MODIFICATION OF PETROCHEMICAL FLUID CATALYTIC CRACKING CATALYST WASTE PROPERTIES BY TREATMENT IN HIGH TEMPERATURE

Valentin Antonovič, Pranas Baltrėnas, Marius Aleknevicius, Ina Pundienė, Rimvydas Stonys

1Vilniaus Gediminas Technical University Institute of Thermal Insulation, Linkmenų str.28, LT-08217, Vilnius, Lithuania. E-mail: futer@centras.lt
2Vilniaus Gediminas Technical University Department of Environmental Protection, Saulėtekio ave. 11, LT-10223 Vilnius, Lithuania. E-mail: pbalt@vgtu.lt

Abstract. Approximately 400 000 tons of waste catalysts are produced by petrochemical industry in fluidized bed catalytic cracking (FCC) process annually. In Lithuania (Mažeikiai Oil Refinery) the waste amounts up to about 200 tons/year. As FCC catalyst is an inorganic aluminosilica zeolite material, the properties of it are important for refractory concrete. This work investigated properties of the waste fired at temperature of 800-1300 °C. It was established that at temperatures higher than 1050 °C, in the waste FCC catalyst the physical and structural changes take place, the zeolitic structure is destroyed and the mineralogical composition undergoes changes, as well as porosity and size of particles. In case of reuse of catalyst waste in refractory concrete, these changes of material can negatively influenced on properties of refractory concrete. One of the promising directions for reuse of waste in refractory material is its modification at temperature of approximate 1000 °C when the porosity of particles changes and, supposedly, the germs of mullite crystals are forming, irrespective of the still dominating zeolitic structure.

Keywords: FCC catalyst waste, zeolite, thermal treatment, refractory concrete.

1. Waste Fluid catalytic cracking catalyst

Approximately 400 000 tons of waste catalysts are produced by the petrochemical industry in fluidized bed catalytic cracking (FCC) process annually (Furimsky 1996). In Lithuania (Mažeikiai Oil Refinery) the waste amounts up to about 200 tons/year. As FCC catalyst is an inorganic aluminosilica zeolite material, the properties of it are important for refractory concrete. This work investigated properties of the waste fired at temperature of 800-1300 °C. It was established that at temperatures higher than 1050 °C, in the waste FCC catalyst the physical and structural changes take place, the zeolitic structure is destroyed and the mineralogical composition undergoes changes, as well as porosity and size of particles. In case of reuse of catalyst waste in refractory concrete, these changes of material can negatively influenced on properties of refractory concrete. One of the promising directions for reuse of waste in refractory material is its modification at temperature of approximate 1000 °C when the porosity of particles changes and, supposedly, the germs of mullite crystals are forming, irrespective of the still dominating zeolitic structure.

Keywords: FCC catalyst waste, zeolite, thermal treatment, refractory concrete.

Figure 1. Scheme of thermal equipment of FCC unit

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.

In some countries the waste catalyst was partly utilized in the rotary furnaces during production of Portland cement clinker (Schreiber et al. 1993), as a filler in asphalt concrete mixes (Lin et al. 1995) or a substitute for kaolin in the industry of ceramic frits (Escardino et al. 1995).

Later investigations showed that the waste catalyst can be used as a fine additive in grouts for various purposes, in concrete and in other cementitious compositions (Su et al. 2000; Hsu et al. 2001; Pacewska et al. 1998; Paya et al. 1999). It is established that FCC catalyst reacts with Ca(OH)₂ (the product of cement hydration) as a pozzolanic material (Pacewska et. al. 2002, Paya et. al. 2003) and increases the compressive strength and other properties of the compositions with Portland cement (Paya et. al. 2001, Wu et. al. 2003, Bukowska et. al. 2004). The pozzolanic properties of FCC waste may be activated, simultaneously improving the strength of cementitious materials by means of waste milling (Pacewska et. al. 2004).

It should be noted that the scientists, who investigate the building materials with waste catalyst, face certain difficulties. In some applications of lime binders the pozzolanic activity of FCC catalyst was not sufficient (Paya et. al. 2004). J. Dweck found (Dweck et al. 2008), that beside the pozzolanic activity which occurs in Portland cement composition, in some cases the compressive strength of pastes containing spent catalyst was lower then that of pastes formed with only cement and water. Supposedly, some elements, like nickel, which is present in the spent catalyst composition, may have limited the pozzolanic activity. Larger amounts of waste in cement compositions require larger water and cement ratio to assure good workability. With a lesser amount of water, only super plasticizers are essential to obtain proper workability of cement paste (Zornoza et. al. 2007).

Generally, it can be stated, that despite the investigations of last 15 years, the problem of utilization and reuse of waste catalyst in building materials is still live. Why?

The generated amount of waste catalyst is very small in comparison with production volume of building materials, therefore, the manufacturers of building materials are not interested in amendment of their production technologies. Besides, depending on the FCC unit and operating conditions, in some cases the concentration of Ni increases up to >2000 mg/kg (Bayraktar 2005). Then, bioleaching can be used for mobilization of nickel from catalyst particles. This means that the reuse of waste catalyst in broad-used building materials must be very careful.

The situation may change in case of the reuse of waste in materials dedicated for industrial purposes, such as refractory materials. These materials are very expensive. So, development of new advantage refractory materials with required properties obtained due to the additive of waste catalyst could give great economical benefit.

FCC catalyst, as a fine additive, was tested in a refractory castable with liquid glass binder (Goberis et al. 1996). However, it was established that along with increase in amount of FCC additive in a 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 FCC catalyst in refractory concretes with alumina cement (Antonović et al. 2005). In comparison with the mentioned above study (Goberis et al. 1996), the polycarboxylate plasticizer were used for reduction of liquid phase in concrete. In this way the positive effect of waste catalyst on strength after hardening of concretes could manifest itself. Yet, at high temperatures the cold crushing strength and thermal shock resistance of concrete was lower than the concrete’s without catalyst.

The method to modify the properties of waste FCC catalyst, 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 waste catalyst) predetermine such properties as low density and big volume (after firing at temperature of >500 °C), stability of dehydrated crystalline zeolithic structures, properties of ion exchange, existence of one-type channels with diameters of molecule size in dehydrated crystals, electric conductivity, gas and vapor adsorption, catalytic properties (Breck et. al. 1976). The temperature modification of zeolitic structure in waste catalyst would enable to change (or to adjust as appropriate) their properties, thus extending the possibilities to develop advantage refractory material.

In study (Tseng et al. 2005) it was showed that pozzolanic activity of FCC catalyst in Portland cement composition could be improved by heat treatment at 450-850 °C. Authors indicated that particle size of the fired catalyst 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.

The goal of this work is to investigate the properties of waste catalytic cracking catalyst received from the joint stock company AB Mažeikiai Nafta (Lithuania) before and after treatment at temperatures of 800-1300 °C and to evaluate the possibilities of modified material to be used as an additive for refractory concrete.

2. Experimental

The microstructure of FCC waste particles was observed by a SEM (EVO50, JEOL JSM-7600F) and their size was measured by a coulter laser size analyzer (Analysette 22, Fritsch Germany). The X-ray phase analyses were carried out using a DRON-7 diffractometer (anode — cooper, anode voltage 30 kV, anode current 8 mA). The phase composition was identified using reference data from ICDD database. For thermoanalytical
studies of FCC catalyst, a STA PT-1600 (Linseis Germany) thermoanalyser was used, operating at temperatures ranging up to 1400 °C in air, at heating rate of 10°C min⁻¹, sample mass of 10 mg. The TG, DSC, curves were registered.

In order to investigate fired FCC waste, it was kept for 5 hours and fired in an electronic controller furnace at temperatures of 750, 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200 °C.

For calorimetric measurements, a differential calorimeter (produced in VGTU Thermal Insulation Institute) was used. The mixes (0.5 g distilled water and 1 g of solid substance) were studied at the starting temperature of 25°C and the heat evolution curves were registered. pH and electrical conductivity of suspensions (distilled water and FCC waste at ratio of 10:1) was measured with a Mettler-Toledo (electrode InLab 410, measurement accuracy for pH 0.01 and an electrode InLab 730 for electrical conductivity with measurement range of 0-1000µS/cm).

3. Results

The chemical composition of waste FCC catalyst was determined to be as follows [mass-%]: Al₂O₃ – 39.4, SiO₂ – 50.1, Fe₂O₃ – 1.3, SO₃ – 2.3, CaO – 0.5, MgO – 0.49, Na₂O – 0.4, K₂O – 0.07, MnOₓ – 0.06; ignition loss –5.4 % (Antonovič et al. 2005). Fig. 2 a shows the scanning electron micrograph (SEM) of FCC waste, indicating that catalyst particles are spherical.

In the waste one can observe a certain amount of destroyed spheres. These are particles of irregular shape (Fig 2 b). The specific surface of FCC catalyst is very large (about 100 m² g⁻¹) (Pacewska et al. 2004). The picture of inner structure of a particle is provided in Fig 2 c.

Though the waste FCC catalyst is not allocated to the group of harmful waste, nevertheless, the waste generated in the joint stock company AB Mažeikių Nafta was evaluated from ecological point of view. By method of atomic absorption spectrophotometry, the concentrations of heavy metals (Ni, Fe, Cr, Pb, Zn) were determined in the waste (Table 1). We can see that except for Fe, the concentration of other metals is very low.

The systematic annual control of Ni concentration in the joint stock company AB Mažeikių Nafta also shows that the concentration of this harmful element in the waste is stably low (Table 2).

Table 1. Results of analysis of heavy metals in waste FCC catalyst

<table>
<thead>
<tr>
<th>N/N</th>
<th>Metal</th>
<th>Concentration detected in mg/kg</th>
<th>Average concentration in mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni</td>
<td>43.59; 44.62; 46.15</td>
<td>44.79</td>
</tr>
<tr>
<td>2</td>
<td>Fe</td>
<td>4839.51; 5333.33; 5777.78</td>
<td>5316.87</td>
</tr>
<tr>
<td>3</td>
<td>Cr</td>
<td>76.92; 71.79; 72.82</td>
<td>73.85</td>
</tr>
<tr>
<td>4</td>
<td>Pb</td>
<td>31.74; 28.97; 33.33</td>
<td>31.65</td>
</tr>
<tr>
<td>5</td>
<td>Zn</td>
<td>28; 40; 48</td>
<td>38.67</td>
</tr>
</tbody>
</table>

Table 2. Ni amount in waste FCC catalyst (periodical testing)

<table>
<thead>
<tr>
<th>Serial number of analysis</th>
<th>Ni in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>187</td>
</tr>
<tr>
<td>2</td>
<td>205</td>
</tr>
<tr>
<td>3</td>
<td>227</td>
</tr>
<tr>
<td>4</td>
<td>322</td>
</tr>
<tr>
<td>5</td>
<td>110</td>
</tr>
</tbody>
</table>

The investigation of distribution of particles in the waste FCC catalyst fired at various temperatures showed (Fig.3) that at firing FCC waste catalyst up to 1000 °C, the diameters of particles remain the same, and the average diameter of particles is ~42 µm. Only after firing at temperature of 1200 °C, one can observe that the diameter of particles decreased to the medium size, ~38 µm.
Diameters of particles, μm

Volume, %

Fig 3. Average diameter of FCC catalyst particles depending on firing temperature (a) and the character of distribution of particles by diameter (b)

By tests of porosity, it was established that the structure of catalyst pores undergoes changes after thermal treatment at temperature of 950 °C (Fig 4). The biggest decrease of porosity of catalyst waste occur after thermal treatment at temperature of 1200 °C.

Fig 4. Pore size distribution for non-treated and treated at different temperature waste catalyst

By X-ray phase analyses (Fig 5), it was established that in waste FCC catalyst, the structure typical to Y zeolite does not change after firing temperatures of 750–900 °C. After firing at temperature of 950 °C the size of main peaks of Y zeolite slightly changes (Fig. 5 a) and a transforms into mullite (1000–1150 °C) and cristobalite (1200 °C).

The more precise information about the changes going in the structure of waste FCC catalyst is shown by thermographic tests (Aleknevičius et al. 2009). Namely, during the firing process, in the curve DSC of thermo-gram (Fig 6) one can see endothermal effect (87 °C) and two exothermal effects (973 °C, 1280 °C).

Fig 5. X—ray diffraction of waste FCC catalyst fired at various temperatures. Y — y zeolite, M — mullite, K — cristobalite

Fig 6. DSC and TG curves of waste FCC catalyst

The endothermal effect at temperature of 87 °C may be explained by desorption of water from catalyst pores and channels (Dweck at al. 2008) (the losses in the mass reach ~4 %). First exothermal effect at temperature near 1000 °C occurs due to crystallization of mullite, the
second exothermal effect occurs at 1280 °C due to crystallization of cristobalite (Fig.6).

Although the mineralogical changes in structure of catalyst are determined after treatment at temperature of 1000 °C, the sharp changes in surface of catalyst particles are observable only after treatment at temperature of 1200 °C when the surface of waste particles changes considerably (Fig.7).

We can see (Fig.7) that after firing at temperature of 1200 °C the surface of catalyst particles is coated richly by new formations generated. These are crystals of mullite, 50–100 nm wide and 100–400 nm long, and crystals of cristobalite of irregular shape.

The performed investigations showed that at temperature higher than 950 °C in waste FCC catalyst phase- and structural changes occur, the zeolitic structure is destroyed and the mineralogical composition, as well as porosity undergoes changes. However, the particle size and surface of catalyst changes considerably only after treatment at temperature of 1200 °C.

At planning to use the FCC catalyst waste as an additive in cementitious materials (refractory mortars and concretes), it is of importance to evaluate the properties of the waste in water suspension, since the characteristics of sorption and electric conductivity have a great influence on hydration of cementitious material.

The decrease of electric conductivity in suspensions of waste treated at temperature 850–1200 °C versus that of non-treated waste suspension means that at this temperature the ion exchange is less activated (Fig 8). We can see that the maximum of heat release rate, which describe the sorption properties of the catalyst, also decreased, when material was treated at temperature >850 °C (Fig.8).

Electric conductivity and maximum of heat release rate are lowest in suspension with material fired at 1200 °C.

Analyse of results of investigation show, that after treatment at temperature of 950 °C, the zeolite Y structure in waste FCC catalyst does not change after firing at temperature of 750–900 °C. The phase conversion of zeolitic structure into mullite at temperature of 1000 °C and into cristobalite at temperature 1200 °C is accompanied by endothermal effects and reduced porosity, while the changes on surface of catalyst particles in shape of new formations sized 50–100 nm (crystals of mullite and cristobalite minerals) are observable after firing at 1200 °C. After firing of waste at 1200 °C, the average diameter of particles decreased from 42 µm to ~38 µm.

Conclusions

1. It was established by spectrophotometry that the concentration of heavy metals (Ni, Fe, Cr, Pb, Zn) in waste FCC catalyst is very low (from 31 to 74 mg/kg), except for Fe, the content of which amounts to 5317 mg/kg.

2. By X-ray phase analyses, it was established that the zeolite Y structure in waste FCC catalyst does not change after firing at temperature of 750–900 °C. The phase conversion of zeolitic structure into mullite at temperature of 1000 °C and into cristobalite at temperature 1200 °C is accompanied by endothermic effects and reduced porosity, while the changes on surface of catalyst particles in shape of new formations sized 50–100 nm (crystals of mullite and cristobalite minerals) are observable after firing at 1200 °C. After firing of waste at 1200 °C, the average diameter of particles decreased from 42 µm to ~38 µm.
3. The investigations of electric conductivity and heat release rate of water suspension of waste FCC catalyst fired at different temperatures show that these characteristics may be controlled by treatment of waste at an appropriate temperature. The control of these properties (utilization of modified waste) would enable to extend the line of concretes for various purposes.

Acknowledgments

The scientific investigations, results of which are presented in this work, were financed by the Lithuanian State Science and Studies Foundation (Project Nano-CSM)

References


Escardino, A.; Amoros, J.; Moreno, A.; Sanchez, E. 1995. Utilizing the used catalyst from refinery FCC units as a substitute for kaolin in formulating ceramic frits, Waste Management and Research 13: 569–578


