THE EFFECT OF FLUID CATALYTIC CRACKING CATALYST WASTE ON REFRACTORY CASTABLE'S PROPERTIES

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The fluid catalytic cracking (FCC) catalyst waste (CW) is eroded catalyst debris from the cracking unit, which is collected by an electrostatic precipitator. CW is zeolite material, which unique properties are underused in refractory castable production technology. This work deals with untreated CW and thermally treated – CWt. The hydration and structure development of cementitous compositions with CW and CWt were investigated. In comparison with CW, CWt is a considerably softer accelerating additive of cement hydration and a certain amount of this additive (10 - 20 %) markedly increases the compressive strength of cementitious stone. The impact of CWt additive on refractory castable properties was investigated. It was established that the increase of CWt additive content causes the increase of castable's compressive strength and decrease of shrinkage, ensures a more compact structure of castable and best thermal durability versus analogical castable without the additive.

INTRODUCTION

The use of different industrial wastes for building materials makes its possible not only to improve major characteristics of such materials but also to solve environmental problems as well. One of such possible wastes is is the petrochemical industrial CW, resulting from fluid catalytic cracking unit. It is mainly composed of Al_2O_3 and SiO_2 and slightly contaminated with metals, including heavy metals such as vanadium and nickel, occurring on the parts per million levels [1]. Moreover, the CW may contain residues of sulphur and carbon compounds, which have not burnt off during the process of catalyst's regeneration.

In the European Waste Catalogue (Commission Decision 94/3/EEC), the spent fluid catalytic cracking catalysts (code 16 08 04) are classified as non-hazardous. In 2006 the European Cracking Catalysts Producers Association (ECCPA) identified the potential reuses of waste catalyst, which include constructional work, cement, insulation materials and metal casting industry.

Investigations showed that the CW can be used as a fine additive in grouts for various purposes, in concrete and in other cementitious compositions [2-5]. It is established that CW reacts with $Ca(OH)_2$ (the product of cement hydration) as a pozzolanic material [6-7] and increases the compressive strength and enhances other properties of the compositions with Portland cement [8-10].

The scientists, who investigate the building materials with CW, face certain difficulties. In some applications of lime binders the pozzolanic activity of CW, was not sufficient [11] and satisfactory workability can be achieved by using superplasticizers [12]. In study [13] it was showed that pozzolanic activity of CW, in Portland cement composition could be improved by heat treatment at 450 - 850°C. Authors indicated that particle size of the treated CW in the temperature range of 25 - 1000°C was found almost the same as that of the untreated, while specific surface area drastically decreased after heat treatment at 850°C. In the study [14] it was found, that besides the pozzolanic activity, which occurs in Portland cement composition, in some cases the compressive strength of pastes containing CW was lower then that of pastes formed with only cement and water. Supposedly, some elements, which are present in the CW composition, may have limited the pozzolanic activity. The reuse of CW (zeolite material with unique sorption, porosity, ion migration in water solution) in materials dedicated for industrial purposes, such as refractory materials is more promising because these materials are very expensive [15]. So, the development of new advanced refractory materials with required properties obtained due to the CW additive could give great economical benefit.

CW, as a fine additive, was tested in the refractory castable with liquid glass binder [16]. However, it was established that along with increase in amount of CW additive in the castable, the demand for liquid glass needed to produce the castable increases considerably as well. This factor affects negatively the thermal and strength properties of such castable at high temperatures.

The efforts were made to use milled CW in refractory castables with aluminate cement. In comparison with the mentioned above study [16], the polycarboxylate plasticizer was used for reduction of liquid phase in conventional refractory castable [17]. In this way the positive effect of CW on strength after hardening of concretes could manifest itself. Yet, at high temperatures the compressive strength and thermal shock resistance of conventional castable was lower than the concrete's without CW. However, milled CW combined with microsilica, reactive alumina and polycarboxylate plasticizer Castament FS-20 in MCC - type castable increased cold crushing strength after hardening as well as after firing at high temperature [18]. It was established that in comparison with the castable without milled CW, the castables with CW added in amount of 2 % and 5 % have the strength characteristics increased up to 25 % [19]. The content of CW above 5 % affects negatively the strength characteristics of castable.

The method to modify the properties of CW, which can more effectively appear in the refractory materials, is heat treatment at temperatures higher than operational temperature of catalyst (700°C). It is known that the particularities of structure of zeolites (such as CW) predetermine such properties as low density and big volume (after firing at temperature of > 500°C), stability of dehydrated crystalline zeolitic structures, properties of ion exchange, existence of one-type channels with diameters of molecule size in dehydrated crystals, electric conductivity, vapor adsorption, catalytic properties [20]. The temperature modification of zeolitic structure in CW would enable to change their properties, thus extending the possibilities to develop a better refractory material.

After treatment at the higher then 700 °C temperature, the organic compounds, remaining in catalyst after the regeneration process (the temperature of the process is ≤ 700°C) are removed from the CW. The X-ray phase analysis [21] show, that after treatment at temperature of 950°C, the size of main peaks of Y zeolite slightly changes, but the zeolitic structure still dominates. By tests of porosity, it was established that after treatment at mentioned temperature porosity decreased and the structure of catalyst pores undergoes changes. Thermographic tests results show, that during the firing process, exothermal effects at temperature 973°C one can see, which occurs due to crystallization of mullite, which mean the brekage of zeolite structure [22]. In this way at temperature > 700°C and ≤ 950°C not only the structure of zeolite can be modified, but also the impurities, that may adversely affect the properties of cementitious material can be removed.

The goal of this work is to evaluate the possibilities to modify the properties of refractory castable using the CW treated at high temperature. For this aim non milled, treated at 950°C CW was used in MCC-type castable with aluminate cement.

EXPERIMENTAL

The chemical composition of untreated (CW) was determined to be as follows (mass %): $Al_2O_3 - 39.4$, $SiO_2 - 50.1$, $Fe_2O_3 - 1.3$, $SO_x - 2.3$, $CaO - 0.5$, $MgO - 0.49$, $Na_2O - 0.2$, $K_2O - 0.07$, $Mn_2O_3 - 0.06$ [16]. It was found by particle size analyser Cilas 1090 LD that non-treated CW and treated at 950°C temperature (CWt) have the average particle diameter (42 μm). X-ray analysis shows that CW is Y zeolite with faujasite structure [22]. Also it was found that the CW and CWt mineralogical composition does not change, but the bulk density has minor differences: for CW 800 kg/m³ and for CWt 785 kg/m³. The catalyst waste particles overview presented in Figure 1. However, weight loss for CWt after treatment at the temperature of 950 °C was 5.2 % [22]. There are other differences between CW and CWt which are observed in the investigations of the CW compositions with water (Table 1). For cement investigations CW and CWt were used, while CWt was used only in castables tests.

The following materials were used for cement and castable samples production:

- *Gorkal 70 aluminate cement.* Content of $Al_2O_3 \geq 70$ %, main mineral phases: CA ($CaO \cdot Al_2O_3$) and CA_2 ($CaO \cdot 2Al_2O_3$), bulk density 1100 kg/m³, specific surface by Blaine method 454 m²/kg, refractoriness not less than 1630°C;

- *Microsilica* from the company RW Silicium GmbH, Germany. Content of SiO_2 not less than 96 % of composition, bulk density 410 kg/m³;

- *Reactive alumina* of type CTC-20, produced by Almatis, Germany. Bulk density 2100 kg/m³;

- *Chamotte aggregate* made by crushing of chamotte bricks, which density 1920 kg/m³. The 0 - 1 mm and 1 - 5 mm fractions of chamotte aggregate were used in refractory castables, bulk density 1260 kg/m³ and 910 kg/m³ respectively;

- *Dispersive chamotte* made by grinding chamotte of the same type in the laboratory ball mill. Bulk density is 1100 kg/m³;

- *Polycarboxilate deflocculant* Castament FS-20 is the commercial product from the company BASF, Germany;

- *Water.* Cement and CW suspensions and pastes were prepared with distilled water, castable with drinking water.
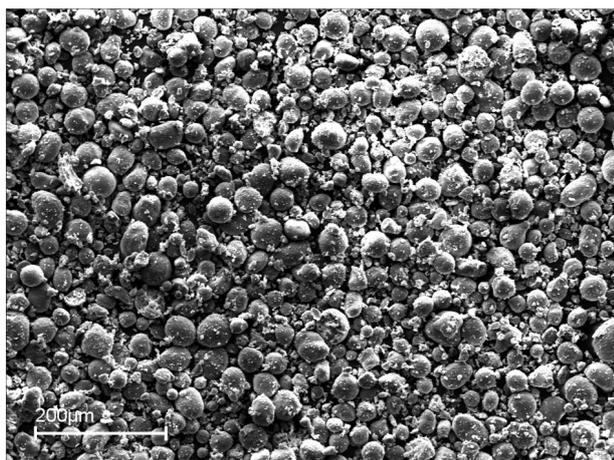
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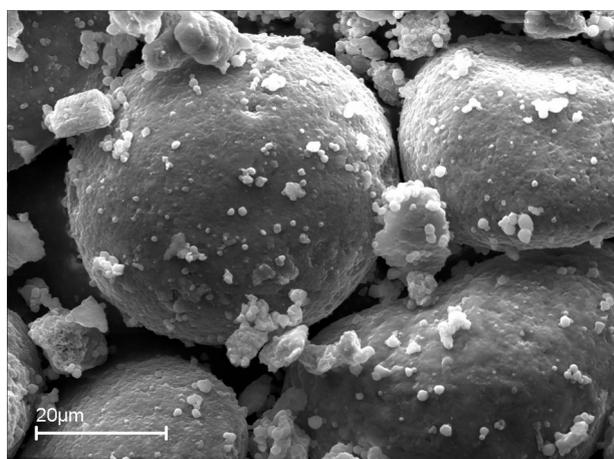
b)

Figure 1. SEM micrograph of CW particles [21].

Table 1. Properties of CW mixture with water.

| | Catalyst type | |
	CW	CWt
Electric conductivity of suspension (distilled water and catalyst at ratio 5:1) [µS/cm]	280	120
Maximum of heat realease rate in calorimeter after mixing with water (distilled water and catalyst at ratio 5:10) [J g^{-1} s^{-1}]	9.8	7.7

For investigations of electric conductivity of (cement – CW) and (cement – CWt) paste compositions (Table 2) with water a device MPC 227 of the company METTLER TOLEDO (electrode InLab 730, measurement range of 0-1000 mS/cm) was used. The solid-water ratio in compositions was 0.35.

Schleibinger Geräte GmbH datalogger with the Pundit 7 ultrasonic pulse indicator was used for investigation of ultrasonic wave velocity (UWV) in pastes and castable samples (Table 2-3). Fresh pastes were set into special ring between two ultrasonic transducers

operating at 10 pulses per second and frequency of 54 kHz. For castable samples UWV measurments were carried out without special ring equipment.

The surface analysis of hardened compositions samples with CW and CWt additives (Table 2) were carried out using scanning electron microscope JEOL JSM-6490LV and JSM-7600F JEOL.

Table 2. Compositions of cement with CW and CWt.

Samples	Cement (g)	CW (g)	CWt (g)
CW - 0	100	0	–
CW - 5	100	5	–
CW - 10	100	10	–
CW - 15	100	15	–
CW - 20	100	20	–
CW - 30	100	30	–
CWt - 5	100	–	5
CWt - 10	100	–	10
CWt - 15	100	–	15
CWt - 20	100	–	20
CWt - 30	100	–	30

For investigations 4 compositions (Table 3) of castable were prepared. After 3 days of curing, the samples (cubes sized 70 × 70 × 70 mm and prism sized 40 × 40 × 160 mm) were dried at temperature of 105 ± 5°C for 48 hours in the electric furnace. Firing process is characterised by heating speed by 3°C/min until maximum firing temperature. Afterwards they were hold for 5 hours at each of investigated temperatures (800°C, 1100°C, 1200°C) in the electronically controlled furnace and finally cooled. Then the compressive strength (LST EN 1402-6) of castable was measured.

Table 3. Composition of MCC-type refractory castable in [%].

| | Composition number | | | |
	B-0	B-2.5	B-5	B-7.5
Cement	12	12	12	12
Microsilica	5	5	5	5
Reactive alumina	5	5	5	5
CWt	0	2.5	5.0	7.5
Dispersed chamotte	15	12.5	10	7.5
Chamotte aggregate	63	63	63	63
Deflocculant*	0.15	0.15	0.15	0.15
Water*	11	11	11	11

* over 100% of dry components

Thermal shock resistance refers to one of the major characteristics of the materials exposed to high temperatures. It indicates their durability under the alternate cycles of heating and cooling. In order to investigate the evolution of thermal shock damage in refractory materials, a new experimental approach has

been proposed. Original express method developed at the VGTU Scientific Institute of Thermal Insulation was applied for investigations of specimens structure changes during thermal cycling. The structure changes and the thermal stability criterion *Rt* was found based on the method of structure changes during thermal cycling with no direct contact of specimens with water. For the thermal stability criterion *Rt* evaluation the specimens with dimensions of 40 × 40 × 160 mm after drying were divided into 3 groups. The 1st group of test specimens were fired at the temperature 800°C and after cooling UWV in the specimens were determined. The 2nd group of specimens were exposed to 3 cycles: they were heated for 35 min. at the 800°C and then cooled for 45 min. on the special water-cooled plate. After cooling UWV in the specimens were determined. The 3rd group of specimens was exposed to 7 similar cycles. The thermal stability criterion *Rt* was determined using the formula:

$$R_t = \frac{\sqrt{V_t^{3C} \cdot V_t^{7C}}}{V_t}$$

where V_t is UWV in the specimen after firing at the temperature 800°C, V_t^{3C} - UWV in the specimen after 3 thermal cycles and V_t^{7C} - UWV in the specimen after 7 thermal cycles.

The UWV measurements help to evaluate the structure changes of specimens during longer thermal cycling after 14 and 21 thermal cycles.

RESULTS AND DISCCUSION

Influence of untreated and treated catalyst waste on cement composition's properties

Electrical conductivity shows a picture of the ionic concentration in water and gives information on the dissolution step of the hydration reaction of cement in water. As electrical conductivity of CW in water is high (Table 1) it has influence on electrical conductivity of cement composition. We can see (Figure 2), that CW additive increases the electric conductivity of cement compositions by 8 - 57 % versus pure cement compositions. The CWt influences considerably less the electric conductivity of cement composition, i.e. when the content does not exceed 10 %, the electric conductivity increases by 8 - 11 %, while at 15 - 20 %, it decreases by 4 - 15 %.

This increase of electrical conductivity in cement compositions caused by CW additives can affect the concrete or mortar paste workability indicators. As indicated in the studies [24], aluminate cement "Gorkal 40" with 5 and 25 % mass of CW in comparison with the reference samples made without CW additive have shown that 5 % content of CW improves workability of mortars while 25 % mass of this waste causes consolidation of mortars with difficulty.
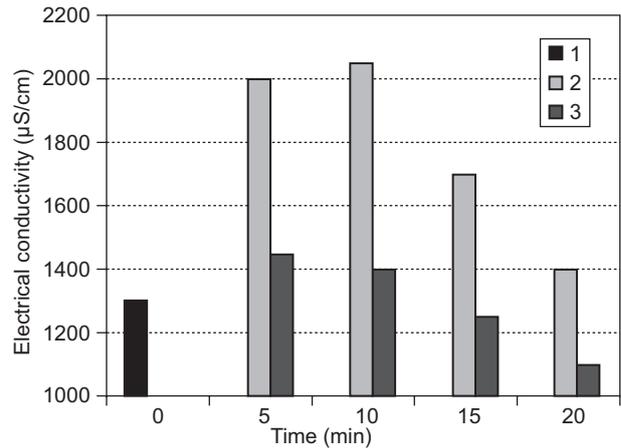

Figure 2. Electrical conductivity of cement paste composition (W/C = 0.35) after 15 min of cement mixing with water: 1 – pure cement paste, 2 – with CW, 3 – with CWt.
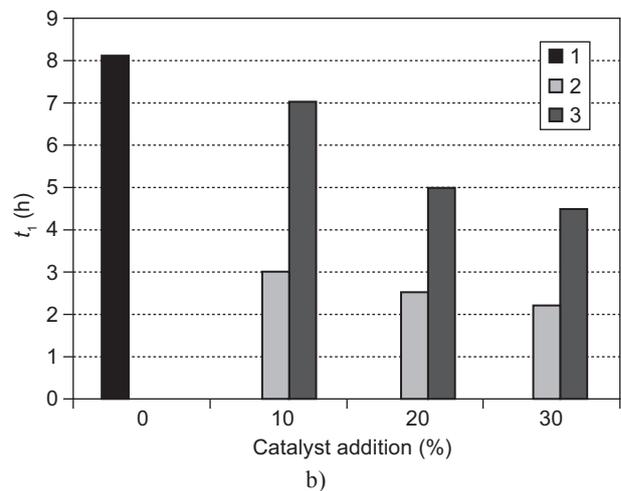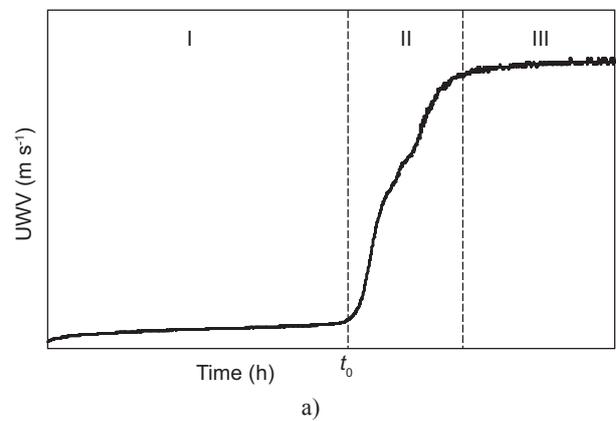

Figure 3. Ultrasonic wave velocity (UWV) curve (a) and initial time (t_0) of drastic change of UWV in cement composition during hardening (b): 1 – pure cement paste, 2 – with CW, 3 – with CWt.

The ultrasonic tests in cement paste (Figure 3) describe the structure formation during hardening of compositions. In the ultrasonic wave velocity (UWV) curve, typical to all cement compositions, one can observe

three steps: Step I when UWV does not practically change for a long period of time (what corresponds to the induction-hydration process), Step II when UWV drastically increases (the crystallization process of

cement hydrates is going on), Step III with almost no changes in UWV. The fact that the CW accelerates the hydration of aluminate cement was shown in other works as well [23-24]. In this work it is observable that CWt is a considerably softer accelerating additive of cement hydration than CW.
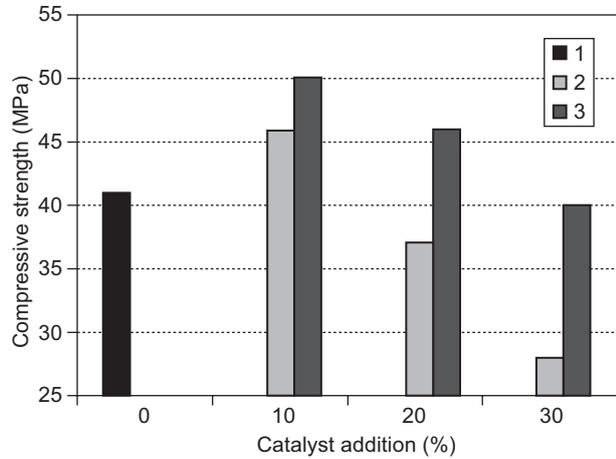
The investigations of the compressive strength in the samples of cementitious stone after 3-days of hardening (Figure 4) showed that the compressive strength in samples with 10 % CW and CWt is higher by 12 and 22 %, respectively, than that of reference sample without additive. Higher amounts of CW and CWt decrease the compressive strength of cementitious stone. It should be also noted that the compressive strength of compositions with CW is considerably lower that that of analogical compositions with CWt, in particular at higher content of additive (20 - 30 %).
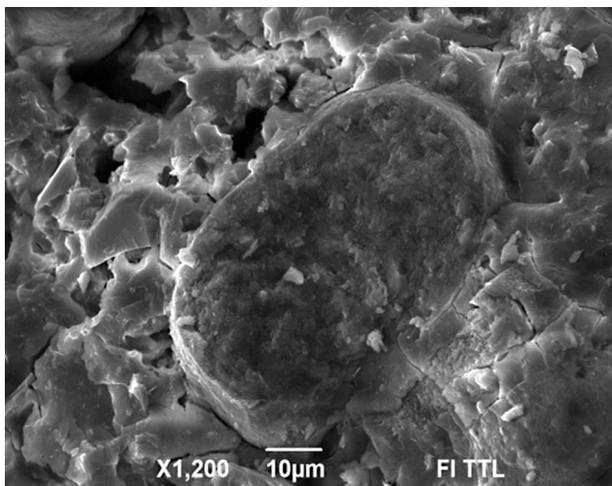
In cement compositions with CW, particles of the latter can be easily identified in the structure of cementitious stone (Figure 5). While analyzing the adhesion between CW particles and cementitious stone, it was

Figure 4. Compressive strength of cement stone after 72 h of hardening (b): 1 – pure cement, 2 – with CW, 3 – with CWt.
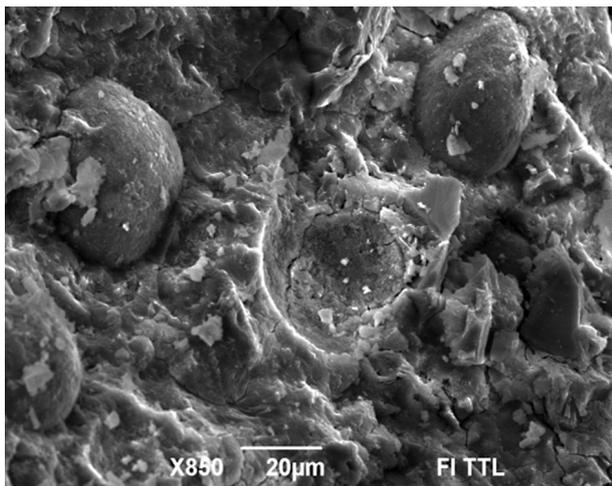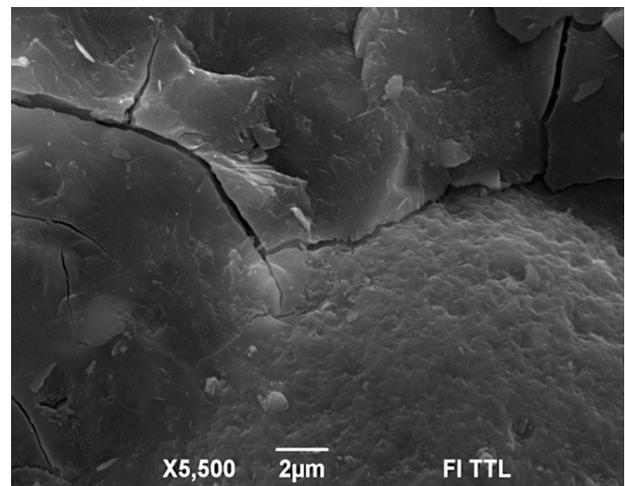

a)
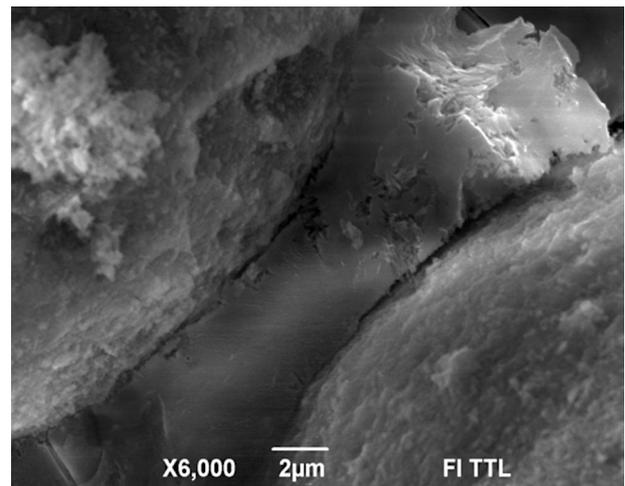
b)

c)

d)

Figure 5. SEM micrograph of cement stone structure with 10 % CW (a, b) and 10 % CWt (c, d).

observed (Figure 5b) that in most cases a tiny gap appears separating these components one from other. Therefore, upon splitting of samples (in preparation for SEM tests), CW particles easily detach from cementitious stone. In the case of CWt particles, they better adhere to cementitious stone, i.e. during the splitting, CWt particles hardly detach from cementitious stone, here and there they split in half (Figure 5c) and a discontinuous gap appears around particles (Figure 5d).

It is obvious that along with growing content of catalyst additive, the number of gaps increases in the structure of compositions causing the compressive strength of samples to decrease (Figure 4).

The performed investigations showed that both CWt and CW accelerate the hydration of cement and that a certain amount of this additive increases the compressive strength of cementitious stone. Nevertheless, in comparison with untreated catalyst, CWt is a considerably softer accelerating additive of cement hydration and that its particles better interact to cementitious stone what positively effects the strength of material.

The investigations of compressive strength in castable samples after 3-days of hardening (Figure 7) showed that CWt additive notably increases the compressive strength versus that of castable without the additive (in particular at 2.5 and 5 % content when the compressive strength increases almost twice). When CWt additive content reaches 7.5 % in castable we can see a noticeable decreasing trend in compressive strength. These results confirm [24] the studies. In the study for the CW content influence on the mortars compressive strength aluminate cement "Gorkal 40" with 5 and 25 % mass of CW and reference samples without CW were prepared. The content of 5 % of CW improves compressive strength after 24 h (about 9.3 %), in the comparison with the mortars without the addition. The content of 25 % of CW in the mortars reduces the strength properties almost twice. As it is pointed in [25] changes in the distribution of aggregate-size and the presence of a non-cohesive zone surrounding the coarse grains and matrix can produce significant differties in the mechanical strength of refractory castables. Therefore, we believe that increase in quantity of additive CWt does not ensure proper relationship between the matrix and filler. After drying at 110°C, the compressive strength of samples of castable of almost all compositions increases, however, a more considerable increase is observable in the compositions without additive or with its minimal content. After treatment at temperature of 800 − 1200°C, the changes in compressive strength in samples of all compositions are insignificant and the earlier observed tendencies remain, i.e. samples of composition B-2.5 differ from others by the highest compressive strength. With increase of CWt additive content in samples, their compressive strength decreases, though in any case it is higher than that of samples of castable without any additive.

Samples of castable with CWt additive did not shrink after burning at temperature of 800°C (Figure 8). The shrinkage was registered only in the sample B-0. By increasing the temperature of treatment up to 1100°C, it was established that the shrinkage of samples B-2.5 amounts to 0.14 %, B-5 to 0.1 %, B-7.5 to 0 %. Upon burning of samples at temperature of 1200°C, we can see the shrinkage of sample B-0 as high as 0.25 %, B-2.5 as 0.2 %, B-5 as 0.15 % and that of B-7.5 as 0.05 %. In the sample with maximum content of additive (B-7.5), the shrinkage is fixed only after burning at 1200°C. These investigations evidenced that CWt additive reduces the shrinkage of castable and that higher CWt amounts in castable causes lower shrinkage.

Thermal shock resistance refers to one of the major characteristics of the materials exposed to high temperatures that are why researchers are interested in this field and it remains high in popularity [26-30]. It indicates sample's durability under the alternate cycles of heating and cooling. Thermal stability describes the castable ability to resist thermal stresses on the structure resulting from the prevailing temperature gradient. The thermal stability criterion R_t was assessed by express
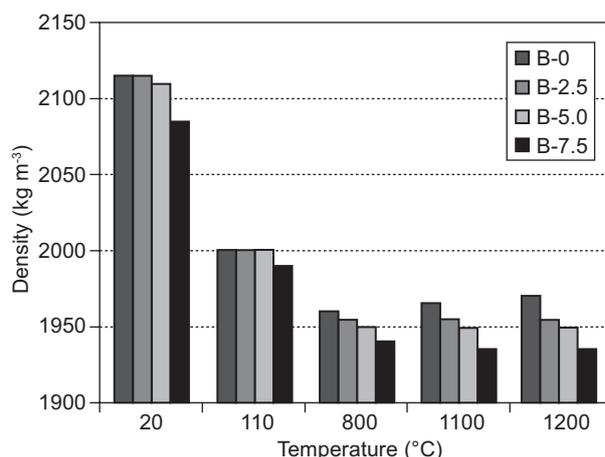

Figure 6. The density of castable after treatment at various temperatures.
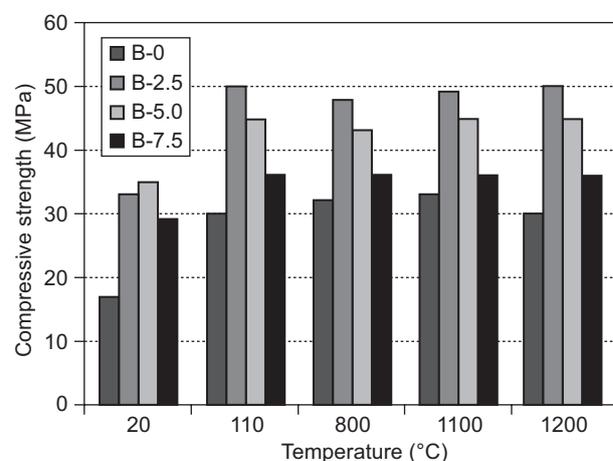

Figure 7. Compressive strength of castable after hardening for 3 days (20) and treatment at different temperatures.

method after 7 thermal cycles, using 21 cycles for exhaustive evaluation of changes in structure of castable, including UWV measurements after 3, 7, 14 and 21 cycles (Figure 9). We can see that after treatment at 800°C (i.e. 0 cycles), the difference in UWV is already observable in samples of castable: B-0 (2650 m/s), B-2.5 (3150 m/s), B-5 (2950 m/s), B-7.5 (2303 m/s). So, the castables B-2.5 and B-5 are distinguished by the densest structure. The main processes of destruction are running in castable during first 3 cycles, and an extremely sharp drop of UWV is observable in samples of castable B-0, while the lowest drop in B-7.5. Upon further cyclic acting on the samples of castable, UWV changes are not so sharp, as here UWV decreases gradually. Rt, which was found by the method TI, also confirms the established tendencies: the highest Rt values are in compositions B-2.5 and B-5. After 21 cycles in the samples of castables B-2.5 and B-5, UWV values are higher by 480 m/s and 285 m/s, respectively, than those of castables B-0 and B-7.5. We can see that R_t (after 7 thermal cycles) well characterizes changes in the structure of castable, meanwhile the further changes in structure continuing the experiment up to 21 cycles, show that the established R_t virtually reflects structural changes and that 7 thermal cycles are sufficient for estimation of thermal durability.
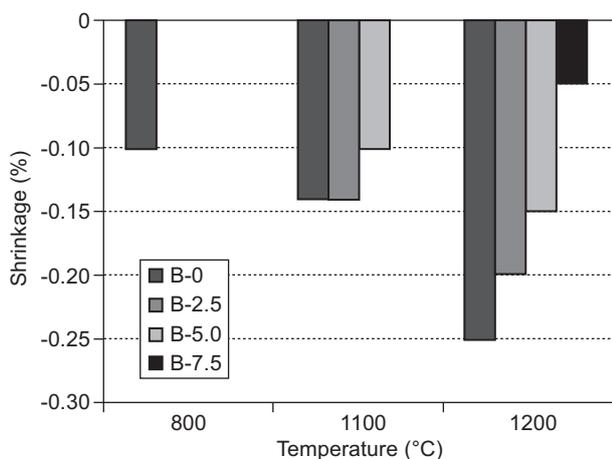

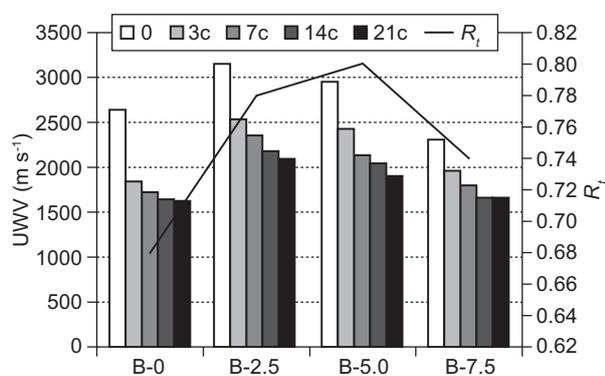Figure 8. The shrinkage of castable samples after treatment at various temperatures.

Figure 9. The UWV of castable samples and R_t after thermal cycles.

CONCLUSIONS

1. It was established that CW additive, irrespective of method of treatment, increases the electric conductivity of cement suspensions. CW additive increases the electric conductivity of cement compositions up to 57 % versus pure cement compositions. Thermally treated CWt catalyst, due to lower content of soluble admixtures, considerably less influences the electric conductivity of cement suspensions, i.e. when CWt content does not exceed 10 %, the electric conductivity increases by 8 - 11 %, when CWt content reaches 15 - 20 %, the electric conductivity decreases by 4 - 15 %.

2. Irrespective of method of treatment, the CW accelerates the hydration of aluminate cement versus that of pure cement. Along with increase in CW and CWt content in cement compositions, a sharp compacting of structure (Step II) occurs and is running quicker, the higher the content of waste is in the composition. Nevertheless, in compositions with CW additive, the structure of samples compacts itself considerably quicker than that with CWt additive.

3. It was established that 10 % CW and 10 − 20 % CWt additive increases the compressive strength of cement compositions after hardening versus cement composi-tions without the additive. Nonetheless, the compressive strength of compositions with CW is considerably lower than that of analogical compositions with CWt additive. Along with increasing content of both additives (20 − 30 %), the compressive strength is decreasing. It is obvious that CWt is a considerably softer accelerating additive of cement hydration than CW and that its particles adhere better to cementitious stone what posi-tively tells on strength of material.

4. It was established that the increase in CWt additive content in MCC-type refractory castable results in a slight decrease (less than 2 %) of density of the castable, as well as in increase of compressive strength (in particular at 2.5 and 5 % content of additives, respectively, where the compressive strength increases almost twice) and in a decrease of shrinkage of castable within the whole range of investigated temperatures (20 - 1200°C) versus analogical castable without the additive.

5. It was established that upon impact of long-term thermal cycles (21 cycles), the 2.5 - 5 % CW$_t$, of additive in the castable, ensures a more compact structure of castable and such a structure is less damaged by the processes of thermal destruction. The estimated R_t shows that the compositions of castable with 2.5 and 5 % CWt additive are distinguished by best thermal durability versus analogical castable without the additive.

REFERENCES

1. Pacewska B., Bukowska M., Wilińska I., Swat M.: Cem. Concr. Res. *32*, 145 (2002).
2. Su N., Fang H., Chen Z., Liu F.: Cem. Concr. Res. *30*, 1773 (2000).
3. Hsu K.C., Tseng J.S., Ku F.F., Su N.: Cem. Concr. Res. *31*, 1815 (2001).
4. Paya J., Monzo J., Borrachero M.: Cem. Concr. Res. *29*, 1773 (1999).
5. Allahverdi A.,Vakilinija S., Gharabeglu P.: Ceramics-Silikaty *55*, 161 (2011).
6. Pacewska B., Wilinska I., Bukowska M., Nocun-Wczelik W.: Cem. Concr. Res. *32*, 1823 (2002).
7. Paya J., Monzo J., Borrachero M.V., Velazques S.: Cem. Concr. Res. *33*, 603 (2003).
8. Paya J., Monzo J., Borrachero M.V.: Cem. Concr. Res. *31*, 57 (2001).
9. Wu I., Wu W., Hsu K.: Cem. Concr. Res. *33*, 245 (2003).
10. Bukowska M., Pocewska B., Wilińska I.: Cem. Concr. Res. *34*, 759 (2004).
11. Paya J., Monzo J., Borrachero M.V., Velazques S.: Adv. Cement. Res. *16*, 123 (2004).
12. Zornoza E., Garces P., Monzo J., Borrachero M.V., Paya J.: Adv. Cement. Res. *19*, 117 (2007).
13. Tseng Y.S., Huang C.L., Hsu K.C.: Cem. Concr. Res. *35*, 782 (2005).
14. Dweck J., Pinto C.A., Buchler P.M.: J. Therm. Anal. Calorim. *92*, 121 (2008).
15. Kuznetsov D., Lysov D., Nemtinov A., Shaleiko A., Korol'kov V.: Refr. Indust. Ceram. *51*, 61 (2010).
16. Goberis S., Stuopys A.: Interceram. *45*, 16 (1996).
17. Antonovič V., Goberis S., Pundiene I., Stonis R.: Ceramika (Polski biuletyn ceramiczny) *88*, 143 (2005).
18. Pundiene I., Goberis S., Antonovich V., Stonis R.: Refr. Indust. Ceram. *47*, 330 (2006).
19. Hommer H.: J. Eur. Ceram. Soc. *29*, 1847 (2009).
20. Stonis R., Pundiene I., Antonovič V., Goberis S., Aleknevičius M.: Mater. Sci. Medžiagotyra *14*, 59 (2008).
21. Breck D.: *Zeolite Molecular Sieves*. Maskva:Mir, 1976.
22. Antonovič V., Pundienė I., Stonys R., Čėsnienė J., Kerienė J.: J. Civ. Eng. Manag. *16*, 595 (2010).
23. Vasiliev P., Ojuva A., Grins J., Bergström L.: J. Eur. Ceram. Soc. *30*, 2977 (2010).
24. Aleknevičius M., Antonovič V.: Chem. Technol. *51*, 33 (2009).
25. Pacewska B., Nowacka M., Wilin´ska I., Kubissa W., Antonovich V.: J. Therm. Anal. Calorim. *105*, 129 (2011).
26. D´ıaz L.A., Torrecillas R., Simonin F., Fantozzi G.: J. Eur. Ceram. Soc. *28*, 2853 (2008).
27. Damhofa F., Brekelmans W.A.M., Geers M.G.D.: J. Eur. Ceram. Soc. *29*, 309 (2009).
28. Martinovic S., Dojcinovic M., Dimitrijevic M., Devecerski A., Matovic B., Volkov Husovic T.: J. Eur. Ceram. Soc. *30*, 3303 (2010).
29. Ghassemi Kakroudi M., Huger M., Gault C., Chotard T.: J. Eur. Ceram. Soc. *29*, 2211 (2009).
30. Antonovič V., Shyukshta M., Pundiene I., Stonys R.: Refract. Ind. Ceram. *52*, 279 (2011).