Analysis of waste coal from the enterprises of Kemerovo region as raw materials for production of ceramic materials

A Yu Stolboushkin, D V Akst, O A Fomina, A I Ivanov and V A Syromyasov
Siberian State Industrial University, 42 Kirov Street, Novokuznetsk, 654007, Russia
E-mail: daniel_axt@mail.ru

Abstract. The analysis of waste coal from mining enterprises of Kemerovo region as raw materials for production of building ceramics is given. The results of studies of material, chemical and mineralogical compositions of waste coal from Abashevskaya processing plant (Novokuznetsk) are presented. It was established that the chemical composition of waste coal refers to aluminosilicate raw materials with a high content of alumina and coloring oxides, the residual carbon content in the wastes is 12-25 %. According to the granulometric composition the waste coal is basically a sandy-dusty fraction with a small amount of clay particles (1-3 %). Additional grinding of coal waste and the introduction of a clay additive in an amount of up to 30 % are recommended. The results of the study of the mineral composition of waste coal are presented. Clay minerals are represented in the descending order by hydromuscovite, montmorillonite and kaolinite, minerals-impurities consist of quartz, feldspar fine-dispersed carbonates. The results of the investigation of ceramic-technological properties of waste coal, which belong to the group of moderately plastic low-melting raw materials, are given. As a result of a comprehensive study it was been established that with chemical, granulometric and mineralogical compositions waste coal with the reduced residual carbon can be used in the production of ceramic bricks.

1. Introduction
As a result of the work of many enterprises from mining, energy and metallurgical industries of Kemerovo region there is an ecological disturbance. A huge amount of industrial wastes have been accumulated today [1 - 3]. In the south of Kuzbass in Novokuznetsk administrative area the annual output of waste coal from Myskovskaya and Kuznetsk coal processing plants is about one million tonnes, from Abashevskaya plant – more than 400 thousand tonnes. There are problems with the placement of slurries from coal-enrichment wastes at Shchedrukhinskaya plant [5].

Simultaneously with the “industrial pollution” of Kemerovo Region there is a shortage of natural resources for the construction industry [6]. Therefore, for the first half of the 21st century the creation of new “green” technologies with efficient utilization of heavy industry waste is important for the production of building materials [7, 8]. A positive example is the successful operation of a unique factory for the production of ceramic bricks from 100 % wastes of coal-enrichment at Abashevskaya factory in Novokuznetsk [9].

The authors carried out research into the manufacture of bricks from carbon waste with a different content of residual carbon and proposed a scheme for obtaining additional fuel for burning ceramic products [9, 10]. The technological idea of the authors is to organize deep processing of waste coal directly at a brick factory. At the same time the secondary enrichment of wastes is carried out to produce energy coal for the plant operation.
Waste coal is characterized by an unstable composition and high content of coal. This can cause problems in the manufacture of bricks and lead to the destruction of the material during firing. Consequently, an important stage in the development of wall ceramics technology from technogenic raw materials is a complete study of the composition and properties of coal waste.

The aim of the work was to conduct a comprehensive study of waste coal as a potential technogenic raw material for the production of ceramic bricks.

2. Methods and materials
The coal wastes from Abashevskaya plant, which were obtained by processing coal from four coal mines in Kemerovo region: Erunakovo coal mine, Uskovo coal mine, Esaulskaya coal mine, Osinnikovskaya coal mine, were analyzed as raw materials. For the study of carbon waste methods of physical and chemical analysis were used: X-ray fluorescence; X-ray diffraction; IR absorption spectroscopy; complex thermal analysis and laser granulometry. The numbering of waste coal samples is given in table 1.

| Sample | Enterprise                  | Initial particle size, mm |
|--------|-----------------------------|---------------------------|
| 1      | Erunakovo coal mine         | 5-100                     |
| 2      | Uskovo coal mine            | 5-100                     |
| 3      | Esaulovka coal mine         | 5-50                      |
| 4      | Osinniki coal mine          | 5-150                     |

Waste coal in its initial form is a large-lump material (table 1, figure 1).

X-ray fluorescence (XRF) was done for four samples of waste coal using spectrometer Shimadzu XRF 1800. The chemical composition is given in table 2.
The chemical composition of waste coal is related to aluminosilicate raw materials with a high content of alumina (14.72-15.28 wt.%). The carbon content is 11.2-22.1 wt. %. The amount of alkali and alkaline earth metal oxides in the samples is 6.3-11.0 wt. %. According to the content of coloring oxides in the calcined state waste coal is referred to a group of raw materials with a high content of coloring oxides.

In the diagram of clays for industrial applications, depending on their chemical composition [11], the samples belong to raw materials suitable for the production of building ceramics. The limitation is a high content of residual carbon (more than 10 % by weight) for all samples which implies the need for their secondary enrichment. The work of the brickyard on the raw materials from waste coal and the authors’ research showed that the content of carbonaceous particles in the composition of the batch should not exceed 5-6 wt. %, which ensures their complete burn-out and the absence of a black core during firing of ceramic masses [10].

### 3. Results and discussion
The granulometric composition of the four waste coal samples after two-stage grinding in the jaw crusher and laboratory runners is provided in table 3 and in figure 2.

| Sample | Mass fraction of the components (%) | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MnO$_2$ | MgO | CaO | K$_2$O | Na$_2$O | LOI* |
|--------|-----------------------------------|--------|--------|-------------|------------|--------|-----|-----|--------|--------|------|
| 1      | 51.30 0.76 14.72 2.91 0.06 1.44 1.26 2.80 0.81 23.31 |
| 2      | 58.49 0.76 15.07 3.07 0.11 1.73 3.28 3.07 1.30 12.99 |
| 3      | 55.68 0.75 15.28 3.23 0.07 1.69 2.01 3.40 1.00 16.63 |
| 4      | 56.87 0.78 15.17 3.98 0.13 1.96 4.78 2.94 1.36 12.01 |

*LOI – loss on ignition

### Table 3. Granulometric composition of waste coal samples.

| Sample | Fraction content in %, particle size in mm | >1.0 | 1.0-0.5 | 0.5-0.1 | 0.1-0.05 | <0.05 |
|--------|-------------------------------------------|------|--------|---------|----------|-------|
| 1      |                                           | 12.8 | 39.52  | 30.96   | 10.91   | 5.81  |
| 2      |                                           | 0.0  | 7.79   | 54.76   | 21.2    | 16.25 |
| 3      |                                           | 0.31 | 17.08  | 52.1    | 17.73   | 12.88 |
| 4      |                                           | 5.07 | 30.66  | 38.52   | 14.89   | 10.86 |

![Figure 2](image-url) **Figure 2.** Histograms of the particles content depending on the size of wastes.
Studies of the granulometric composition of waste coal showed that the samples have almost the same particle size distribution. Carbon waste consists of a sandy-dusty fraction and a small amount of particles smaller than 1 μm (1-3 %). According to the diagram of clays for industrial applications depending on the particle size distribution [12] the material is not suitable for the production of ceramic bricks and needs to be adjusted for the fractional composition. The authors recommend an additional grinding of coal waste in a rod-type mill and the introduction of a clay additive in the amount up to 30 %.

The mineral composition of the waste coal was studied by X-ray diffraction (XRD) methods; and complex thermal analysis. Thermograms of coal waste are given in figure 3. Thermal analysis of four samples of waste coal showed the same endothermic effect in the temperature range of 88.3-100.1 °C. The thermal effect is associated with the removal of adsorbed water, while the mass loss is 1.27-2.86 % (figure 3). The DTA curve shows exothermic effects at temperatures of 367.4-370.7 °C and 449.5-460.7 °C which correspond to the processes of pyrolysis and carbon burn-out. The total weight loss in these reactions is 7.72-9.49 %.

![Figure 3. TG and DTA curves of the waste coal samples.](image)

The second endothermic effect in samples 1, 3 at a temperature of 550.2-560.8 °C is associated with the removal of interlayer water and the destruction of the crystalline lattice of layered silicates. The absence of this effect in samples 2 and 4 can be explained by the simultaneous occurrence of an exothermic oxidation reaction in the temperature range 500-650 °C. The oxidative reaction is caused by a shift in the temperature peak of the coal burn-out reaction and is explained by a higher content of clay minerals (table 2). The reaction of removal of OH groups from the lattice of hydromuscovite slows down the process of carbon burn-out. In this regard the oxidation of carbon occurs at temperatures 100-150 °C higher (figure 3).

The endothermic reaction of decarbonization of waste coal samples occurs at a temperature of 803.4-821.8 °C, and the mass loss in the samples is 1.25-3.16 %. At a temperature of 1000 °C the total mass loss in waste coal samples is 12.01-23.31 % and depends on the amount of carbonaceous particles (table 2).
X-ray diffraction of four waste coal samples was done using Shimadzu LabX XRD-6000 spectrometer. The XRD results are given in figure 4 and table 4.

**Figure 4.** XRD analysis of the average waste coal samples.

| Sample | Name of minerals                                                                 | Impurities          |
|--------|----------------------------------------------------------------------------------|---------------------|
| 1      | Hydromuskovit, kaolinite, montmorillonite                                        | Quartz, calcium feldspar Calcite, chlorite |
| 2      | Hydromuskovit, kaolinite, montmorillonite                                        | Quartz, calcium feldspar Siderite, calcite, chlorite |
| 3      | Hydromuscovit, montmorillonite, kaolinite                                         | Quartz, calcium feldspar Hematite, calcite, chlorite |
| 4      | Hydromuskovite, kaolinite                                                        | Quartz, calcium feldspar Calcite |

According to XRD analysis the samples of waste coal have the following mineralogical composition: quartz (d/n = 0.425, 0.334, 0.223, 0.128), kaolinite (d/n = 0.710, 0.357; 0.234); hydromuscovite (d/n = 0.447, 0.239, 0.150); calcium feldspar (d/n = 0.636, 0.319, 0.183) and montmorillonite (d/n = 1.390, 0.448, 0.167). Calcites are identified as impurities (d/n = 0.303, 0.209, 0.160), chlorite (d/n = 1.380, 0.353, 0.280), siderite (d/n = 0.279, 0.172) and hematite (d/n = 0.271, 0.169).

The results obtained are confirmed by thermal analysis of four samples. Minerals of hydromica group are predominant from layered silicates. The impurities are predominantly quartz-feldspar in nature with an insignificant amount of dispersed carbonates.

In the study of ceramic-technological properties the ductility of finely grinded waste was determined (table 5). Definitions were carried out by two methods: according to GOST 21216.1-93 “Clay raw materials. Method for plasticity determination” and Pfefferkorn method.
Table 5. Plasticity of finely grinded waste coal*

| Sample | Humidity, % | Plasticity index | Classification according to GOST 9169-75 |
|--------|-------------|------------------|------------------------------------------|
| 1      | 11.8        | 22.8             | 11.0                                    |
|        | 11.2        | 22.4             | 11.2                                    |
| 2      | 11.8        | 19.7             | 7.9                                     |
|        | 11.1        | 18.6             | 7.5                                     |
| 3      | 12.4        | 22.6             | 10.2                                    |
|        | 11.9        | 21.8             | 9.9                                     |
| 4      | 11.0        | 17.5             | 6.5                                     |
|        | 10.3        | 16.7             | 6.4                                     |

*Values according to GOST 21216.1-93 (numerator), values by Pfefferkorn method (denominator)

To determine the ceramic-technological properties of waste coal ceramic samples-cylinders were prepared by the method of semi-dry pressing. From the grinded waste coal with moisture of 8-9 % raw samples were pressed at a pressure of 15-17 MPa. The dried samples were fired at a temperature of 1000 °C.

The physical and mechanical properties of ceramic samples from waste coal are presented in table 6.

Table 6. Physical and mechanical properties of ceramic samples from waste coal.

| Sample | Air shrinkage, % | Fire shrinkage, % | Average density, kg/m³ | Compressive strength, MPa | Water absorption, % | Strength-density ratio |
|--------|------------------|-------------------|------------------------|---------------------------|---------------------|------------------------|
| 1      | 1.0              | 0.6               | 1693                   | 6.2                       | 16.1                | 3.7                    |
| 2      | 1.6              | 0.9               | 2053                   | 32.4                      | 10.7                | 15.8                   |
| 3      | 1.2              | 0.7               | 1764                   | 8.1                       | 15.5                | 4.6                    |
| 4      | 1.5              | 0.9               | 1984                   | 21.7                      | 10.5                | 10.9                   |

The comparative analysis showed a wide dispersion in the physical and mechanical properties of ceramic samples depending on a number of waste coal sample. The compressive strength of waste coal samples 1, 3 is 6-8 MPa, for samples 2, 4 is 21-32 MPa. The difference in strength is more than 3 times due to the high content of carbonaceous particles in samples 1, 3 (figure 2).

During firing waste coal samples 1, 3 carbon does not burn out which leads to low strength. During testing a black core is observed inside the samples. Incomplete burn-out of C disrupts the sintering of ceramic material from waste coal. For samples 1, 3 the water absorption was increased by 1.5 times with an average density of 1700-1750 kg/m³.

4. Conclusions
The conducted researches of four samples of coal waste from Abashevkaya plant established:

- according to the chemical composition the samples refer to aluminosilicate raw materials with high alumina content, coloring oxides, the residual carbon content in the waste is 12-25 %;
- according to the granulometric composition the samples have mainly a sandy-dusty fraction with a small amount of clay particles (1-3 %);
- mineral composition of waste coal is represented by clay minerals: hydromuscovite, montmorillonite and kaolinite. Minerals-impurities consist of quartz, feldspar, fine-dispersed carbonates. In a small amount there are chlorite, siderite and hematite;
- according to the ceramic-technological properties the samples belong to the group of moderately plastic low-melting raw materials.
As a result of a comprehensive study of the waste coal from mining companies of Kemerovo region it is established that waste coal can be used in the production of ceramic bricks with the corrected composition of batch.

Acknowledgements
The results of the research were obtained within the framework of the state assignment of the Ministry of Education and Science of the Russian Federation, the code of the project No. 7.7285.2017 / 8.9 “Fundamental research in the field of building ceramic composites with a matrix structure based on technogenic and natural raw materials”

References
[1] Petrov I V et al 2013 Proc. Int. Conf. on Ecology. Nature Management. Economy (Moscow: Rolix) pp 43–56
[2] Rakhimov R Z et al 2009 Building Materials 12 8–11
[3] Chernyshov E M 2010 Proc. XV Int. Sci. Conf. on Achievements and Problems of Materials Science and Modernization of the Construction Industry (Kazan: Kaz-SASU) 1 8–9
[4] Ivanov A The Enrichment Factory harmed the Environment for Millions http://nk-tv.com/128049.html
[5] Kikava O Sh et al 1997 Environment and Industry of Russia 12 23–8
[6] Rasskazov V F et al 2009 Glass and Ceramics 1 5–9
[7] Shpirt M Ya 1986 Wasteless Technology. Utilization of Wastes of Extraction and Processing of Solid Fossil Fuels (Moscow: Nedra) p 255
[8] Burmistrov V P et al 1989 Building Materials 8 18–9
[9] Storozenko G I et al 2013 Building Materials 4 57–61
[10] Stolboushkin A Yu and Storozenko G I 2011 Building Materials 4 43–6
[11] Avgustinik A I 1975 Ceramics (Leningrad: Stroyizdat) p 592
[12] Stolboushkin A Yu, Karpacheva A A and Ivanov A I 2011 Wall Ceramic Products on the Basis of Waste Coal and Iron-containing Additives (Novokuznetsk: Inter-Kuzbass) p 156