VILNIUS GEDIMINAS TECHNICAL UNIVERSITY

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THE INFLUENCE OF OIL CRACKING CATALYST WASTE ON THE PROPERTIES OF REFRACTORY CASTABLES

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Marius ALEKNEVIČIUS

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Introduction

Topicality of the problem. One of the priorities in management of waste is to turn waste into products or secondary raw materials for production. This is a rational and effective way to manage a wide line of technogenic waste, which may be useful for making of various products including building materials.

The fluidized bed catalytic cracking catalyst (FCCC) is technognic waste of oil refining industry, aluminosilicate zeolite material. During the technological process FCCC is contaminated by various impurities including heavy metals, what may lead to various problems (toxical, technological and others) if FCCC is to be used in building materials. In terms of toxicity, its use in building materials for industrial purposes is most appealing. Since the resistance of FCCC to temperature is up to 1750 °C, it can be used in refractory castables.

This work deals with the possibility not only to reuse FCCC in refractory castables, but also to take advantage of FCCC zeolite properties for modification of physical, mechanical, thermal and other characteristics of these castables.

The object of research. The research object is FCCC waste, refractory binder material and refractory castables with a FCCC additive.

Main objective. To develop a medium cement refractory castable using, as an additive, fluidized bed catalytic cracking catalyst waste – zeolite.

Main tasks. To achieve the objective of the work, the following tasks should be solved:

1. To investigate the properties of FCCC and to determine the effect of high temperatures on mineral composition, structure and other characteristics of this material.
2. To assess the impact of FCCC on the properties of refractory binders with aluminate cement:
   a) to investigate how FCCC effects cement hydration,
   b) to investigate how FCCC effects the formation of structure during hardening and after treatment at high temperatures.
3. To develop a refractory castable modified by a FCCC additive, to determine its physical, mechanical and thermal characteristics.
4. To test the new refractory castable under the real operating conditions of thermal equipment.

Research methodology. In this work the main properties of refractory castable were determined basing on the LST EN 1402-(2–8):2004 standards. The optical and scanning electron microscopy, X-ray diffraction, thermographic,

dilatometric, porosimetric, ultrasonic analyses were employed to assess the structure of materials.

The differential scanning calorimeter and the egzothermal temperature measurement technique were used to measure the hydration heat of binders.

Scientific novelty. While preparing the dissertation, the following new results for the materials engineering science were obtained:

1. The investigated effect of temperature of 800–1200 °C on the properties of catalytic cracking catalyst waste allows to determine that FCCC waste is revelant as an additive in refractory materials.
2. It was found that the zeolite structure of FCCC changes the aluminate cement hydration: after mixing with water, the heat release rate increases immediately as well as the crystallization process rate and the impact on the structure of hydrates is observed.
3. The interaction mechanism between FCCC, aluminate cement and water was explained.
4. The mineral composition and structure changes were determined for aluminate cement and FCCC binder after treatment at high temperatures.
5. The new medium cement refractory castable was developed using FCCC as a modifying additive of castable properties.

Practical value. The medium cement refractory castable with chamotte fillers was developed. It can be used for lining of various thermal equipment (in industries of oil, ceramics, chemicals, energy and other), for replacement of chamotte brick masonry or conventional castables. The use of FCCC in refractory materials allows to solve efficiently the problem of waste disposal.

Defended propositions

1. The catalyst waste additive of zeolite structure changes the aluminate cement hydration, effects the formation of structure during hardening and after treatment at high temperatures.
2. Catalyst waste can be disposed of not only as an additive in refractory castables but also used as a valuable additive to improve physical, mechanical properties and performance of advanced medium cement refractory castable.

Scope of scientific work. The dissertation consists of introduction, five chapters and a summary of results. It also contains two annexes.

The volume of the work is 98 pages excluding annexes. The text makes use of 14 numbered formulas, 49 figures and 14 tables, as well as 110 references.

1. Fluidized bed catalytic cracking catalyst waste and its application fields

The performed literature review of researches on FCCC and usage of FCCC in various concretes shows: FCCC is a zeolite material with unique properties (sorption, porosity, ion migration in water solution), which is presently underused in the production of cementitious materials. It was also found that until now FCCC was not used in refractory castables, regardless of the suitability of its characteristics (chemical composition, particle size).

Subject to operating conditions and catalytic cracking type, FCCC may be contaminated by heavy metals (Ni), therefore, its reuse is desirable in materials for industrial purposes – refractory castables.

2. Raw materials. Research methodology

This dissertation makes use of two types of calcium aluminate cement: Gorkal 70 and Gorkal 40 made by the company "Gorka", Poland.

Gorkal 70 aluminate cement. Content of Al_2O_3 70 %, main mineral phases: CA ($CaO \cdot Al_2O_3$) and CA_2 ($CaO \cdot 2Al_2O_3$), bulk density 1100 kg/m^3, specific surface by Blaine method 454,8 m^2/kg, refractoriness not less than 1630 °C.

Gorkal 40 aluminate cement. Content of Al_2O_3 40 %, main mineral phases: CA ($CaO \cdot Al_2O_3$), ferrite phase, $C_{12}A_7$, C_2AS, bulk density 1160 kg/m^3, specific surface by Blaine method 345,5 m^2/kg, refractoriness not less than 1280 °C.

Microsilica from the company RW Silicium GmbH, Germany. Content of SiO_2 not less than 96 % of composition, bulk density 410 kg/m^2.

Reactive alumina of type CTC-20, produced by Almatis, Germany. Bulk density 2100 m^2/kg.

Chamotte aggregate made by crushing of chamotte bricks, density 1920 kg/m^3. The 0–1 mm and 1–5 mm fractions of chamotte aggregate were used in refractory castables, bulk density 1260 kg/m^3 and 910 kg/m^3 respectively.

Dispersive chamotte made by grinding of chamotte of same type in the laboratory ball mill. Bulk density is 1100 kg/m^3.

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

Water. Cement and FCCC suspensions and pastes were prepared with distilled water, mortar and castable with drinking water.

The compositions of studied binders are shown in the Table 1, and those of castables in the Table 2.

Table 1. The compositions of FCCC and cement binders in mass %

Composition	AC	NK5	NK10	NK15	NK20	NK30	NK100
Cement	100	95	90	85	80	70	0
FCCC	0	5	10	15	20	30	100

Table 2. The composition of refractory castables in mass %

Cement	Microsilica	Reactive alumina	FCCC	Dispersive chamotte	Chamotte aggregate	Deflocculant*	Water*
12	5	5	0	15,0	63	0,15	11,5
12	5	5	2,5	12,5	63	0,15	11,5
12	5	5	5,0	10,0	63	0,15	11,5
12	5	5	7,5	7,5	63	0,15	11,5

* – over 100 % of dry components.

In this work the main properties of refractory castable were determined basing on the LST EN 1402-(2–8):2004 standards. The optical and scanning electron microscopy (JEOL JSM-6490LV, Hitachi S4800, EVO50, JEOL JSM-7600F), X-ray diffraction (DRON7), thermographic (Linseis STA PT-1600), dilatometric (Linseis L76), porosimetric (Poremaster PM-33-12), ultrasonic (Pundit 7) analyses were employed to assess the structure of materials.

The differential scanning calorimeter and the egzothermal temperature measurement technique developed by the company Alcoa were used to measure the hydration heat of binders.

X-ray analysis was performed by means of diffractometer DRON-7 with copper anticatode, nickel filter, anode voltage 30 kV, anode current 12 mA, goniometer apertures (0,5; 1,0; 1,5) mm. For decoding of peaks, the ICDD database was used.

Thermal analysis The TG, DTG, DSC, DDSC curves were registered by thermo analytical instrument Linseis STA PT-1600 up to 1400 °C, temperature

rise rate 10 °C/min, air as heating environment for samples in furnance, weight of samples 30–75 mg.

Thermal stability factor was determined based on methodology developed by the Science Institute of Thermal Insulation of Vilnius Gediminas Technical University. For this purpose, the ultrasonic pulse velocity was measured after treatment of samples at 800 °C temperature and rapid cooling between two water cooled plates.

The selected analytical equipment and methodologies allow to examine the structure of the material under investigation, to disclose the processes taking place during hydration and after treatment at high temperatures.

3. Research on the properties of catalyst waste

FCCC, the aluminosilicate material, largely (89,5 %) consists of SiO_2 and Al_2O_3 minerals. The chemical composition of FCCC waste was determined to be as follows [in mass %]: SiO_2 – 50,1; Al_2O_3 – 39,4; SO_x – 2,3; Fe_2O_3 – 1,3; CaO – 0,5; MgO – 0,49; Na_2O – 0,2; K_2O – 0,07; Mn_2O_3 – 0,06. Average particle size was 42 µm.

X-ray analysis shows that FCCC is Y zeolite with faujasite structure (Fig. 1).

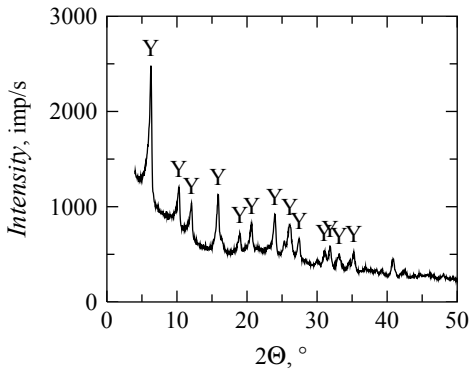


Fig. 1. The X-ray diffraction pattern of FCCC

The ecological study was carried out with FCCC coming from the oil refinery AB "Mazeikių nafta", Lithuania. The atomic absorption spectrophotometry was used to find out the concentration of heavy metals Ni, Fe, Cr, Pb, Zn in the waste

(Table 3). The results show that the concentrations of metals are very low except for Fe. This means that material is suitable for the production of binding material.

Table 3. The results of the analysis of the presence of heavy metals in FCCC

Metal	Average concentration, mg/kg
Ni	45
Fe	5300
Cr	74
Pb	32
Zn	39

As the studied binders are intended to be used at temperatures from 800 °C to 1300 °C, it was important to determine what processes are taking place in FCCC material at these temperatures.

At the initial stage of the temperature treatment of FCCC, water vapor is emmited from FCCC pores and channels what is shown by endothermic effect at 87 °C (Fig. 2). This process takes place up to 500 °C and is accompanied by a sudden loss in mass, 3,5 %. After decomposition of zeolite crystal lattice, the formation of mullite occurs, this formation is accompanied by the exothermic effect which is observed at the temperature of 973 °C. A broad exothermic peak is visible at the temperature of 1282 °C, evidencing the formation of cristobalite.

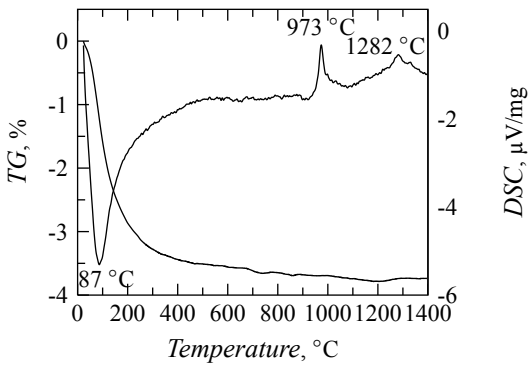
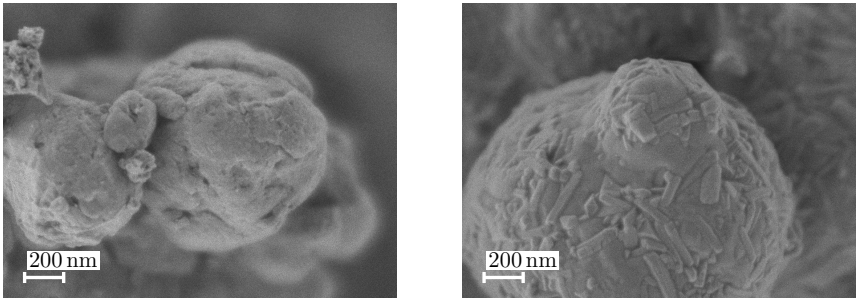


Fig. 2. Thermographical DSC and TG curves of FCCC

Although mineral changes in the structure of FCCC take place after its treatment at 1000 °C, nevertheless, the dramatic changes on the particle's surface are observed only at 1200 °C (Fig. 3). New structures are forming at this temperature on the surface of FCCC. These stuctures are 50–100 nm wide and 50–100 nm long mullite crystals.



a) b)

Fig. 3. SEM images of FCCC particles after treatment at the following temperatures: a) 1100 °C; b) 1200 °C

The results of research as well as porosity, calorimetric, and electro-conductivity measurements of FCCC-water suspensions show that when FCCC is treated at the temperature up to 950 °C, the zeolite structure is dominating (X-ray analysis). Nonetheless, treatment at 973 °C results in breakage of zeolite structure and formation of the germs of mullite crystals, as well as in change of porosity and decrease in electro-conductivity and sorption. After treatment at 1200 °C temperature, the zeolite structure is fully destroyed, and electic conductivity and sorption become similar to those of conventional castable additives such as ground chamotte, mullite, and other.

4. The influence of catalyst waste on aluminate cement binder hydration and properties

FCCC, as all zeolite materials, is good sorbent. Due to sorption, immediately after mixing FCCC with water, a considerably greater quantity of heat is released (Fig. 4a, curve NK100) in comparison with that of aluminate cement. In the binder with aluminate cement FCCC exerts a great influence on heat release what is not observed in the binder without this additive. We can see (Fig. 4a) that

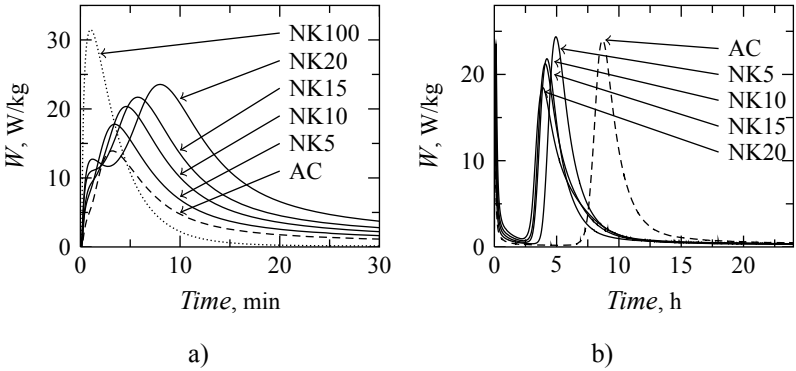


Fig. 4. The heat release rate (W) of cement pastes with FCCC, a) – in 0,5 h; b) – in 24 h

along with increase of FCCC content from 5 % to 20 %, the heat release also is growing, at once after mixing with water, from 14 W/kg to 23 W/kg in the first 10 min. Most likely, for this reason, the induction period of hydration of binders (at constant heat release) is cut down almost twice (Fig. 4b) and the crystallization of hydration products is going faster (a second sudden effect of heat release). Though the cement content is decreased thank to increase of FCCC, the quantity of heat released in 24 h almost equals to that of the binder without additive, approximately 240 kJ/kg. That means that FCCC additive not only accelerates the hydration of cement, but also stimulates the process of crystallization (additional heat release).

It was found that the samples with FCCC additive hardened much earlier than those without additive (Table 4). So the hardening (1,8 h) of the sample with the maximum quantity of FCCC (NK30) comes to an end earlier by more than 3 times than the binder without a FCCC additive (6 h).

Table 4. The setting time of cement binders in h

AC	NK10	NK20	NK30
6	5	3,5	1,8

The X-ray analyses show that peaks of CAH_{10} and C_2AH_8 hydrates are low in intensity in binders with FCCC in comparison with the binder without a FCCC

additive. The degree of hydration of such binders can be assessed by the peak intensity of the CA phase. The higher the intensity of the peak of not reacted phase, the lower the degree of cement hydration. In the X-ray diffraction patterns of NK10 and NK20 compositions, the main peak of CA phase (d = 0,297 nm) is significantly higher in the AC composition without a FCCC additive. However, the intensity of this peak in the binder with 30 % of FCCC is close to that of AC composition.

It was found by means of thermal analysis that the maximum loss in mass after treatment of cement binders up to 1000 °C is found in binder without a FCCC additive, approximately 22,6 %, while in binder with 10 % of FCCC – 16,3 %, with 20 % of FCCC – 17,5 % and 30 % of FCCC – 19,7 %. This means that the degree of hydration (bound water in hydrates) is lower in binders with a FCCC additive than in the AC composition (without a FCCC additive).

The analysis of adhesion between FCCC particles and cement stone shows that in many cases a gap between them is formed, separating these components (Fig. 5). These gaps have width of 50–100 nm (Fig. 5). Upon analysing the surface of FCCC (Fig. 5), it was found that it is covered by dense and fine cement hydration products. Furthermore, in the area of a gap, in the contact zone, characteristic needle-shaped crystal hydrates are formed (Fig. 6). Their loose arrangement (Fig. 6) suggests that the emerged gap provoked their formation.

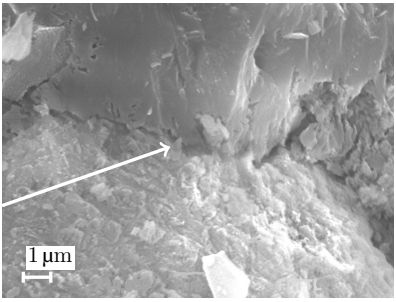


Fig. 5. The zone between a FCCC particle and cement matrix in cement stone with 10 % of FCCC

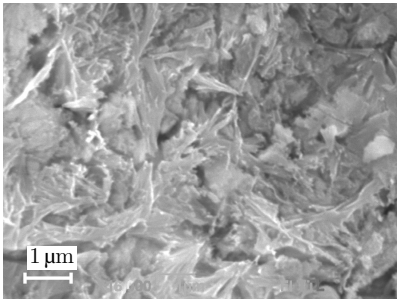


Fig. 6. The structure of the contact zone between cement stone and FCCC particle in a binder with 10 % of FCCC

To improve the adhesion of FCCC particles with cement stone 0,1 % and 0,2 % of Castament FS-20 polycarboxilate deflocculant were added to binder with

10 % of FCCC. In binders with deflocculant FCCC particles very well adhered to the cement matrix and no gaps formed around particles. As for the binders without deflocculant (Fig. 6), as well as for the binders with deflocculant, the formation of crystal hydrates occur in the contact zone between FCCC particles and cement matrix. However, in case of deflocculant, their layout is much denser than in the sample without deflocculant.

Basing on the results of research, the diagram of interaction between FCCC, aluminate cement and water can be drawn. At the first stage, FCCC sorbs water (Fig. 7a), at the second stage after the start of the formation of crystal hydrates, some water from FCCC particles is released (Fig. 7b). Due to it, at the third stage the layer of crystal hydrates is formed around FCCC particles (Fig. 7c).

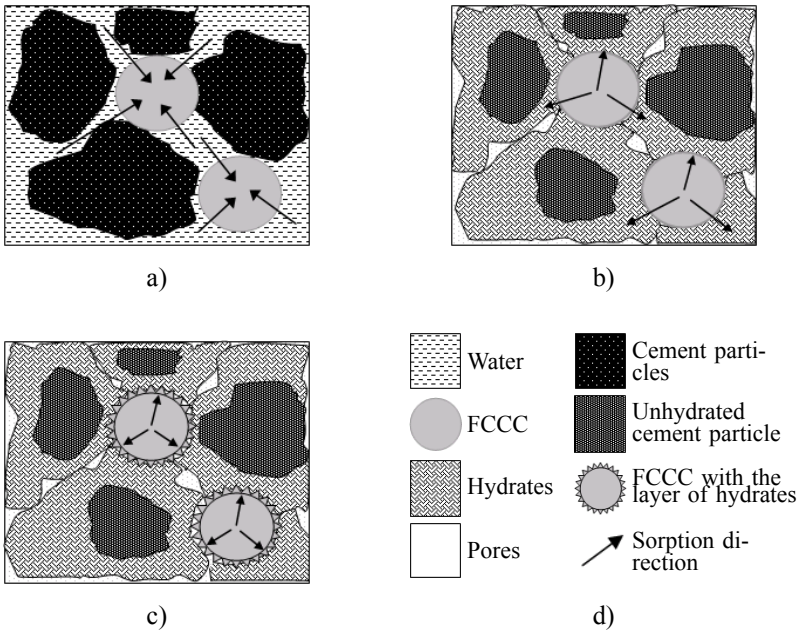
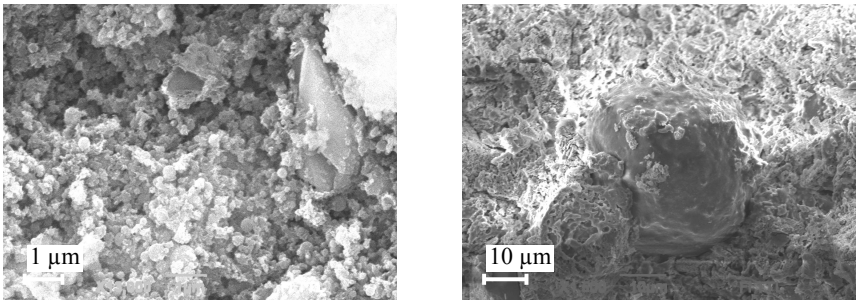


Fig. 7. The diagram of hardening for the binder with aluminate cement and FCCC: a) immediately after mixing with water; b) formation of cement stone structure; c) formation of hydrate layers around FCCC particles; d) legend

The effect of temperature on the properties of binder was studied. In the process of dehydration (100 °C), the decay of CAH_{10} and C_2AH_8 hydrates and

the formation of cube-shaped C_3AH_6 crystal hydrates takes place. This transformation is observed in the contact zone between FCCC particles and cement matrix (Fig. 8a). Long particles (Fig. 6) are transforming into cube-shaped particles of the average size of 250 nm (Fig. 8a).



a) b)

Fig. 8. The SEM image of the binder of cement stone with 10 % of FCCC: a) in the contact zone after treatment at 100 °C and b) 1200 °C temperature

After treatment of binder at 900–1200 °C temperature, the FCCC additive induces greater contraction of binder, in comparison with binder without a FCCC additive, from 1,5 % to 2,2 %. At 1200 °C the anorthite is formed in the binder: the higher the content of a FCCC additive, the higher the intensity of peak is observed in the X-ray diffraction pattern. The contraction and transformations result in the improved contact between FCCC particles and cement matrix (Fig. 8b) and in the absense of gaps in contrast to untreated binder (Fig. 6).

5. The influence of catalyst waste on the properties of medium cement refractory castable

The results of the investigation of binders enable to design medium cement refractory castables. Such castables were developed using aluminate cement containing 70 % and 40 % of Al_2O_3 and a FCCC additive, respectively 2,5 % and 5,0 %. It was found that a FCCC additive, due to its zeolite structure, increases the intensity of the hydration of MCC castable: the time of the maximal temperature of exothermic process shortens about 2–3 times, and the value of this temperature increases 2–9 °C, subject to type of cement used.

The results show that the compressive strength of castables increases up to 40 % after curing for 3 days. The compressive strength after treatment at various temperatures depends on the type of aluminate cement. Using aluminate cement containing 70 % of Al_2O_3, the compressive strength of castable with 2,5 % of a FCCC additive is the highest within range of temperatures studied (Fig. 9a). While increasing the content of FCCC in castable, the compressive strength decreases. The highest compressive strength of castables with aluminate cement containing 40 % of Al_2O_3 after treatment at 800 °C and 1200 °C temperatures is achieved with 5 % of a FCCC additive (Fig. 9b).

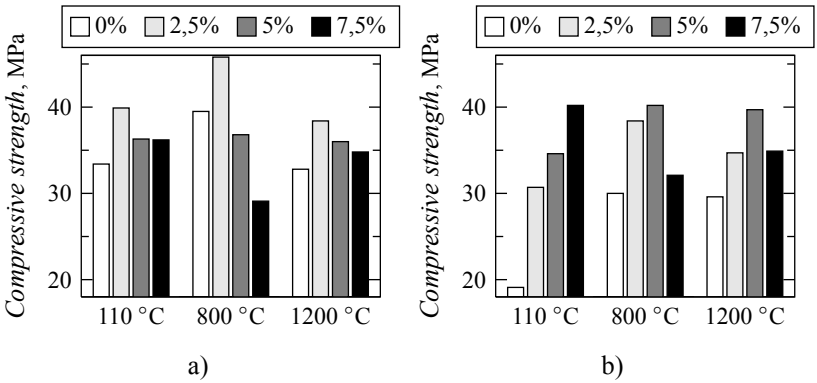


Fig. 9. The compressive strength of castable after treatment at various temperatures with aluminate cement containing: a) 70 % and b) 40 % of Al_2O_3

The thermal stability factor of castables with a FCCC additive is higher in castable with cement containing 70 % of Al_2O_3 – at 800 °C temperature with 2,5 % of a FCCC additive is 0,79, while without an additive 0,7, meanwhile in castable with cement containing 40 % of Al_2O_3 and 5 % of a FCCC additive 0,73 and without an additive 0,67.

Experimental tunnel kiln car lining blocks made of medium cement refractory castable with aluminate cement containing 70 % of Al_2O_3 and 2,5 % of a FCCC additive were made (approximately 2 t) at the factory AB "Palemono keramika", Lithuania in November 2006.

Blocks were in operation for about 3 years and withstood about 400 cycles until significant breakage (large gaps, and separated pieces of castable falling). The new castable lining allowed to increase the durability of the car lining about 2 times in comparison with that of conventional castable blocks.

The accomplished research and development work at the ceramics factory enables to reuse FCCC as an additive in refractory castable.

General conclusions

1. The investigated effect of 800–1200 °C temperature on the properties of catalytic cracking catalyst waste, allows to describe waste, as a proper additive for refractory materials. It was assessed that the zeolite structure at 1000 °C temperature transforms into mullite, and after treatment at 1200 °C cristobalite forms, the 10 % decrease of an average diameter and of about 2 times decrease in porosity is observed.
2. The carried out study of binding material consisting of aluminate cement containing 70 % of aluminium oxide and catalytic cracking catalyst waste shows the following:
   - catalyst waste exerts an impact on aluminate cement hydration: immediately after mixing with water (V/C = 0,5), the heat release rate increases 20–40 % in proportion to the quantity of catalyst 5–20 % in cement paste; the crystallization process is accelerated about 2 times, the changes in the ratio of CAH_{10} to C_2AH_8 hydrates are observed. The temperature of endothermic effect accompanying the dehydration of these hydrates grows from 153 °C up to 170 °C along with increase in content of catalyst from 10 % up to 30 %.
   - The temperatures have the following effect on aluminate cement stone with catalyst waste: after treatment at 100 °C temperature in the area between catalyst waste particles and cement stone cube-shaped particles of the average size of 250 nm were formed. After treatment at 1200 °C in the structure of contact zone, small crystals are still prevailing. By increasing the catalyst content in cement stone from 0 % to 20 % and after treatment at 800–1200 °C temperature, one can observe the contraction of a sample from 1,5 % up to 2,2 %, also at this temperature in the binder with a catalyst waste additive in comparison with the binder without the additive, the anorthite is formed.
3. The mechanism of interaction between catalytic cracking catalyst waste, aluminate cement containing 70 % of aluminium oxide and water was explained:
   - after mixing the dry ingredients with water, the catalyst waste, due to its high sorption properties, absorbs a certain amount of water used

for mixing. In result, the saturation of solution with cement mineral ions occurs earlier than in solution without a catalyst waste additive. This also causes the earlier formation of cement crystal hydrates;
- after the start of the formation of crystal hydrates, some water from catalyst waste particles is released into the cement matrix and takes part in the further cement hydration process. There is an additional release of heat, due to it the hardening of binders is accelerated;
- water around catalyst waste particles is released and around these particles a crystal hydrate layer is formed, up to 100 nm wide.

4. Medium cement refractory castables were developed using aluminate cement containing 70 % and 40 % of aluminium oxide and a catalytic cracking catalyst waste additive, 2,5 % and 5,0 %, respectively. It was found that the advantages of new castable over castable without a catalytic cracking catalyst waste additive are the following:
   - Faster by 6 h hardening of castable with aluminate cement containing 70 % of Al_2O_3 and 13,5 h with 40 %;
   - up to 40 % higher compressive strength after curing for 3 days;
   - up to 20 % higher compressive strength at operating temperature of 1200 °C using aluminate cement containing 70 % of Al_2O_3;
   - higher thermal stability: in castable with cement containing 70 % of Al_2O_3 the thermal stability factor at 800 °C temperature is 0,75–0,79, without a catalyst waste additive 0,70.
5. The dry castable mixture was produced (approximately 2 t), it was used to manufacture tunnel kiln car lining blocks at the factory AB "Palemono keramika", Lithuania. It was found that the used new castable allowed to increase the durability of the car lining about 2 times. The accomplished research and development work at the ceramics factory enables not only to reuse catalytic cracking catalyst waste in refractory castables, but also to use it, as a valuable additive, for improvement of physical, mechanical properties and performance of advanced medium cement refractory castables.

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NAFTOS KREKINGE NAUDOTO KATALIZATORIAUS POVEIKIS UGNIAI ATSPARIŲ BETONŲ SAVYBĖMS

Mokslo problemos aktualumas. Paskutinio dešimtmečio tendencija – ugniai atsparių medžiagų naudojimo mažėjimas. Tai lėmė pramonės, naudojančios ugniai atsparias medžiagas, o ypač metalurgijos, restruktūrizacija, naujų efektyvių medžiagų sukūrimas, globalizacijos procesas. Kita tendencija – forminės medžiagos (plytos, blokai ir kiti gaminiai) keičiamos ugniai atspariais betonais, kurių konstrukcijos (išklojos) turi svarbių privalumų: sutaupoma laiko ir lėšų šiluminiams agregatams statyti, remontuoti ir eksploatuoti, palengvėja šiluminių agregatų projektavimas iš monolitinių konstrukcijų, nes naudojamos nesudėtingos išklojų pagaminimo technologijos. Tikimasi, kad ateityje forminių medžiagų panaudojimas tebemažės, o betonų poreikis pastoviai didės. Todėl aktualu kurti naujos kartos ugniai atsparius betonus, kurių technologijoje siekiama kuo labiau sumažinti cemento ir vandens kiekius, naudojant įvairius efektyvius priedus.

Naujųjų ugniai atsparių betonų savybės – mechaninės, terminės ir kt. akivaizdžiai pranašesnės nei forminių gaminių bei įprastinių betonų. Reikia pažymėti, kad tokie betonai yra labai jautrūs gamybinėms sąlygoms: aplinkos temperatūrai, maišymo parametrams, vandens kokybei ir kt., dėl to kartais nepavyksta pagaminti kokybiško produkto. Tai rodo, kad naujų betonų hidratacijos procesas sunkiai valdomas, nepavyksta deramai reguliuoti struktūrų formavimosi mikro ir nano lygmenyje.

Naujos kartos betonų gamybai reikia tokių priedų, kurie galėtų modifikuoti betono reologines savybes, cemento hidratacijos procesą (reguliuojant rišimosi laikus) ir betono struktūros formavimąsi kietėjimo metu. Veikiant aukštoms temperatūroms yra aktualu, kad tokie priedai efektyviai veiktų kietafazėse reakcijose, mažintų destrukcijos procesus eksploatacijos temperatūrose. Dėl ypatingų savybių (gera sorbcija, didelis savitasis paviršius, tinkami dalelių matmenys ir cheminė sudėtis), naftos krekinge naudoto katalizatoriaus (NK) priedas ugniai atspariame betone galėtų atlikti aukščiau minėtas funkcijas.

Planuojant naudoti NK ugniai atspariose medžiagose, reikia pažymėti, kad šios medžiagos, kurių sudėtyje yra nemažai Al ir Si oksidų, yra brangios, todėl NK naudojimas turi ne tik ekologinį ir technologinį, bet ir ekonominį pagrindą.

Tyrimų objektas. Darbo tyrimų objektas yra NK atliekos, ugniai atspari rišamoji medžiaga ir ugniai atsparūs betonai su NK priedu.

Darbo tikslas. Sukurti vidutinio cemento kiekio ugniai atsparų betoną su naftos kataliziniame krekinge naudoto katalizatoriaus priedu – ceolitu.

Darbo uždaviniai. Darbo tikslui pasiekti iškelti šie uždaviniai:

1. Ištirti NK savybes, nustatyti aukštų temperatūrų poveikį šios medžiagos mineralinei sudėčiai, struktūrai ir kitoms charakteristikoms.
2. Nustatyti NK poveikį ugniai atsparių kompozicijų su aliuminatiniu cementu savybėms:
   a) ištirti NK poveikį cemento hidratacijos procesui,
   b) ištirti NK poveikį struktūros formavimuisi kietėjimo metu ir aukštose temperatūrose.
3. Sukurti ugniai atsparų betoną modifikuotą NK priedu, nustatyti pagrindines jo fizikines, mechanines ir termines charakteristikas.
4. Išbandyti naują ugniai atsparų betoną realiomis eksploatacinėmis salygomis šiluminiuose agregatuose.

Tyrimų metodika. Pagrindinės ugniai atsparaus betono savybės šiame darbe buvo nustatomos remiantis LST EN 1402-(2-8):2004 standartais. Medžiagos struktūrai vertinti buvo naudojami optinės ir skenuojančios elektroninės mikroskopijos, rentgenografinės, termografinės, dilatometrinės, porozimetrinės bei ultragarsinės analizės metodai.

Rišamųjų medžiagų hidratacijos šilumai įvertinti naudota diferencinė kalorimetrija ir egzoterminio proceso temperatūros nustatymo metodika.

Mokslinis naujumas. Rengiant disertaciją buvo gauti šie medžiagų inžinerijos mokslui nauji rezultatai:

1. Ištirtas 800–1200 °C temperatūros poveikis kataliziniame krekinge naudoto katalizatoriaus savybėms, leidžiantis nustatyti NK atliekų panaudojimo ugniai atspariose medžiagose tinkamumą.
2. Nustatyta, kad ceolitinė NK priedo struktūra veikia aliuminatinio cemento hidrataciją: padidina šilumos išsiskyrimo greitį iškart po sumaišymo su vandeniu, pagreitina kristalizacijos procesą, daro įtaką besiformuojančiai hidratų struktūrai.
3. Išaiškintas naudoto katalizatoriaus, aliuminatinio cemento ir vandens sąveikos mechanizmas.
4. Nustatyti aliuminatinio cemento ir NK rišamosios kompozicijos mineralinės sudėties ir struktūros kitimai aukštose temperatūrose.
5. Sukurtas naujas vidutinio cemento kiekio ugniai atsparus betonas, panaudojant betono savybes modifikuojantį NK priedą.

Praktinė reikšmė. Sukurtas vidutinio cemento kiekio ugniai atsparus betonas su šamoto užpildais, kuris gali būti naudojamas įvairių šiluminių agregatų (naftos, keramikos, chemijos, energetikos ir kitose pramonėse) išklojose, pakei-

čiant šamotinių plytų mūrą arba morališkai pasenusius įprastinius betonus. NK panaudojimas ugniai atspariame betone leidžia efektyviai (ekologiniu ir ekonominiu požiūriu) išspręsti šių atliekų utilizavimo problemą.

Ginamieji teiginiai

1. Ceolitinę struktūrą turintis naudoto katalizatoriaus priedas keičia aliuminatinio cemento hidrataciją, veikia struktūros formavimąsi kietėjimo metu ir aukštose temperatūrose.
2. Naudotas katalizatorius gali būti ne tik utilizuojamas ugniai atspariuose betonuose, bet ir naudojamas kaip vertingas priedas gerinantis pažangių vidutinio cemento kiekio betonų fizikines, mechanines bei eksploatacines savybes.

Disertacijos struktūra. Darbo apimtis yra 98 puslapiai, neskaitant priedų, tekste panaudotos 14 numeruotų formulių, 49 paveikslai ir 14 lentelių. Rašant disertaciją buvo panaudota 110 literatūros šaltinių.

Disertaciją sudaro įvadas, penki skyriai, bendrosios išvados, naudotos literatūros ir autoriaus publikacijų disertacijos tema sąrašai. Taip pat yra du priedai. Įvadiniame skyriuje aptariama tiriamoji problema, tyrimo objektas ir metodika, darbo aktualumas, formuojami darbo tikslai bei uždaviniai, aprašomas darbo mokslinis naujumas, nurodoma darbo rezultatų praktinė reikšmė, įvardijami ginamieji teiginiai. Įvado pabaigoje pristatomos disertacijos tema autoriaus paskelbtos publikacijos ir pranešimai konferencijose ir disertacijos struktūra. Pirmasis skyrius skirtas literatūros apžvalgai. Skyriaus pabaigoje formuluojami apibendrinimai ir išvados. Antrajame skyriuje aprašytos naudotų žaliavų charakteristikos, naudoti metodai ir įranga. Trečiajame skyriuje pateikiami naudoto katalizatoriaus tyrimai. Ketvirtajame skyriuje nagrinėjamas naudoto katalizatoriaus poveikis aliuminatinio cemento kompozicijų hidratacijai ir savybėms. Penktajame skyriuje aprašomi naudoto katalizatoriaus poveikio vidutinio cemento kiekio ugniai atsparaus betono savybėms tyrimai.

Bendrosios išvados

1. Ištirtas 800–1200 °C temperatūros poveikis kataliziniame krekinge naudoto katalizatoriaus savybėms leidžia apibūdinti šias atliekas kaip tinkančias naudoti ugniai atspariose medžiagose. Nustatyta, kad ceolitinė struktūra 1000 °C temperatūroje virsta į mulitą, o 1200 °C – susidaro kristobalitas, 10 % sumažėja katalizatoriaus dalelių vidutinis skersmuo ir iki 2 kartų sumažėja jų poringumas.

2. Atlikti rišamosios medžiagos, susidedančios iš 70 % aliuminio oksido turinčio aliuminatinio cemento ir naudoto katalizatoriaus, tyrimai leidžia konstatuoti:
   - naudotas katalizatorius daro įtaką aliuminatinio cemento hidratacijai: užmaišius cemento tešlą su vandeniu (V/C = 0,5) šilumos išsiskyrimo greitis didėja 20–40 % proporcingai katalizatoriaus kiekiui 5–20 % tešloje; apie 2 kartus pagreitėja kristalizacijos procesas, pasikeičia susidariusių CAH_{10} ir C_2AH_8 hidratų santykis. Šių hidratų dehidrataciją lydinčio endoterminio efekto temperatūra, padidinus katalizatoriaus priedo kiekį nuo 10 % iki 30 %, padidėja nuo 153 °C iki 170 °C.
   - Veikiant aliuminatinio cemento akmenį su naudotu katalizatoriumi temperatūra nustatyta, kad po kaitinimo 100 °C temperatūroje naudoto katalizatoriaus dalelių ir cemento akmens sąlyčio zonoje susiformuoja vidutinio 250 nm skersmens kubinės formos dalelės. Po degimo 1200 °C temperatūroje sąlyčio zonos struktūroje ir toliau vyrauja smulkiakristalinė struktūra. Didinant cemento akmenyje katalizatoriaus kiekį nuo 0 % iki 20 % po degimo 1200 °C temperatūroje padidėja kompozicijos susitraukimas nuo 1,5 % iki 2,2 %, taip pat šioje temperatūroje cemento akmenyje su naudotu katalizatoriumi, palyginti su kompozicija be priedo, formuojasi anortitas.
3. Išaiškintas naudoto katalizatoriaus, 70 % aliuminio oksido turinčio aliuminatinio cemento ir vandens sąveikos mechanizmas:
   - sumaišius sausus komponentus su vandeniu naudotas katalizatorius dėl savo gerų sorbcinių savybių įgeria dalį sumaišimui sunaudoto vandens. Dėl to tirpalo įsisotinimas cemento mineralų jonais pasiekiamas greičiau, anksčiau prasideda cemento kristalohidračių formavimasis nei kompozicijoje be naudoto katalizatoriaus priedo;
   - pradėjus formuotis kristalohidračiams dalis vandens iš naudoto katalizatoriaus dalelių patenka į cementinę matricą ir yra naudojama tolesniame cemento hidratacijos procese. Vyksta papildomas šilumos išsiskyrimas, pagreitinantis kompozicijos kietėjimą;
   - dėl atsilaisvinusio iš naudoto katalizatoriaus dalelių vandens aplink šias daleles susiformuoja kristalohidračių zonos, kurių plotis siekia iki 100 nm.
4. Sukurti vidutinio cemento kiekio ugniai atsparūs šamotbetoniai su 70 % ir 40 % aliuminio oksido turinčiais aliuminatiniais cementais ir naudoto

katalizatoriaus priedu atitinkamai 2,5 % ir 5,0 %. Nustatyta, kad naujo betono pranašumai palyginti su betonu be naudoto katalizatoriaus priedo yra:

- 6 h greitesnis betono kietėjimas naudojant 70 % Al_2O_3 turintį aliuminatinį cementą ir 13,5 h – 40 %;
- iki 40 % didesnis gniuždymo stipris po 3 parų kietėjimo;
- iki 20 % didesnis gniuždymo stipris eksploatacinėje 1200 °C temperatūroje, kai naudojamas 70 % Al_2O_3 turintis aliuminatinis cementas;
- didesnis terminis patvarumas: betone su 70 % Al_2O_3 turinčiu cementu terminio patvarumo koeficientas 800 °C temperatūroje – 0,75–0,79, betone be naudoto katalizatoriaus priedo – 0,70.

5. Pagaminta bandyminė sausųjų betono mišinių partija (apie 2 t), kuri panaudota AB „Palemono keramika“ gamyklos tunelinės krosnies vagono išklojai pagaminti. Nustatyta, kad naujo betono panaudojimas leido padidinti vagono išklojos ilgaamžiškumą apie 2 kartus. Atlikti moksliniai tyrimai ir diegiamasis naujos medžiagos darbas keramikos gamykloje sudaro galimybes ne tik utilizuoti naudotą katalizatorių ugniai atspariuose betonuose bet ir naudoti kaip vertingą priedą gerinantį pažangių vidutinio cemento kiekio betonų fizikines, mechanines bei eksploatacines savybes.

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