

PURIFIED WASTE FCC CATALYST AS A CEMENT REPLACEMENT MATERIAL

[#]DANUTĖ VAIČIUKYNIENĖ*, AUDRIUS GRINYS, VITOLDAS VAITKEVIČIUS, ARAS KANTAUTAS

^{*}*Department of Building Materials, Kaunas University of Technology,
Studentų str. 48, LT-51367 Kaunas, Lithuania*

^{**}*Department of Silicate Technology, Kaunas University of Technology,
Radvilėnų str. 19, LT-50254 Kaunas, Lithuania*

[#]E-mail: danute.palubinskaite@ktu.lt

Submitted October 29, 2014; accepted April 15, 2015

Keywords: Purified waste FCC catalyst, Pozzolan, Cement replacement material

Zeolites are commonly used in the fluid catalytic cracking process. Zeolite polluted with oil products and became waste after some time used. The quantity of this waste inevitably rises by expanding rapidly oil industry. The composition of these catalysts depends on the manufacturer and on the process that is going to be used. The main factors retarding hydration process of cement systems and modifying them strength are organic compounds impurities in the waste FCC catalyst. The present paper shows the results of using purified waste FCC catalyst (pFCC) from Lithuania oil refinery, as Portland cement replacement material. For this purpose, the purification of waste FCC catalyst (FCC) samples was treated with hydrogen peroxide. Hydrogen peroxide (H₂O₂) is one of the most powerful oxidizers known. By acting of waste with H₂O₂ it can eliminate the aforementioned waste deficiency, and the obtained product becomes one of the most promising ingredients, in new advanced building materials. Hardened cement paste samples with FCC or pFCC were formed. It was observed that the pFCC blended cements developed higher strength, after 28 days, compared to the samples with FCC or reference samples. Typical content of Portland cement substituting does not exceed 30 % of mass of Portland cement in samples. Reducing the consumption of Portland cement with utilizing waste materials is preferred for reasons of environmental protection.

INTRODUCTION

Fluid catalytic cracking (FCC) is one of the most important conversion processes used in petroleum refineries. It is widely used for the transformation of crude oil to gasoline and other fuel products. Zeolites are commonly used in the FCC process, but when the catalysts are used they degraded [1].

The previous study [2-6] has shown that this residue exhibits excellent pozzolanic properties in Portland cement mixtures. The combination of the research techniques allows determination of the optimal dosage in order to maximize the use of this excellent pozzolan [6]. The pozzolanic activity of equilibrium catalyst (Ecat), one of the FCC catalysts from oil companies increases with calcined temperature initially, reaches a maximum, and afterwards decreases [3]. H. L. Chen et al. in the study [4] shows that the activity of two spent FCC catalysts, i.e., equilibrium catalyst (Ecat), and electrostatic precipitator catalyst (Epcat), were examined and compared. Epcat provides a filling effect on the microstructure and enhances the compressive strength of the resulting mortars. The performance of Epcat is close to or slightly better than that of silica fume.

Pastes and mortars with Epcat were prepared and

cured, and their compressive strengths were measured. The improvement of mortars mechanical properties is attributed to the increase in the hydrated cement paste and, more importantly, improved bonds between the cement paste and aggregate [5]. K. Al-Jabri et al. [7] studies the effect of using FCC spent catalyst, produced from local refineries on the compressive strength of mortars. Encouraging results were achieved when Sohar Refinery's spent catalyst was used as sand replacement. Spent catalysts from both refineries showed negligible effect on the strength of cement mortars when used as partial substitute of cement.

N. Su et al. [8] analyzes the properties of Ecat and Epcat waste catalysts and examines the feasibility of reusing them to substitute part of the cement required in mortar preparation. They can substitute up to 15 % of the cement content in mortar without sacrificing the quality of concrete. In fact, the substituted concrete shows a greater compressive strength, 15 % higher than that without substitution.

The preliminary results of an ongoing project [9] with one of the goals to investigate the viability of using waste FCC catalyst (wFCC) in order to produce low carbon blended cements. Four blended cements were produced for this purpose substituting cement CEM I

42.5R up to 20 % (w/w) by waste FCC catalyst. It was observed that the wFCC blended cements developed similar strength in 28 days compared to the reference cement CEM I 42.5R.

Accelerated carbonation tests have been carried out on Portland cement mortars and pastes, partially substituted with a spent fluid catalytic cracking catalyst (FC3R). This study has revealed that the incorporation of FC3R on mortars produces a significant reduction of the alkaline reserve. Both portlandite and CAH/CASH are transformed, yielding calcium carbonate when FC3R/cement system is carbonated. When the w/b ratio is medium or high, the presence of FC3R accelerates the carbonation process suggesting that the reduction in porosity did not compensate the reduction in the portlandite which act as chemical barrier [10].

Waste FCC has been used as a whole replacement for crushed aggregates in road construction [11], as a pozzolanic material that can be used in reinforced concrete for civil engineering applications exposed to the action of chlorides [12], the production of clinker by substitution of bauxite by waste catalysts [13], in the production of blended calcium aluminate cement [14, 15] and as a supplementary cementitious material in blended cement production [16, 17]. The aim of this work was to investigate the influence of purified waste FCC catalyst as a Portland cement replacement material for cementitious materials.

EXPERIMENTAL

Materials

The Portland cement CEM I 52.R (mineral composition: $C_3S = 56.60\%$, $C_2S = 15.76\%$, $C_4AF = 10.85\%$, and $C_3A = 8.59\%$) and waste FCC catalyst are used in this study.

The zeolite-Y dominates in the waste FCC catalysts. It is an aluminosilicate with a crystalline structure consisting of tunnels and cages, was producing a high surface area. Zeolite polluted with oil products and became waste product after some time used. The quantity of this waste inevitably raises rapidly expanding oil industry. The composition of these catalysts depends on the manufacturer and on the process to be used.

Half of the experiments were done with waste FCC catalysts (FCC), and the other half was performed with purified waste FCC catalysts (pFCC). The purification of FCC samples was done treating hydrogen peroxide. 17 % hydrogen peroxide solution was used there. The FCC and hydrogen peroxide mixture was aged at room temperature for 24 h, then was centrifuged and dried in oven at 100°C. The composition of used raw materials is submitted in Table 1.

The compositions of hardened cement paste samples varied in the contents of FCC or pFCC as supplementary material: 0 %, 10 %, 20 %, and 30 %. The cement and

water ratio (W/C) was constant (W/C = 0.4). The formed test samples, 2 × 2 × 2 cm sized cubes, were hardened for 28 days under the conditions prescribed by the standard. The test procedure of hardened cement paste compressive strength was applied according to the EN 196-1.

Table 1. The oxide composition of used raw materials.

Oxides	Quantity, %		
	CEM I 52.5 R	FCC	pFCC
SiO ₂	20.48	28.71	28.78
Al ₂ O ₃	5.55	63.43	64.60
CaO	63.99	–	–
Fe ₂ O ₃	3.58	2.28	2.28
MgO	3.99	0.81	0.81
SO ₃	0.41	0.55	0.55
Na ₂ O	0.20	0.44	0.44
K ₂ O	1.00	–	–
Na ₂ Oekv.	0.80	–	–
TiO ₂	–	1.56	1.57
C	–	1.26	–
CuO	–	0.95	0.95

Experimental techniques

The X-ray powder diffraction data were collected using DRON-6 X-ray diffractometer equipped with Bragg-Brentano geometry using Ni-filtered Cu K α radiation and graphite monochromator. Operating voltage of 30 kV and emission current of 20 mA were used in the experiments.

Thermographic investigations were carried out using a differential scanning calorimeter *STA 409 PC*, produced by *Netzsch*. The maximum temperature was 1500°C, and the velocity of the increase in temperature was 10°C·min⁻¹.

IR spectra were recorded with Perkin Elmer FT-IR System spectrometer. 1 mg of the substance was mixed with 200 mg of KBr and compressed in a forming press under vacuum for the IR analysis,

Particle size distribution and specific surface area were determined by “Mastersizer 2000” instrument from Malvern. Red light was produced by helium-neon laser and blue light was obtained from a solid phase source.

The compression strength of hardened cement paste was evaluated by on EN 196-1 standard. An automated and computerized ToniTechnik 2020 press was used to evaluate the compression strength of hardened cement paste.

RESULTS AND DISCUSSION

According to the results of granulometric analysis it was established that while the FCC and pFCC particle distribution is identical (a diameter ranging from 0.63 mm to 239 mm, forming a peak at 79.43 mm with

10.25 % of all particles in the histogram), but the specific particle surface of FCC and pFCC are equal to the $S_{FCC} = 0.1403 \text{ m}^2 \cdot \text{cm}^{-3}$ and $S_{pFCC} = 0.1525 \text{ m}^2 \cdot \text{cm}^{-3}$ (Figure 1). This is the fact that oxidation of carbon with hydrogen peroxide does not affect the particle size of the waste but increases their specific surface. It can be concluded that carbon impurities are penetrated inside the waste catalyst particles.

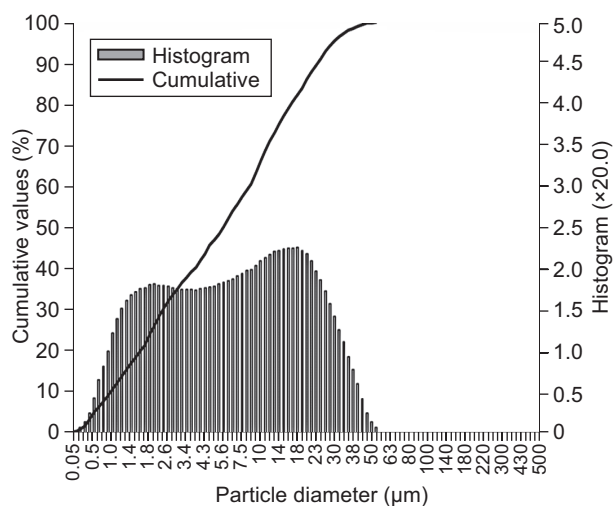
Meanwhile, the Portland cement particle size varied more evenly from 0.05 mm to 52.5 mm, forming two peaks at 1.8 mm (1.75 % of all particles) and at 19.42 mm (2.14 % of all particles) in the distribution histogram. The specific surface of Portland cement was equal to $S_p = 0.599 \text{ m}^2 \cdot \text{cm}^{-3}$. So, Portland cement particles are almost five times finer than the particles of zeolitic waste.

Thermal analyze show changes in FCC and pFCC materials at temperatures above 1000°C. The endothermic effect at temperatures of 89°C and 74°C (Figure 2) may be explained by water desorption from catalyst pores and channels (losses in the mass reach about 3 %). At temperatures about 924°C and 926°C the endothermic effect related with amorphous phase increasing. The exothermal effect at temperatures about 983°C and 974°C occurs due to crystallization of mullite in the structure of FCC and pFCC catalyst waste respectively [18]. The exothermal effect (at temperature about 604°C) was obtained before treating the waste with H_2O_2 (Figure 2a). This effect may be related with oil products pollutants. By acting of zeolitic waste with H_2O_2 the above mentioned exothermal effect at temperature about 604°C disappear. Therefore, by acting of waste with H_2O_2 for the oxidation reaction it can eliminate the oil products pollutants in zeolitic waste catalyst.

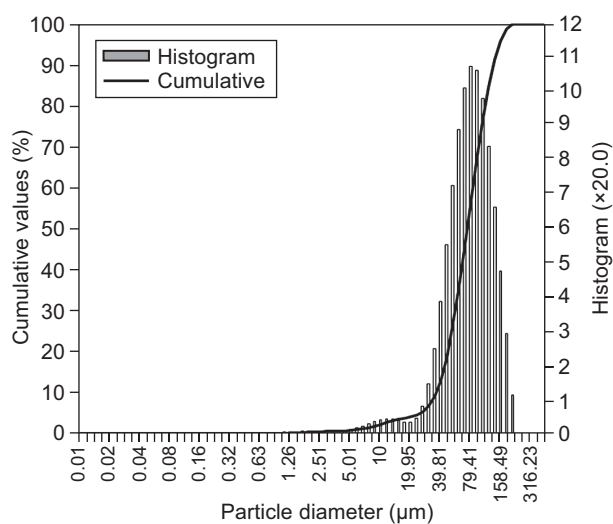
X-ray diffraction analysis results of the hardened cement paste samples (Figure 3) show that portlandite, calcium silicate hydrate, alite, belite and calcite, as well as small amount of calcium aluminum carbonate hydrate dominated in the hardened cement paste, where 10 % of Portland cement were replaced with FCC or pFCC. The same mineral composition prevails in reference sample without Portland cement supplementary material.

The X-ray diffraction patterns presented in curve 1 and curve 2 (Figure 3) shows that the highest peak of portlandite with 0.493 nm interplanar distance is the same in the reference sample and in the sample where 10 % of Portland cement is replaced with FCC. It can be stated that FCC accelerates cement hydration process, when less Portland cement were used in the samples.

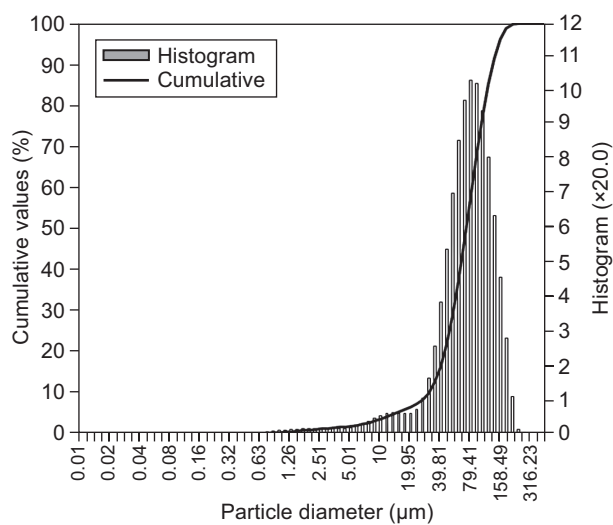
The portlandite peak decreases When 10 % of Portland cement is replaced with pFCC (Figure 3, curve 3). The reduction of that peak can be explained by the replacement of Portland cement with investigated zeolitic waste i.e. lower amount of Portland cement is used. But on the other hand it can be stated that pFCC is pucolanic material and binds portlandite to secondary calcium silicate hydrates during the hydration.



a) Portland cement



b) FCC



c) pFCC

Figure 1. Particle size distribution for a) Portland cement, b) FCC and c) pFCC.

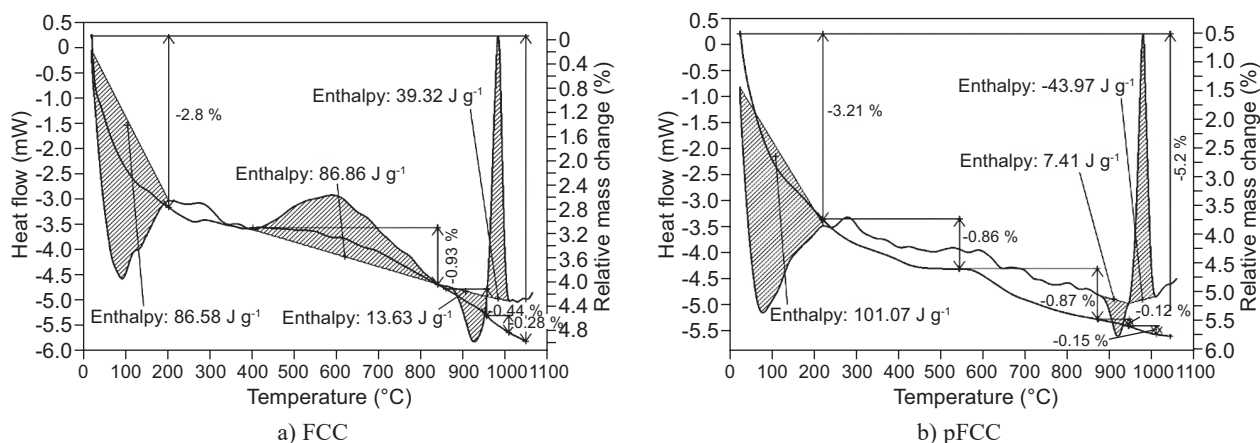


Figure 2. DTA curves of zeolitic waste catalyst: FCC (a) and pFCC (b).

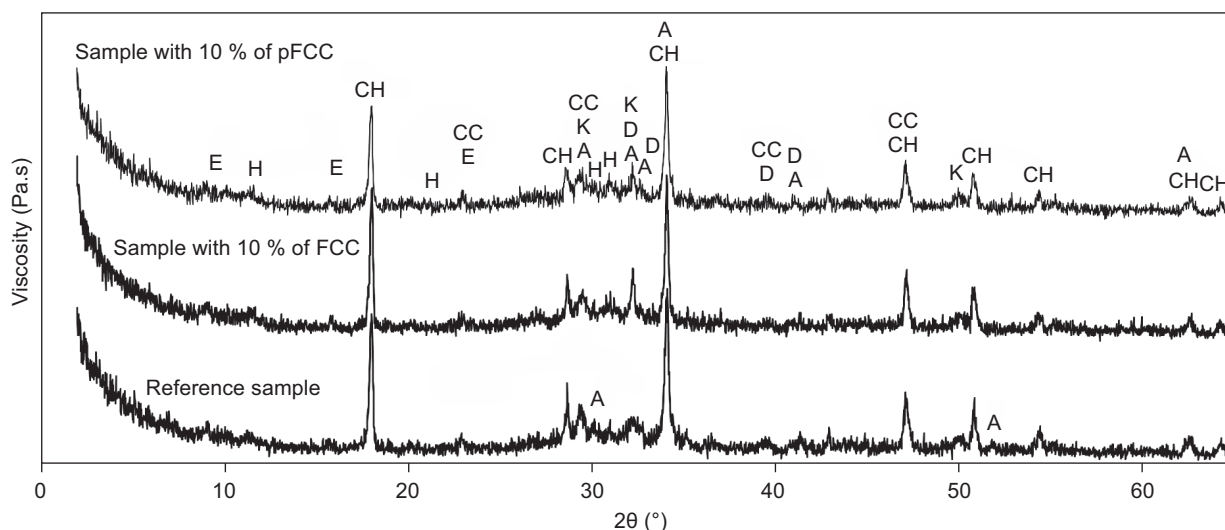


Figure 3. X-ray diffraction patterns of hardened cement paste after 28 days. Notes: CH – portlandite; A – alite; K – calcium silicate hydrate; D - belite; E - ettringite; CC – calcite, H – calcium aluminum carbonate hydrate..

Thermal analysis was carried out with hardened cement paste samples containing 10 % of FCC and with 10 % of pFCC. The thermograms (Figure 4) showed that endothermic peaks of DSC curves in the temperature range between 100°C and 200°C indicated the elimination of water at C-S-H phase and calcium aluminosilicate hydrates. The second intensive endothermic peak with the temperature maximum about 463°C indicated the

dissociation of portlandite $\text{Ca}(\text{OH})_2$.

The weight loss of the reference sample without zeolitic material, associated with $\text{Ca}(\text{OH})_2$ decomposition, was 3.96 %. So, if assuming into portlandite, it would be 16.28 %, according to mass losses (Table 2). Similar quantity of portlandite is estimated according to the DSC method. In the samples with supplementary materials (FCC or pFCC) the quantities of portlandite decrease till

Table 2. Quantity of portlandite in the hardened cement paste after 28 days*.

Amount of zeolitic waste [%]	Data according to the TG method		Data according to the DSC method	
	Mass losses at 407 - 483°C [%]	W ($\text{Ca}(\text{OH})_2$) [%]	Peak area at 439-483°C [$\text{J} \cdot \text{g}^{-1}$]	W ($\text{Ca}(\text{OH})_2$) [%]
0	3.96	16.28	142.98	15.10
10 FCC	3.24	13.32	122.59	12.95
10 pFCC	3.44	14.14	121.86	12.87

*the quantities of $\text{Ca}(\text{OH})_2$ were calculated according to [19] methodology

13.32 % and 14.14 % respectively. It can be observed that the consumption of portlandite was due to the pozzolanic reaction occurring, when FCC or pFCC was incorporated and the formation of smaller amount of hydration products because of lower concentration of Portland cement in the system. The third endothermic peaks, close to 723-728 °C, are attributed to the decomposition of carbonated phases and calcite CaCO_3 .

Figure 5 show the development of compressive

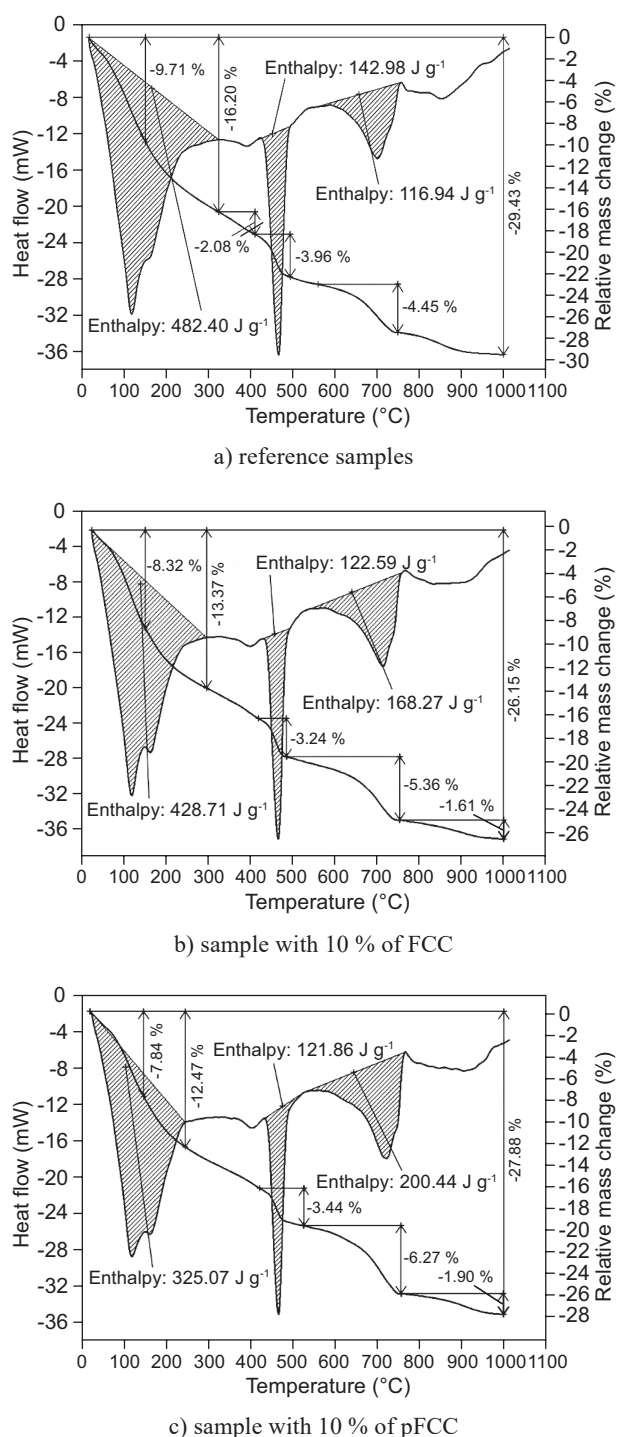


Figure 4. DTA curves of hardened cement paste after 28 days: a) reference samples, b) sample with 10 % of FCC and c) pFCC.

strength of the hardened cement paste in relation to the Portland cement replacement level for the case of FCC or pFCC. Concerning the use of FCC or pFCC, the replacement of 10 % and 20 % zeolites led to higher compressive strengths. The compressive strength begins to decrease insignificantly in case the amount of FCC supplementary material is higher, i.e. 30 %. Compressive strength increase slightly from 44 Mpa till 45.92 Mpa using pFCC as supplementary material. Better results of compressive strength were observed in the samples with pFCC. The best compression strength of 65.25 MPa was with 10 % of pFCC by comparing with reference sample which has compression strength of 46.80 MPa in investigated conditions.

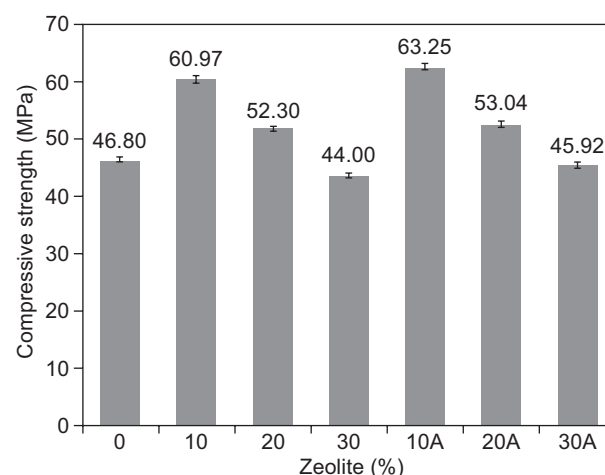


Figure 5. The influence of FCC and pFCC supplementary material content on compressive strength after 28 days of hardened cement paste.

CONCLUSIONS

Hardened cement paste samples with investigated zeolitic waste treated with hydrogen peroxide showed higher compression strength than the samples with untreated waste FCC catalyst. It was experimentally confirmed that the possible replacement level of Portland cement with purified waste FCC catalyst is from 10 till 30 %. The compression strength increases in all cases. The highest compression strength was obtained when 10 % of Portland cement was replaced with pFCC. It increases about 35 % by comparing with reference samples strength. A pozzolanic reaction with calcium hydroxide $\text{Ca}(\text{OH})_2$, liberated during cement hydration, undergo when the pFCC are incorporated in Portland cement mixtures. This reaction produces cement-like hydrated products responsible for the development of mechanical strength.

It provides some new knowledge about the organic impurity in used FCC and its effect on cement performance.

REFERENCES

1. Gary J.H., Glenn E.H.: *Petroleum Refining: Technology and Economics*, 4th ed., p. 437, CRC Press, 2001.
2. Garcés P., Glasser F.P., Brew D.R., Zornoza Gómez E.M.I.L.I.O., Paya Bernabeu J.J.: *Advances in Cement Research* 23, 105 (2011).
3. Tseng Y.S., Huang C.L., Hsu K.C.: *Cement and concrete research* 35, 782 (2005).
4. Chen H.L., Tseng Y.S., Hsu K.C.: *Cement and concrete composites* 26, 657 (2004).
5. Wu J.H., Wu W.L., Hsu K.C.: *Cement and Concrete Research* 33, 245 (2003).
6. Payá J., Monzó J.M., Borrachero M.V., Velázquez S.: *Advances in Cement Research* 25, 112 (2013).
7. Al-Jabri K., Baawain M., Taha R., Al-Kamyani Z.S., Al-Shamsi K., Ishtieh A.: *Construction and Building Materials* 39, 77 (2013).
8. Su N., Fang H.Y., Chen Z.H., Liu F.S.: *Cement and Concrete Research* 30, 1773 (2000).
9. Costa C., Marques P.: *Cement Industry Technical Conference 2012 IEEE-IAS/PCA 53rd*, 1 (2012).
10. Zornoza E., Payá J., Monzó J., Borrachero M.V., Garcés P.: *Construction and Building Materials* 23, 1323 (2009).
11. Taha R., Al-Kamyani Z., Al-Jabri K., Baawain M., Al-Shamsi K.: *Journal of hazardous materials*, 229-230, 122 (2012).
12. Zornoza E., Garcés P., Payá J., Climent M.A.: *Cement and Concrete Research* 39, 126, (2009).
13. Al-Dhamri H., Melghit K.: *Journal of hazardous materials* 179, 852 (2010).
14. Pacewska B., Nowacka M., Aleknevičius M., Antonovič V.: *Procedia Engineering* 57, 844 (2013).
15. Pacewska B., Nowacka M., Wilińska I., Kubissa W., Antonovich V.: *Journal of thermal analysis and calorimetry* 105, 129 (2011).
16. Zornoza E., Garcés P., Monzó J., Borrachero M.V., Payá, J.: *Advances in cement research* 19, 117 (2007).
17. Torres Castellanos N., Torres Agredo J.: *Ingeniería e Investigación* 30, 35 (2010).
18. Antonovič V., Baltrėnas P., Aleknevičius M., Pundienė I., Stonys R. in the 10th International Conference „Modern Building Materials, Structures and Techniques”, p. 6–12 Technika, Vilnius 2010.
19. Eisinas A., Baltakys K.: *Cheminė technologija* 50, 18 (2009). (In Lithuanian)