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USE OF WASTE OF FERROALLOY PRODUCTION FOR OBTAINING OF GASOIL CRACKING CATALYST

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ABSTRACT

In this work obtaining of gasoil cracking catalyst from ferroalloy production waste is described. Results of research of original ash-slime and prepared catalyst by methods of scanning electron microscopy, X-Ray analysis, Auger spectroscopy are showed. The selectivity by amount of liquid phase products of 99.16% wt. with the conversion of 51.43% wt. are reached resulting the process of catalytic cracking of gasoil at the temperature of 450°C and atmospheric pressure.

Key words: Elemental analysis, Spectrograms, Gasoil cracking, Waste, Catalyst.

INTRODUCTION

According to the Ministry of Environmental Protection of RK in Kazakhstan about 700 million tons of industrial wastes are annually formed. As reports, the Ministry of environmental protection, "in the country more than 22 billion tons of waste, from them more than 16 billion tons of technogenic mineral formations and about 6 billion tons of dangerous wastes are accumulated". The problem of utilization of industrial wastes is actual not only for the Republic of Kazakhstan, but also for a huge number of other countries with the developed industrial sphere[1]. Waste of metallurgical production is of special interest because of the composition. It is known that the composition of waste of the ashes and slimes of metallurgical production includes a number of valuable elements, in particular transitional metals, such as chrome, iron, manganese, vanadium, titanium, etc. The content of some of the listed elements in waste of metallurgical productions reaches such level that dumps can be considered as secondary deposits for mining of these valuable metals[2].

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Utilization of wastes of metallurgical factories is necessary for creation of the closed production processes with the maximum economic and ecological efficiency[3,4]. Closed production processes in metallurgy mainly are based on use of waste in production of construction materials. It is known for a large number of works, in which researches of properties of various construction materials created from the metallurgical waste[5,6].

However, valuable elements, which are parts of waste, used not enough effectively at production of construction materials from that kind of waste. Deeper extraction of valuable metals with the subsequent use of the rest of poor ore for production construction materials is more effective way. However, it isn't always energetically favorable. Earlier, we presented results of research of ash-slime waste composition of Aksu ferroalloy plant (AFP) using the X-ray spectral analysis. It was shown that rather high amount of transitional metals-chrome, iron and manganese is a part of waste. It is known, that these metals are catalytically active. Therefore, industrial wastes of AFP can be used for obtaining catalysts for various petrochemical processes. The technique of preparation of the catalyst on the basis of waste of ferroalloy production without stage of extraction of metals and only using various methods of processing of material of waste is economically justified. In that case, relative low cost of utilization process remains and efficiency of use of waste valuable components increases because of their catalytic activity joins. It is natural that the cost of the catalyst is much higher, than the cost of construction materials. Besides economic efficiency of utilization of ferroalloy production waste increases in the offered way many times taking into account that various types of catalysts can be synthesized for various processes, which can lead to receiving valuable products of chemical processing and synthesis.

In this work, we represent a technique of preparation of the catalyst based on the waste of AFP, results of research of samples of the catalyst with physical and chemical methods, results of experiments on cracking of gasoil with use of the obtained catalyst.

EXPERIMENTAL

Element analysis, electron microscopy, auger spectroscopy

Element analysis, electron microscopy and Auger spectroscopy researches were carried out on scanning electron microscope JEOL JSM-6610 (Japan) using Japan Computer X-ray analyser JCXA 733.

Catalyst preparing

The received ash-slime mass was washed out with distilled water for separation of small organic particles. Then non-activated clay-calcite (1/8 part) and sodium silicate as

binder were mixed with moist ash-slime mass. The mass was molded with laboratory extruder to obtain cylindrical granules with a diameter of 1.5-2 mm and a length of 10-15 mm. After that granules were dried up at 100-150°C for 5 hrs at a speed of rise in temperature of 25-30°C per hr, then calcinated at a temperature of 200°C for 1 hr, at 300°C for 1 hr, at 400°C for 1 hr, at 500°C for 5 hrs. The calcination is carried out at a temperature higher than the temperature of the catalytic reaction.

The method of catalytic cracking of gasoil

The catalyst was prepared on the basis of AFP waste, used in the reaction of catalytic cracking of gasoil (240-350°C) on a laboratory flow-through installation (Fig. 1) with a fixed bed catalyst. Catalyst volume – 75 mL. The process temperature is from 450 to 500°C. The pressure is atmospheric. The volumetric feed rate of raw materials – 1.5 mL/min.

The raw materials move using the metering pump (2) in the reactor (3) filled with the studied catalyst at the set temperature. In the reactor above and below the catalyst bed, there are quartz layers (10 mL). Raw material, passing through a layer of quartz is heated to working temperature, and contacts in the form of a steam phasea catalyst layer. The reaction products come to the cooler (4). After cooling the reaction products come to separators high (5) and low (6) pressure, and the liquid fraction is collected in the receiver (8) (Fig. 1).

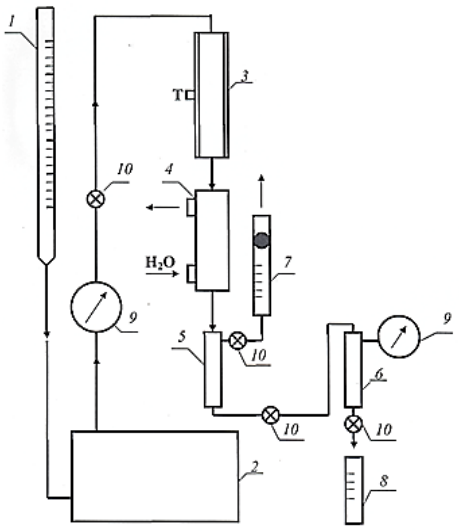

Fig. 1: Laboratory flow-through installation for catalytic cracking of gasoil

1 – buret; 2 – metering pump; 3 – reactor; 4 –cooler; 5 –high-pressure separator; 6 –low-pressure separator; 7 –rotameter; 8 –receiver; 9 –manometers; 10 –cocks

RESULTS AND DISCUSSION

Element analysis

Element analysis was performed twice. At first, composition of samples of waste obtained from AFP was researched. Then composition of prepared catalyst was researched.

The element analysis of waste samples was made using a method of the X-ray spectral analysis. The spectrum of each sample was taken three times. An average value used as a result. The elements were irregular distributed in the territory of ash-slime repository. For the expression of the average waste composition the concentrations of elements in each sample were summarized. The results of the analysis are expressed as average values and are presented in Table 1.

Table 1: Element composition of waste of AFP

S. No.	Element	Containing (wt.%)
1	O	46.18
2	Si	34.16
3	Mg	5.01
4	Ca	4.44
5	Mn	2.18
6	Cr	1.73
7	K	1.41
8	Zn	1.38
9	Al	1.23
10	Fe	1.01
12	Na	0.54
13	S	0.4
14	Cl	0.26
15	Sn	0.06

The results show rather high content of catalytically active metals such as Cr, Mn, Fe. This fact indicates that the obtained material can be used for the preparation of catalysts for various processes of the chemical industry.

The catalyst was prepared from waste material by formation and calcination according to the method described above. The results of element analysis of the granules of the catalyst are presented in Table 2.

Table 2: Element composition of granules of the catalyst

S. No.	Element	Containing (wt.%)
1	O	49.67
2	Si	33.83
3	Mg	5.03
4	Ca	1.09
5	Mn	1.47
6	Cr	1.50
7	K	1.63
8	Zn	1.31
9	Al	1.42
10	Fe	1.01
12	Na	0.93
13	S	0.45
14	Cl	0.67

Visible differences in the content of some elements such as tin, calcium are presented due to irregular distribution of elements on the territory of ash-slime repository. This results in the fact that the element can be contained in a single granule in trace amounts or absent. However, it is clear that the content of the main catalytic elements (Mn, Cr, Fe) remains almost constant. This indirectly indicates the uniformity of their distribution in the waste mass.

Auger spectroscopy and electron microscopy

The distribution of the element on the catalyst surface is one of important indicators. In the best case, the distribution should be uniform. However, there may be some crystallites, resulting in the observed non-uniform accumulation of the element in small areas of the surface of the catalyst granule.

Modern physical-chemical methods of analysis simply allow quantification of the surface. For example, Auger spectroscopy allows to obtain data on the concentrations of atoms of various elements and gives an indication of the distribution of atoms on the surface[g].

We investigated the distribution of catalytically active metals included in the catalyst composition on the surface of catalyst granules, using the method of Auger spectroscopy (Fig. 2, 3). The results show good uniform distribution of Cr and Fe. It was also found that manganese presents a bit larger crystallites, which are distributed less uniformly. By electron microscopy, it was discovered that the thermal treating of catalyst granules leads to a change in the surface. In Fig. 4 a. large non-uniform particles are visible. The calcinating leads to an increase in the surface porosity of the catalyst and the dispersion of the particles on its surface (Fig. 4 b). It is known that the extended surface and high dispersion of particles of the active phase lead to an increase in catalytic activity.

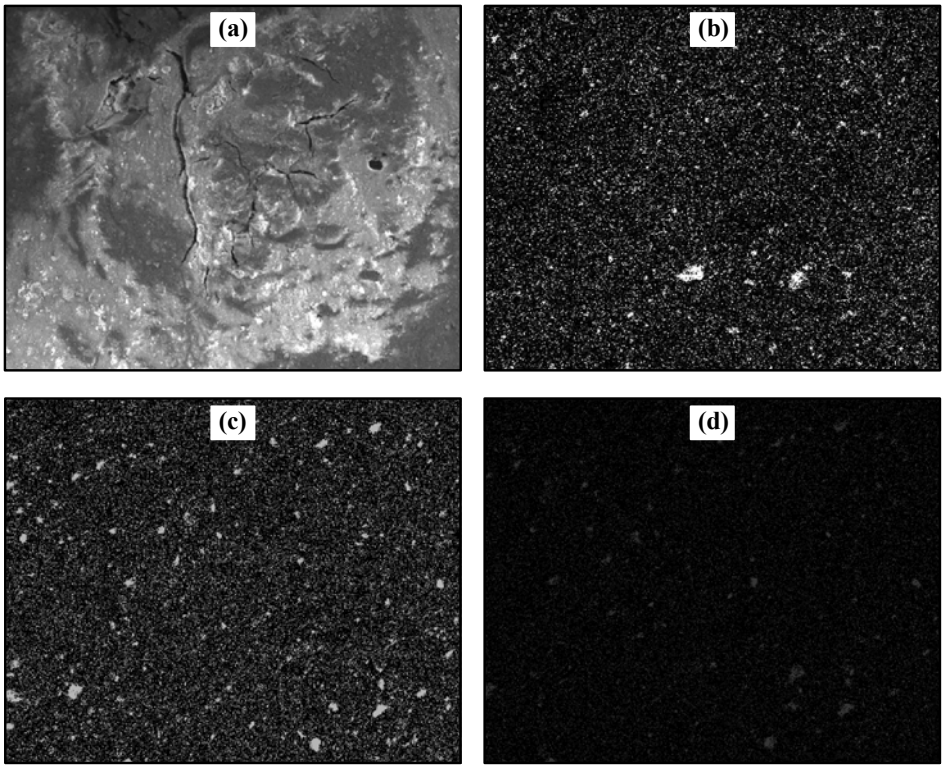

Fig. 2: The distribution of elements on the lateral surface of the catalyst granule (a) electron microphotograph, (b) Mn, (c) Cr, (d) Fe

Thus, the results of electron microscopic analysis indicate activating effect of a calcination stage in the process of catalyst preparation.

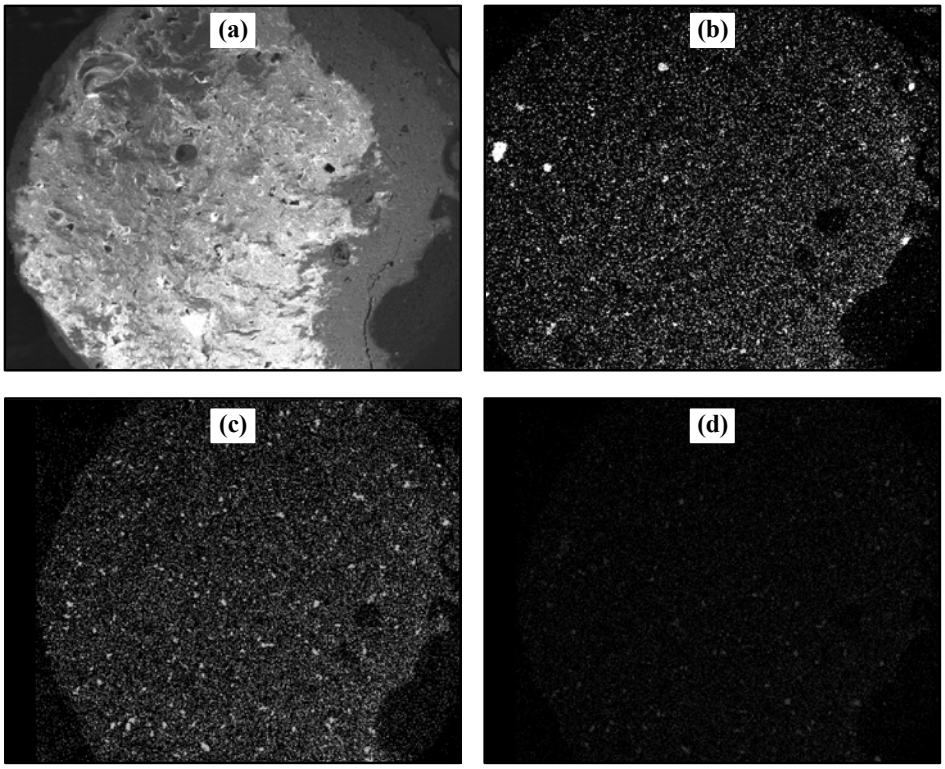

Fig. 3: The distribution of elements on the cross-cut surface of the catalyst granule (a) electron microphotograph, (b) Mn, (c) Cr, (d) Fe

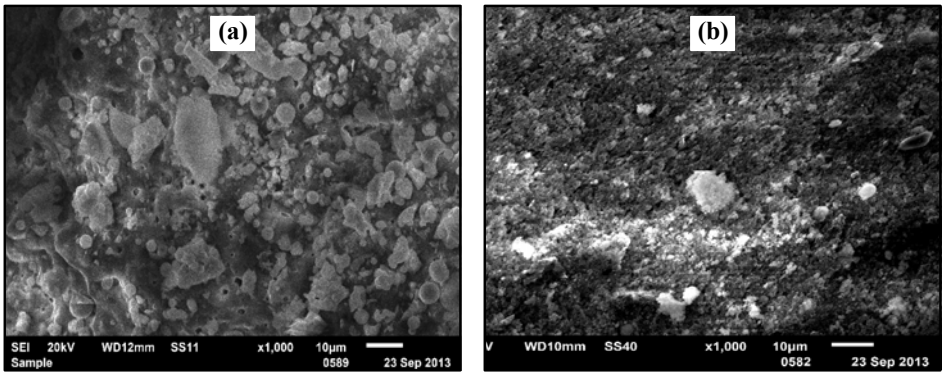

Fig. 4: Electron microphotographs of samples (a) the original waste sample, (b) the thermal-treated granular catalyst

The catalytic cracking of gasoil

The obtained catalyst used in the catalytic cracking of gasoil (diesel fuel 240-350°C) on stationary laboratory installation. The experiment was performed at temperature of 450°C and 500°C.

The experimental results are shown in Table 3. It is revealed that at more high temperature higher depth of transformation is reached, and at a temperature of 450°C; higher selectivity on an output of liquid-phase products. Thus, the catalyst based on waste of AFP shows a high activity and selectivity in the catalytic cracking of gasoil.

Table 3: Activity of catalyst based on waste of AFP in the process of catalytic cracking of gasoil (pressure = 690 mm Hg, mass of raw material = 40 g)

Temp. (^oC)	The yield of cracking products (wt.%)					The depth of conversion (wt.%)	The selectivity on the output of liquid products (%)
	Gas	Benzine (Start of boiling - 200^oC)	Middle distillate (200-270^oC)	Gasoil (270-350^oC)	Residuum (> 350^oC)		
500	2.00	23.99	29.48	18.28	26.25	55.47	96.39
450	0.43	18.92	32.08	44.98	3.59	51.43	99.16

The study confirms the assumption of the possible catalytic activity of ash-slime of ferroalloy production in the process of oil stock refining. The catalytic activity of this waste is due to the appropriate elemental composition and surface structure. In the process of gasoil cracking on the obtained catalyst high activity (the depth of conversion of raw material is about 55%) and selectivity (the output of liquid products is reached 99%) are reached at atmospheric pressure and temperature of the process of 450-500°C.

Thus, processing of ash-slime of ferroalloy production allows to obtain a valuable product; the catalyst for cracking of gasoil, which confirms the high economic efficiency of the proposed method of utilization of this type of industrial waste.

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