical composition of fired body III (20 % of calcite waste) – A- anorthite, D – dmisteinbergite, Mi - mica

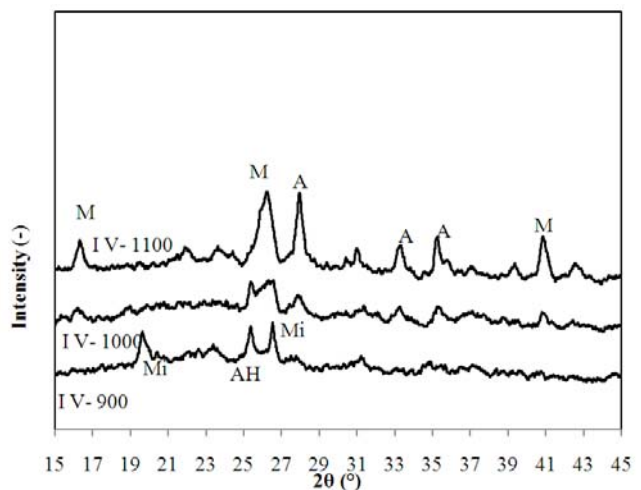


Fig. 7 Mineralogical composition of fired body III (20 % of fly ash) – A- anorthite, AH - anhydrite, Mi - mica

IV. CONCLUSION

The aim of experimental work was to evaluate the effect of addition of CaO from various sources on the properties of fired body.

Mechanical properties of four types of samples (reference sample without calcite waste, sample with 10 wt.%, sample with 20 wt.% of the calcite waste and sample with 20 wt.% of class C fly ash) were investigated after their firing at 900, 1000, 1100 and 1200°C. It was found that:

The addition calcite waste to clay significantly reduces the firing shrinkage and at lower temperatures (up to 1000°C) reduces the porosity of the fired body. With increasing the firing temperature, the porosity of the body does not change significantly, only its flexural strength is improved.

CaCO₃ content in the mixture at lower temperatures leads to the formation of polymorphic modifications of anorthite, called dmisteinbergite.

Class C fly ash addition is useful for use at high firing temperatures (1200°C). Water absorption is under 2%.

Anorthite and mullite are the main crystalline phases of the samples fired at 1200°C. The higher the temperature of the firing and the higher the amount of calcite, the more anorthite is created in the samples.

A presence of calcite waste decreases a sample contraction during sintering.

Water absorption decreases with the increase of the firing temperature, but the sample with the content of calcite 10 wt.% shows approximately constant absorptivity.

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