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Carbonation of Alumina Cement-bonded Conventional Refractory Castable in Fireplace

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It was determined by verification by in situ analysis that combustion products of firewood in fireplaces cause carbonation of alumina cement-bonded conventional refractory castable and accelerate its destruction. The carbonation of hydrated cement (Gorkal 40) paste was modeled in a laboratory conditions: having been fired at various temperatures (300 ºC – 950 ºC) the specimens were curing in humid conditions for two days. It was determined by X-ray analysis that the hydrates CAH_{10}, C_2AH_8 and C_3AH_6 change into a mineral $C_{12}A_7$ after the cement paste are fired at 300 ºC – 800 ºC temperatures. The amount of the mineral depends on the firing temperature. In humid conditions $C_{12}A_7$ hydrates and carbonizes, consequently calcium carboaluminate hydrate forms. In the composition of cement and microsilica (9 %) carbonation of cement hydrates noticeably slow down at the same conditions. Carbonized minerals are not identified when the specimens are fired at 500 ºC –850 ºC temperatures.

Keywords: alumina cement-bonded castable, carbonation, X-ray analysis, microsilica.

INTRODUCTION

Domestic boilers, furnaces and fireplaces that are heated by biofuel (fire-wood, wood waste, peat) are widely used in Lithuania. The observations show, that the lining of such furnaces, which is made using conventional alumina cement-bonded castable, has not long durability. Having been exploited for some time, it destructs. In cases when gas or fuel oil is used to heat up furnaces, the exploitation period of analogical linings is 2 – 3 times longer than in cases when biofuel is used.

One of the reasons that cause this destruction might be carbonation of alumina cement hydration phases. It is known that the main hydration phases forms during the reaction between alumina cement and the water are as follow: CAH_{10} (forms at the temperature <21 ºC), C_2AH_8 and AH_3 (21 – 35 ºC), C_3AH_6 and AH_3 (>35 ºC) [1]. CAH_{10} and C_2AH_8 are meta-stable therefore depending on temperature and other factors that change into C_3AH_6 and AH_3. It is indicated [2] that refractory castable start to deteriorate by peeling-off of material due to carbonation if it is not exploited, i.e. not fired for a long time after its production. The practical observations [2] of refractory castable reveal the following tendencies:

1. Carbonation occurs easily in lightweight castables, but hardly at all in dense castables;
2. Carbonation occurs easily in not dried products and hardly at all in dried castables;
3. Carbonation occurs easily in an environment with high temperature and humidity;
4. When not dried products are exposed to rain, the carbonation rate is highly accelerated.

The carbonation of alumina cement's phases is thought to occur by the following reactions [3]:

$$CAH_{10}+CO_2+xH_2O \rightarrow CaCO_3+Al_2O_3\cdot yH_2O+(10+x-y)H_2O; \quad (1)$$

$$C_2AH_8+2CO_2+xH_2O \rightarrow 2CaCO_3+Al_2O_3\cdot yH_2O+(8+x-y)H_2O; \quad (2)$$

$$C_3AH_6+3CO_2+xH_2O \rightarrow 3CaCO_3+Al_2O_3\cdot yH_2O+(6+x-y)H_2O. \quad (3)$$

In various works [4 – 6] the influence of curing temperature (5 ºC – 60 ºC) on the carbonation of hydrates was analyzed. It is being stated that the rate of carbonation is higher at 20 ºC temperature when not stable CAH_{10} is in composition. However, the carbonation of C_2AH_8 is considerably higher when humidity is increased [2]. C_3AH_6 distinguishes as having the lowest rate of carbonation.

It is known that under the influence of temperature hexagonal hydrates (CAH_{10} and C_2AH_8) converse to cubic hydrates (C_3AH_6). For this reason the porosity of cement paste increases and the compressive strength decreases. The literature [6 – 8] says that in most cases newly formed carbonates increase the compressive strength of such compositions. It is pointed out that a considerable amount of carbonates forms due to the fact that CO_2 may penetrate the porous structure of the material much easier.

In certain conditions carbonation causes an absolute destruction of the material. It was noticed [2] that the specimen of castable partially immersed into the water totally destructs due to strong carbonation in the area where it contacts with the water. Carbonation also causes a large-scale destruction of alumina cement materials because Na^+, K^+ ions participate in alkaline hydrolysis [7-9].

Approximately 15 % of CO_2 and 25 % of H_2O form in combustion products of firewood, therefore, it might be forecasted that a repeated hydration of cement's minerals may occur in such conditions. Thus, due to the influence of CO_2, H_2O, KOH and NaOH, which are in combustion products, the carbonation may start.

In order to determine the reasons of destruction that take place in the refractory products, which are made using alumina cement-bonded castable and exploited in furnaces and fireplaces, which are heated by burning wood waste, verification in site and laboratory analysis were carried out.

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EXPERIMENTAL

Experimental work was performed using alumina cement "Gorkal 40", which is manufactured in Poland. The content of Al_2O_3 in cement is not less than 40 %. The main mineral phases are: CA, the ferrite phase, $C_{12}A_7$, C_2AS; bulk density is 1160 kg/m^3, specific surface 0.310 m^2/g – 0.380 m^2/g, refractoriness – not less than 1280 °C.

Microsilica from "Elkem ASA (Norway), SiO_2 makes up not less then 98 % of its composition, bulk density 410 kg/m^3, specific surface 15 m^2/g, L.O.I ~2 % at the temperature of 750 °C.

In order to determine the influence of temperature and water vapors upon the process of castable's destruction, X-ray analysis of cement paste (composition A, alumina cement with W/C ratio = 1) and cement paste with the additive of 9 % of microsilica (composition B) was carried out. There were two stages of the specimens' tests: first, the specimens that had cure 24 hours in normal condition and had been fired at various temperatures that varied from 300 °C up to 950 °C, were analyzed; second, the same specimens after firing had been curing in humid conditions (above water) for two days and only then their roentgenograms were recorded. The quantitative changes of separate minerals were estimated according to the intensity of diffraction peaks.

The X-ray analysis was carried out by X-ray-diffractometer DRON-2 with a cooper anticathode and nickel filter, the voltage of anode 30 kV, current of anode 8 mA, slits of the goniometer – 0.5; 1.0; 0.5 mm, the speed of recording of X-ray-diffraction patterns – 600 mm/min. The phase composition was defined using the ASTM card index of data.

In this work a conventional chamotte concrete of the following composition was used (mass %): chamotte 0 mm – 1 mm – 30; chamotte 1 mm – 5 mm – 30; disperse chamotte – 15; alumina cement – 25; water – 14.5.

Castable cubes of the size (70 × 70 × 70) mm were formed. After 3 days of normal curing, the samples were dried at a temperature of 105 °C ±5 °C for 48 hours. Next, they were kept for three hours under the investigated temperatures 300 °C, 600 °C and 800 °C respectively in an electronic controller furnace and cooled. Then the hardness of castable samples and cold compressive strength were determined. The hardness of the castable was estimated using Rockwell apparatus TP 5043 according to GOST 24622-81.

RESULTS AND DISCUSSION

Practical observation showed, that alumina cement-bonded castable blocks of boilers that are heated by biofuel disintegrate and fracture (Fig. 1).

In order to determine the reasons of destruction of conventional castable, verification by in situ analysis of castable plate was carried out. 25 mm thickness plates were set in a fireplace. The fireplace has been heated 4 hours per day during 100 days. Each day 20 kg of firewood were being burned down. The humidity of the firewood was approximately 50 %.

The temperature of the castable plate inner surface during its exploitation reached up to ~800 °C, outer – ~500 °C. It has to be noted that the fireplace was working cyclically: the castable was being heated up from 20 °C up to 800 °C and cooled down again. It means that the influence of combustion products CO_2, KOH, NaOH, H_2O upon the material might be different at the moments of fluctuation of temperature.

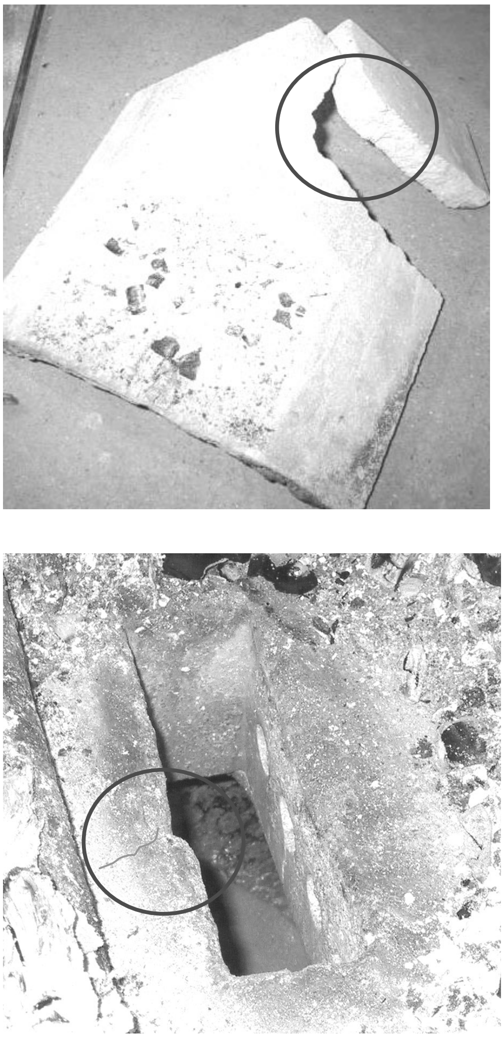

Fig. 1. Examples of castable products destruction in boiler (size (40 × 20 × 5) cm and (60 × 40 × 10) cm)

After 100 days of exploitation the plates were removed from the fireplace and analyzed in a laboratory. The analysis of castable plate showed, that the inner structure of the plate that was affected by combustion products differs greatly from the "cold" side, which leaned against metal shell of the fireplace. The castable of inner side of the plate was grey and fragile. The castable of the outer side was reddish and strong enough. It was determined that the hardness of the plate's inner and outer sides differ greatly after the exploitation: outer – 12.5 HB while inner only ~6 HB.

The hardness of the castable fired at laboratory conditions depending on the temperature might reach up to 15 HB – 30 HB. As it might be noticed (Fig. 2) temperature negatively affects the hardness of the castable: after heating at 110 ºC – 800 ºC temperatures this value decreases 15 % – 45 % (it is due to the dehydration). It has to be noted that the values of the castable's hardness correlate very well with the values of castable's cold crushing strength (Fig. 2). The difference between the values of exploited and not exploited castable hardness showed, that not only temperature but also other factors influence the material destruction during the exploitation. These factors we aimed to reveal in this work.

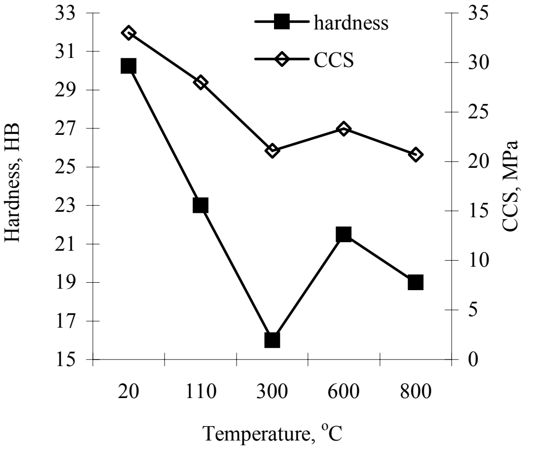

Fig. 2. The dependence of castable hardness and cold crushing strength (CCS) upon the temperature

According to the X-ray analysis of the inner and outer sides of exploited castable plate the following phases were identified: CA, $C_{12}A_7$, C_3AH_6 and C_4AcH_{11} – calcium carboaluminate hydrate ($3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$). This result shows that carbonation occurred in chamotte castable.

Aiming to understand the mechanism of the plate destruction the X-ray analysis of hydrated cement paste was carried out.

After one day of the hardening process of cement paste in the X-ray diffraction pattern of the specimen of composition A hydrates CAH_{10} and C_2AH_8 dominate, ferrite phase as well as gehlenite (C_2AS) are unchanged, and mineral CA not identified.

After firing at the interval of 300 °C – 950 °C temperatures minerals $C_{12}A_7$ and CA were determined, and C_3AH_6 was determined only after firing at 300 °C temperature because it disintegrates at the temperature of 360 °C (Fig. 3). The results might be explained by dehydration scheme of cement mineral hydrates [10]:

$$CAH_{10} \rightarrow C_2AH_8 + AH_3\,; \tag{4}$$

$$C_2AH_8 + AH_3 \rightarrow C_3AH_6 + 2AH_3\,; \tag{5}$$

$$C_3AH_6 + 2AH_3 \rightarrow C_{12}A_7 + CA + H\uparrow\,. \tag{6}$$

Concluding the experiments it may be stated that in dehydrated paste $C_{12}A_7$ mineral forms. This mineral of alumina cement is one of the fastest reacting with water [11]. The amount of this mineral depends on the temperature.

Amount of $C_{12}A_7$ increased when the specimens were fired at the temperatures 600 °C – 900 °C and decreased after 950 °C. It can be notice that CA intensively crystallizes in the composition after firing at 900 °C.

The decrease of $C_{12}A_7$ after firing at 900 °C may be explained by the intensive reaction of CA. The formula of the reaction is as follows [10]:

$$C_{12}A_7 + 5A \rightarrow 12CA\,. \tag{7}$$

When the specimens are fired and cured in humid conditions, C_3AH_6 considerably increases and C_4AcH_{11} appears. It can be seen that C_3AH_6 persists up to 950 °C. The biggest amount of C_4AcH_{11} was identified in the interval of 500 °C – 800 °C temperatures. The higher amount of C_3AH_6 and newly formed C_4AcH_{11} in the specimens, which were cured in humid conditions, explains the lower amount of $C_{12}A_7$ in them (Fig. 4).

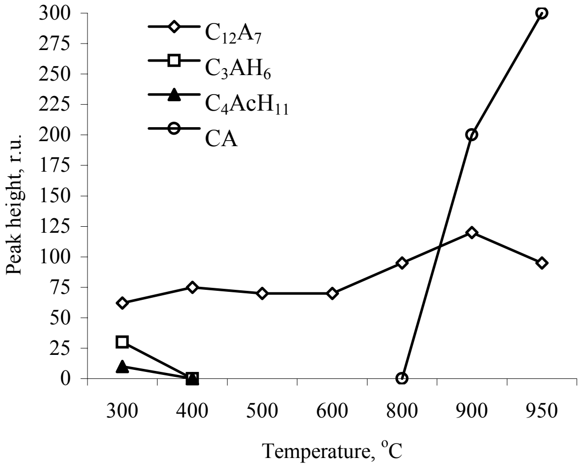

Fig. 3. Changes of peak height of minerals (C_3AH_6 ($d = 0.229$ nm), $C_{12}A_7$ ($d = 0.220$ nm), C_4AcH_{11} ($d = 0.76$ nm) and CA ($d = 0.297$ nm)) representative peak after firing

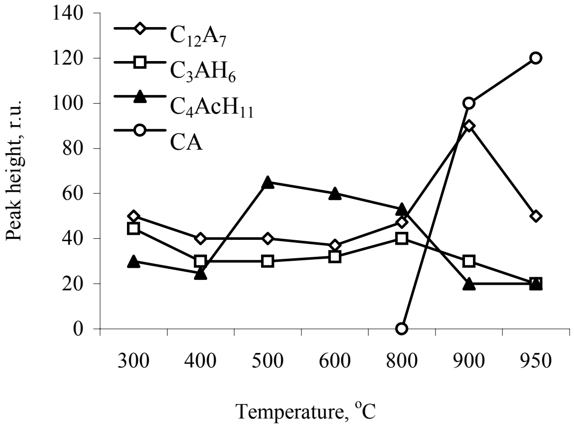

Fig. 4. Changes of peak height of minerals (C_3AH_6 ($d = 0.229$ nm), $C_{12}A_7$ ($d = 0.220$ nm), C_4AcH_{11} ($d = 0.76$ nm) and CA ($d = 0.297$ nm)) representative peak after firing and curing in humid conditions

It can be concluded that $C_{12}A_7$ in humid conditions (as one of the most active minerals of cement) easily hydrates and carbonates further forming C_3AH_6 and C_4AcH_{11}. The volume of newly formed minerals is considerably higher than $C_{12}A_7$. It is obvious that cyclic changes (dehydration at high temperatures, repeated hydration and carbonation in humid conditions, and dehydration of carbonates) of mineral volume may cause a destruction of castable's structure during exploitation of fireplaces or furnaces.

The changes of minerals are different in composition B with the additive of microsilica.

After the hardening process of 24 hours C_2AH_8, CAH_{10}, unchanged gehlenite and ferrite phase as well as CAS_mH_n (it is the product of the reaction between microsilica, minerals of cement and the water) were identified in the specimens of composition B.

After firing at the interval of 300 °C – 850 °C temperatures $C_{12}A_7$ and C_2AS were observed. The quantitative changes are reflected in Fig. 5. Unlike in hydrated cement paste (composition A) in fired specimens of composition B C_3AH_6 is not identified. $C_{12}A_7$ mineral in composition with the additive of microsilica forms according to this scheme [10]:

$$CAH_{10}+CAS_mH_n+S \rightarrow C_2AH_8+AH_3+CAS_mH_n+S; \tag{8}$$

$$C_2AH_8+CAS_mH_n+S \rightarrow C_3AH_6+2AH_3+CAS_mH_n+S; \tag{9}$$

$$C_3AH_6+2AH_3+CAS_mH_n+S \rightarrow C_{12}A_7+CA+H+CAS_mH_n+S. \tag{10}$$

It has to be noted that an intensive additional crystallization of gehlenite is noticed at 850 °C temperature. At this temperature the reactions take place according to this scheme [10]:

$$C_{12}A_7+S \rightarrow C_2AS+A . \tag{11}$$

A small amount of CA_2 and CA also appears (these peaks are not shown in Fig. 5 and Fig. 6).

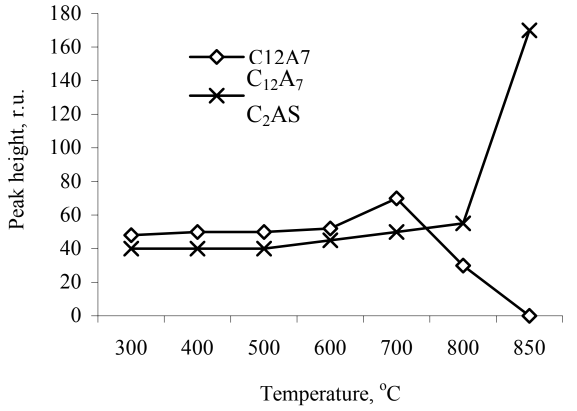

Fig. 5. Changes of peak height of minerals $C_{12}A_7$ ($d = 0.220$ nm) and C_2AS ($d = 0.285$ nm) representative peak after firing

In the specimens cured in humid conditions (Fig. 6) mineral C_3AH_6 forms, but it's amount is smaller than in the specimens of composition A. After firing at 800 °C this mineral is not found any more in the specimens cured in humid conditions.

C_4AcH_{11} mineral has not been identified in the fired specimens, but a small amount of it was found in the specimens that were cured in humid conditions, however, after firing at 500 °C it is not observed (Fig. 6).

After firing at 850 °C $C_{12}A_7$ has not been identified as well as amount of gehlenite considerably increased in any of the specimens (neither in fired nor in cured in humid conditions).

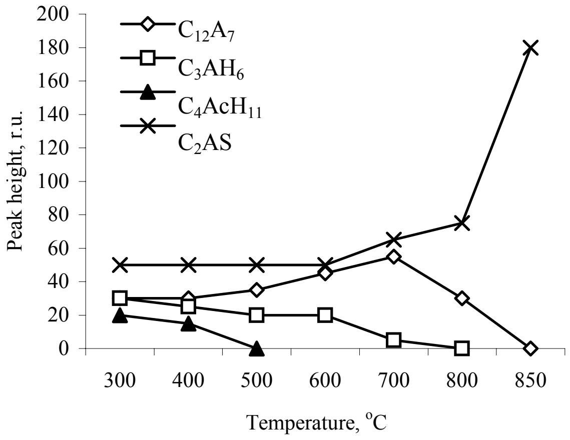

Fig. 6. Changes of peak height of minerals (C_3AH_6 ($d = 0.229$ nm), $C_{12}A_7$ ($d = 0.220$ nm), C_4AcH_{11} ($d = 0.76$ nm) and C_2AS ($d = 0.285$ nm) representative peak after firing and curing in humid conditions

Mineral gehlenite at high temperature forms by the same scheme (11).

The analysis show that in the cement paste (composition A), cement hydrated phases carbonate up to the temperature of 900 °C. As a result of the reaction between the additive of microsilica and the minerals of alumina cement „Gorkal 40", which takes place during the hardening, drying and firing process, the resistance to moisture content as well as to the influence of CO_2 is increased: in the composition B that had been fired at 500 °C – 900 °C temperatures after the repeated hydration carbonates do not form any more and gehlenite, that crystallized additionally, grants better features of the composition due to its low reacting abilities.

CONCLUSIONS

1. The verification by in situ analysis of conventional alumina cement-bonded castable plates was carried out. It was determined that the compressive strength of the castable and its hardness is considerably lower in the area of the contact with combustion products than in the outer side.
2. Laboratory analysis of hydrated alumina cement paste showed that calcium carboaluminate hydrate (C_4AcH_{11}) forms in the paste, which was cured for two days in humid conditions after it has been fired.
3. It was determined that the additive of microsilica increases the resistance of cement paste to the carbonation. In the specimens after firing and curing in humid condition small quantity of carbonated calcium hydroaluminate is identified only below 500 °C temperature.

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