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Preliminary Chemical Activation of Ash Waste with Release of Carbon Concentrate

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Research has been carried out to obtain carbonaceous concentrate from ash from the combustion of Ekibastuz coals by the flotation method. To increase the efficiency of flotation, a preliminary chemical activation of ash in a sodium bicarbonate solution was used, which made it possible to change the phase composition and mineral structure. Upon activation, the phases of aluminum silicate-silymanite and hedenbergite disappeared, changes occurred in mullite towards a decrease in the content of silica in it, the content of free silica increased from 8.7 to 36.1 %, and the calcite phase appeared. As a result of studies, it was determined that the optimal temperature of chemical activation is 150 °C, a further increase in temperature leads to insignificant changes in the phase composition. At a temperature of 150 °C, phase transformations in ash are completed with a duration of 60 - 90 min. After chemical activation of the ash, the carbon content in the carbonaceous concentrate obtained during flotation doubled. The richest carbonaceous concentrate with a carbon content of 52.9 % was obtained using kerosene and MIBC (Methylisobutylcarbinol).

1. Introduction

Coal fly ash (CFA), also generally regarded as waste, is the lightweight fraction of the incombustible material or ash formed after combustion of coal in coal-fired power plants. It is typically spherical in shape and ranges from 1 to 150 lm in particle size. This material is driven out of the boilers with flue gases owing to its light weight and gets captured and recovered by gas cleaning devices like electrostatic precipitators before the gases are exhausted to the atmosphere. Generally, the total ash content of the coals used in most power generation plants range between 30 and 40 % and fine CFA can make up to 80 % of the total ash content, this gives a perspective of how much CFA gets generated during coal combustion. CFA has been largely regarded as an environmental pollutant with very limited industrial applications. However, the relative abundance of Al_2O_3 in the ash is significant enough to justify an attempt to exploit it commercially and the potential success of such an initiative would vastly boost a lot of economies. The potential presented by developing another alternative source of alumina from CFA would supplement bauxite resources, significantly reduce the volume of ash disposal; realize savings on disposal and landfill costs, and lessen the potential for environmental damage. Worldwide, it is estimated that coal combustion in power plants provides about 41 % of the electricity generation (WCA., et al.,2014). producing more than 800 Mt of CFA per annum of which approximately 500 Mt is generated in China, 140 Mt in India, 115 Mt in the United States & European Union (Yao et al.,2014), and South Africa produces about 40 Mt. In South Africa, Eskom and Sasol are the major producers of CFA. Eskom, according to its 2010 annual report, combusted 122,7 Mt of coal and generated a net of 215,940 GWh power with emission of 0.39 kg M Wh-1 of particulate matter, most of which is in the form of coal fly ash (CFA). It is estimated that only 30 % of the CFA produced finds use (Montes-Hernandez et al., 2009), and the balance is disposed of in controlled land fills or stockpiled in waste containment facilities resulting in serious environmental liability. Despite the environ mental pollution it causes and its potential harmful effect on life on earth, fly ash production is still increasing, since many power plants through out the world still rely heavily on

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coal combustion. Some of the CFA is used as a raw material in cement production and as partial replacement for cement in concrete (Heidrich et al., 2013), in the ceramic manufacturing, in the production of catalysts and catalysts support, and as an adsorbent in pollution abatement (Blissett et al., 2012). Chemical and mineralogical compositions of CFA are highly variable due to the variability of the sources of the coal, its pre-treatment, and the operational parameters during its combustion in the power generation plants. However, on average it contains between 25 and 30 % Al_2O_3, making it a potential alternative source of alumina for aluminum production after bauxite which contains about 50 % Al_2O_3 (Authier-Martin et al., 2001). Therefore, the availability of CFA as a substitute or to augment bauxite will not only have environmental benefits, but also potentially expand the raw materials base for the aluminum industry.

Today, the fuel base of the Pavlodar region of the Republic of Kazakhstan is represented by the large Ekibastuz coal field. In Pavlodar oblast alone, over 500 Mt of such waste have been accumulated in ash dumps (Bitimbaev et al., 2018). Disposal and recycling of ash is of great ecological and economic importance. Of particular interest from the side of metallurgy are iron, aluminum, silicon and underburning contained in the ash composition (Mal’chik and Litovkin, 2015). When coal is burned, a significant amount of unburned or partially burnt coal particles, called “underburning”, appears in the ash. The recovered underburning is a valuable component and can be used as a secondary fuel in the manufacture of fuel briquettes (Alexandrova et al., 2016), and is also used in the construction of some elements of nuclear power plants (Kizilshtein et al., 2016). Flotation is an effective method for recovering unburned coal particles (Ryabov et al., 2013).

There are various methods of pretreatment of high-silica aluminosilicate raw materials before leaching. In the work (Guo et al., 2013), thermal activation calcination was performed with the addition of NaOH and Na_2CO_3. The results showed that the addition of NaOH and Na_2CO_3 obviously improved the extraction of alumina. The maximum extraction of alumina reached ~ 60 % when calcined at 600-900 °C with the addition of NaOH and could reach 82 % at 900 °C with the addition of Na_2CO_3. The results obtained showed that NaOH and Na_2CO_3 contribute to the decomposition of the polymer phases. Mixed additives containing NaOH and Na_2CO_3 had a better activating effect on coal fly ash. In the work (Han et al., 2018), unburned carbon is first removed from the ash using an effective surfactant, humic acid, at the foam flotation stage. The maximum carbon removal rate is 93.20 ± 0.05 %. Then, at the metallurgy stage, the glass phase is leached in a carbon-free product with mixed acid solutions (HF: H_2SO_4 = 3:1). In the work (Valeev et al., 2019), a combined ash treatment process was developed to remove spent coal fly ash from coal-fired power plants. Ash treatment included three stages: 1) magnetic separation of the iron-containing fraction, 2) separation of carbon by flotation and 3) extraction of aluminum by autoclave leaching with hydrochloric acid. The results of the study showed that the fly ash consists mainly of quartz, mullite and magnetite. It was found that the magnetic fraction isolated at the first stage was enriched with magnetite (more than 20 wt.%), the carbon content in the concentrate after flotation in the folds reached 27 wt.%, and 90-95 % of aluminum can be extracted by autoclave acid leaching. The maximum digestion rate of the glass phase was 97.40 ± 0.16 %. The work of the author (Sapinov et al., 2020) indicates positive results when using a vibration installation to intensify the leaching and cementation process in order to extract valuable components from productive solutions. The proposed technology made it possible to efficiently extract valuable components from man-made raw materials.

As a result of the literature review on the processing of ash and slag waste, it was shown that for the efficiency of the process of enrichment and leaching of ash and slag waste, a method of pretreatment of the starting material is proposed, with the release of a carbon concentrate for further extraction of valuable components (aluminosilicate product, alumina). In this work, in order to increase the efficiency of flotation, a method of preliminary chemical activation of the feedstock was used, which makes it possible to change the phase and mineral structure. For the treatment of ash and slag waste using the chemical activation method, an expensive firing process is not required, as well as a large amount of limestone and soda ash for the dosage and binding of silica. The method consists in the processing of raw materials in an autoclave with a solution containing 120 – 150 g/dm^3 of sodium bicarbonate at a temperature of 120–200 °C (Abdulvaliev et al., 2017). The processing mode depends on the composition of the feedstock. At temperatures of 60 – 200 °C, sodium bicarbonate decomposes according to the reaction:

$$2NaHCO_3 \leftrightarrow Na_2CO_3 + H_2O + CO_2 \qquad (1)$$

This reaction is reversible. When carrying out the process of chemical enrichment in an autoclave, all the components of decomposition and formation of sodium bicarbonate are in the volume of the solution in an active freshly formed form. During processing, the components of aluminosilicate raw materials react with the solution, form water-soluble hydrocarbonate salts and leave the mineral structure. Further, due to the high temperature, they decompose with the formation of less soluble carbonates, which serve as the basis for the formation of a new mineral structure. The required content of sodium bicarbonate in the solution of 120 – 150 g /dm^3 is selected taking into account its solubility limit.

Formulation of the problem. The aim of the research was to obtain carbonaceous concentrate from ash from the combustion of Ekibastuz coals by the flotation method. To increase the efficiency of flotation, preliminary chemical activation of the ash was carried out, which made it possible to change the phase composition and mineral structure.

2. Material and methods

For research, samples were taken from ash dumps of the Eurasian Energy Company (JSC "EEC") from the combustion of Ekibastuz coal. Chemical composition of the initial averaged ash sample, wt. %: 55.0 SiO_2; 20.04 Al_2O_3; 2.30 Fe_2O_3; 1.36 CaO; 0.4 MgO; 0.71 TiO_2; 0.50 K_2O; 0.62 SO_3; 0.7 Na_2O. The bulk is represented by the class -0.25 + 0.1 mm, the amount of which is about 60.0 %. The size of the ash material allows for further hydrochemical processing without preliminary grinding. In physicochemical studies of feedstock and processed products, X-ray phase, X-ray fluorescence and chemical analyzes were used. Semi-quantitative X-ray phase analysis was performed on a D8 Advance diffractometer (BRUKER) using copper Cu – K_α radiation at an accelerating voltage of 36 kV and a current of 25 mA. X-ray fluorescence analysis was performed on a Venus 200 wave dispersion spectrometer (PANalyical B.V., Holland). The chemical analysis of the samples was performed on an Optima 2000 DV inductively coupled plasma optical emission spectrometer (Perkin Elmer, USA).

Chemical activation of ash was carried out by treatment with a solution containing 120–150 g/dm^3 of sodium bicarbonate at a temperature of 120–200 °C and duration of 60 min. Flotation beneficiation was carried out on laboratory flotation machines of the Mekhanobr Technica type with a chamber volume of 3.0 dm^3. Enrichment was carried out on the initial size of ash and slag waste, with a chamber volume of 1 dm^3 and a sample weight of 150 g (T: W = 1/3) with a pulp aeration of 10 dm^3/ min using a MIBC foaming agent. The foaming agent consumption was 20 kg/t. A cheap and effective reagent, kerosene (Ryabov et al., 2016) and SBX (sodium butyl xanthate), was chosen as a collector. The collector consumption varied within 5-10 kg/t. The impeller rotation speed was 2,500 rpm.

3. Results and discussion

To determine the optimal conditions for the chemical activation of ash in a sodium bicarbonate solution, the dependence on temperature and duration was studied. The phase composition of ash after chemical activation in a sodium bicarbonate solution depending on temperature for a duration of 60 min is shown in Table 1.

Table 1: Phase composition of ash after chemical activation in sodium bicarbonate solution depending on temperature

Name	Activation temperature, °C	Composition		
		Component	Formula	%
Initial ash		Sillimanite	Al_2SiO_5 ,	32.5
		Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	27.2
		Hedenbergite	$CaFe+2Si_2O_6$	12.4
		Hematite	Fe_2O_3	6.7
		Quartz	SiO_2	8.7
Ash after activation	100	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	61.8
		Hematite	Fe_2O_3	8.1
		Quartz	SiO_2	25.8
		Calcite	$CaCO_3$	4.2
Ash after activation	120	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	39.3
		Hematite	Fe_2O_3	8.0
		Quartz	SiO_2	33.2
		Calcite	$CaCO_3$	5.2
Ash after activation	150	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	44.3
		Hematite	Fe_2O_3	7.9
		Quartz	SiO_2	36.1
		Calcite	$CaCO_3$	5.3
Ash after activation	200	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	49.6
		Calcite	$CaCO_3$	5.3

Studies of the change in the phase state of ash after activation, depending on temperature, showed, on an X-ray diffractometer, the analysis of which revealed that, as a result of chemical activation, changes occurred in the mineral structure of the ash:
- the phases of aluminum silicate - silymanite and hedenbergite have disappeared;
- there have been changes in mullite towards a decrease in the content of silica in it;
- the content of free silica has increased from 8.7 to 36.1 %;
- the calcite phase appeared.

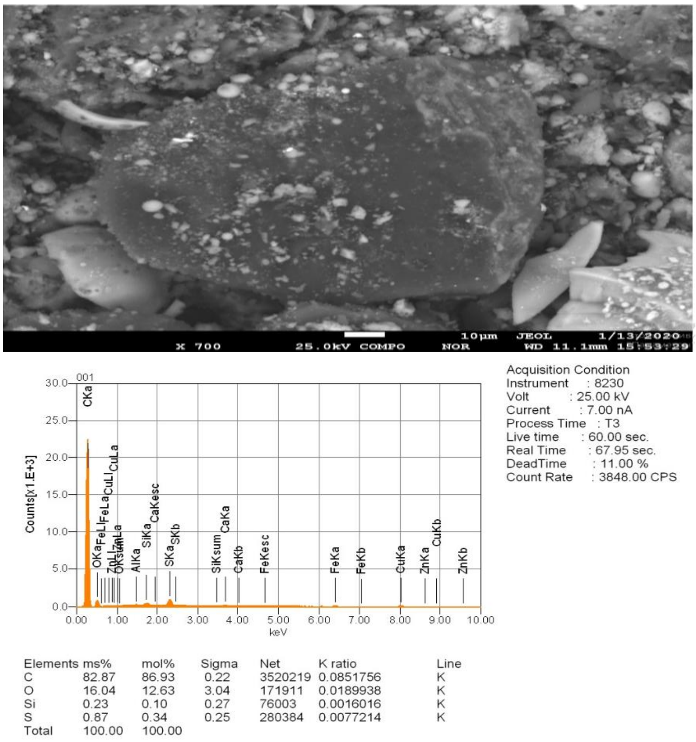
From the obtained dependence it follows that the optimal temperature of chemical activation can be considered 150 °C, since a further increase in temperature leads to insignificant changes in the phase composition. The chemical composition of the ash did not change during activation. The phase composition of ash after chemical activation at 150 °C, depending on the duration of chemical activation, is shown in Table 2.

Table 2: Phase composition of ash depending on the duration of chemical activation

Duration	activation time, min.		Composition	
		Component	Formula	%
	20	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	12.5
		Hematite	Fe_2O_3	8.0
		Quartz	SiO_2	36.0
		Calcite	$CaCO_3$	5.3
	40	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	11.8
		Hematite	Fe_2O_3	7.9
		Quartz	SiO_2	36.0
		Calcite	$CaCO_3$	5.4
	60	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	44.3
		Hematite	Fe_2O_3	7.9
		Quartz	SiO_2	36.1
		Calcite	$CaCO_3$	5.3
	90	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	44.8
		Hematite	Fe_2O_3	8.1
		Quartz	SiO_2	36.0
		Calcite	$CaCO_3$	5.2
	120	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	44.9
		Hematite	Fe_2O_3	7.9
		Quartz	SiO_2	36.1
		Calcite	$CaCO_3$	5.3
	240	Mullit	$Al(Al_{0.83}Si_{1.08}O_{4.85})$	44.9
		Hematite	Fe_2O_3	8.0
		Quartz	SiO_2	36.0
		Calcite	$CaCO_3$	5.3

Studies have shown that at a temperature of 150 °C, changes in the phase composition of the ash end in the range from 90 to 120 min. Research has been carried out on the effect of chemical activation of ash on the degree of extraction of carbonaceous concentrate. When extracting carbonaceous concentrate, a basic flotation scheme with concentrate cleaning was used. Investigations of the flotation recovery of carbonaceous concentrate were carried out with different reagent modes. A distinctive feature of the experiments was that the first and second experiments were carried out on the initial ash without the use of chemical activation, the third and fourth experiments after the chemical activation of the ash at a temperature of 150 °C and a duration of 90 min. The weight of the initial ash sample was 150 g. The duration of the main flotation was 5 minutes, the duration of re-cleaning of the rough concentrate was 2.5 min.

From the results obtained, it follows that the chemical activation of ash makes it possible to obtain a carbon concentrate almost twice as rich during flotation. The richest carbon concentrate with a carbon content of 52.9 % at an output of 87.43 % was obtained using kerosene and MIBC (experiment 3) using chemical activation of ash. A carbon concentrate with a carbon content of 26.60 % at a yield of 79.62 % was obtained without the use of chemical activation of ash. Figure 1 shows the results of the energy dispersion analysis of carbon concentrate with an increase of 700.



Acquisition Condition
Instrument : 8230
Volt : 25.00 kV
Current : 7.00 nA
Process Time : T3
Live time : 60.00 sec.
Real Time : 67.95 sec.
DeadTime : 11.00 %
Count Rate : 3848.00 CPS

Elements	ms%	mol%	Sigma	Net	K ratio	Line
C	82.87	86.93	0.22	3520219	0.0851756	K
O	16.04	12.63	3.04	171911	0.0189938	K
Si	0.23	0.10	0.27	76003	0.0016016	K
S	0.87	0.34	0.25	280384	0.0077214	K
Total	100.00	100.00				

Figure 1: Carbon concentrate (magnification 700)

4. Conclusions

The method of chemical activation of raw materials in sodium bicarbonate solution made it possible to change the initial phase composition of the ash. The phases of aluminum silicate - silymanite and hedenbergite disappeared, there were changes in mullite towards a decrease in the content of silica in it, the content of free silica increased from 8.7 to 36.1%, and a calcite phase appeared. The optimum temperature for chemical activation is 150 °C, a further increase in temperature leads to insignificant changes in the phase composition. At a temperature of 150 °C, phase transformations in ash are completed with a duration of 60 - 90 min. After chemical activation of the ash, the carbon content in the carbonaceous concentrate obtained during flotation doubled. The richest carbonaceous concentrate with a carbon content of 52.9 % was obtained using kerosene and MIBC. Thus, the chemical composition of ash and slag waste practically does not change during activation, but there is a change in the phase composition. After activation, due to changes in the phase composition and disintegration, conditions are created for effective enrichment and leaching of ash.

The method of chemical activation of ash and slag waste makes it possible to increase the efficiency of the enrichment or leaching operation by changing the phase composition, separating the surface layer of silicate rock and disintegrating the processed material. The authors plan to continue their research in this direction for the subsequent extraction of valuable components, including the production of alumina from ash and slag waste by pyro-hydrometallurgical methods. These areas are promising.

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