Magnetite concentrate from coal fly ash of Kashirskaya GRES - the raw material for the production of metal products by reduction smelting

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Abstract. Coal fly ash is a hazardous waste of heat power engineering. The complex processing of it includes several stages, such as carbon flotation and magnetic separation of iron. This study focuses on carbon extraction by flotation method and iron by magnetic separation method from Kashirskaya GRES coal fly ash with subsequent reduction smelting of it. At optimal conditions were obtained carbon concentrate with 37% C and magnetic concentrate with 61% Fe2O3. The high-quality steelmaking pig iron with low P and S and high alumina slag were obtained at 1400 °C after reduction smelting mixture magnetic, and carbon concentrates.

The magnetite concentrate production from coal fly ash (CFA) is a mandatory part of its complex recycling. [1]. These wastes usually contain a small amount of iron oxides (5-10% Fe2O3) but can contain until to 20-25% Fe2O3, it comparable with the amount of iron oxides content in the titanomagnetite ore. The CFA is a raw material for the magnetic concentrate production by magnetic separation. According to expert estimation, more than 15 million tons of Fe2O3 in these wastes already accumulated in Troitskaya, Reftinskaya and Verkhnetagilskay thermal power stations (TPS) ash ponds and near 2 million tons of Fe2O3 in Kashirskaya GRES and Moscow power plant in Russia.

It is was reported earlier [2], that from the CFA can be obtaining a good-quality iron concentrates for cast iron production. The present study shows a flow sheet for producing the magnetic concentrate and the cast iron from Kashirskaya GRES CFA. The chemical and phase compositions of the CFA Kashirskaya GRES sample determined by chemical and X-Ray diffraction methods are represented in table 1.

Table 1. The chemical and phase compositions of CFA

| Compositions | SiO2 | Al2O3 | Fe2O3 | MgO | TiO2 | P2O5 | S | C |
|--------------|------|-------|-------|-----|------|------|---|---|
| Chemical composition | 50,0 | 21,5 | 8,13 | 1,32 | 0,75 | 0,76 | 0,10 | 14,07 |
As can be seen, the main components of CFA are SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, but it also contains more than 8% of Fe\textsubscript{2}O\textsubscript{3} and 14% C. Table 1 also shown that the iron exists in the CFA in oxides form and distributed between magnetite, hematite and wustite.

For magnetic concentrate producing, initial CFA was treatments according to a flow sheet represented in figure 1.

![Figure 1. The flow sheet of CFA enrichment.](image)

To determine the necessity of a preliminary CFA classification was separated by a dry classification on eight fractions with subsequent chemical analyses of them. The chemical composition of fractions represents in table 2.

**Table 2.** The chemical compositions of different fractions CFA after dry classification.

| Grain-size fraction, \(\mu\)m | Yield, \% wt. | Content of component, \% wt. | S | C |
|-------------------------------|--------------|-----------------------------|---|---|
| + 160                         | 10.0         | SiO\textsubscript{2}: 47.0, Al\textsubscript{2}O\textsubscript{3}: 19.2, Fe\textsubscript{2}O\textsubscript{3}: 5.44, MgO: 1.22, TiO\textsubscript{2}: 0.67, P\textsubscript{2}O\textsubscript{5}: 0.23, S: 0.16, C: 25.0 |
| - 160 + 125                   | 6.0          | SiO\textsubscript{2}: 54.0, Al\textsubscript{2}O\textsubscript{3}: 21.7, Fe\textsubscript{2}O\textsubscript{3}: 9.86, MgO: 1.53, TiO\textsubscript{2}: 0.82, P\textsubscript{2}O\textsubscript{5}: - , S: - , C: 7.7 |
| - 125 + 100                   | 44.0         | SiO\textsubscript{2}: 49.0, Al\textsubscript{2}O\textsubscript{3}: 20.4, Fe\textsubscript{2}O\textsubscript{3}: 8.24, MgO: 1.43, TiO\textsubscript{2}: 0.75, P\textsubscript{2}O\textsubscript{5}: - , S: - , C: 15.4 |
| - 100 + 80                    | 23.0         | SiO\textsubscript{2}: 50.3, Al\textsubscript{2}O\textsubscript{3}: 20.8, Fe\textsubscript{2}O\textsubscript{3}: 7.48, MgO: 1.33, TiO\textsubscript{2}: 0.74, P\textsubscript{2}O\textsubscript{5}: - , S: - , C: 15.0 |
| - 80 + 56                     | 6.0          | SiO\textsubscript{2}: 52.0, Al\textsubscript{2}O\textsubscript{3}: 22.3, Fe\textsubscript{2}O\textsubscript{3}: 8.24, MgO: 1.47, TiO\textsubscript{2}: 0.79, P\textsubscript{2}O\textsubscript{5}: 0.38, S: 0.10, C: 6.7 |
| - 56 + 45                     | 7.5          | SiO\textsubscript{2}: 51.6, Al\textsubscript{2}O\textsubscript{3}: 23.0, Fe\textsubscript{2}O\textsubscript{3}: 9.52, MgO: 1.64, TiO\textsubscript{2}: 0.90, P\textsubscript{2}O\textsubscript{5}: - , S: - , C: 4.2 |
Table 2 indicates that difference in various fractions' chemical compositions is insignificant. Therefore, the magnetic separation process of CFA was performed without preliminary dry classification. The chemical analyses indicated that U and Th in CFA are not above the statutory value of LOC for powder materials, so the magnetic concentrate is not a toxic material.

For extraction of iron from CFA, laboratory experiments for its enrichment were performed using the different magnetic separators type:

- an electromagnetic separator with high magnetic field strength;
- a high-intensity separator with permanent magnets;
- an electromagnetic belt separator (ED - separator).

The best results obtained using the electrodynamic belt separator [3]; thus, it was used for CFA enrichment, as shown in figure 1. As can be seen, from figure 1, producing of magnetic concentrate from CFA include magnetic separation by electrodynamic belt separator, mild attrition of magnetic concentrate (cleaning the surface of magnetic spheres from sludge), hydraulic classification (remove of sludge). From initial CFA with 8.13% Fe₂O₃ (table 1), the magnetic concentrate with 62.8% Fe₂O₃ and 53.4% of Fe₂O₃ recovery obtained. After attrition and hydraulic classification content of Fe₂O₃ in magnetic concentrate increased to 66.56 %, recovery decreased to 51.9 %.

The dry magnetic concentrate was separated by classification on classes with 80 μm particles sizes that lead to obtaining a product with content of Fe₂O₃ near 70% with a recovery of it from initial CFA near 38%. The fraction with particles sizes smaller than 80 μm contains more than 60% Fe₂O₃. The total iron recovery in both products exceeds 50%. It should be mentioned that by dry classification of magnetic concentrate can be obtained narrower fractions of magnetic spheres (table 3).

### Table 3. The content of Fe₂O₃ and SiO₂ in different fractions of magnetic spheres.

| Grain-size fraction, μm | Yield, % wt | Fe₂O₃, % wt Content | Recovery | SiO₂, % wt Content | Recovery |
|-------------------------|-------------|----------------------|----------|-------------------|---------|
| + 125                   | 5.8         | 48.8                 | 4.2      | 30.2              | 10.1    |
| - 125 + 100             | 4.5         | 56.4                 | 3.8      | 24.1              | 6.2     |
| - 100 + 80              | 20.6        | 63.9                 | 19.8     | 19.9              | 23.5    |
| - 80 + 63               | 19.5        | 68.0                 | 18.9     | 17.4              | 19.5    |
| - 63 + 45               | 14.6        | 70.0                 | 15.4     | 15.4              | 12.9    |
| - 45 + 30               | 24.0        | 72.1                 | 26.0     | 14.4              | 19.8    |
| - 30 + 20               | 9.0         | 72.0                 | 9.7      | 12.4              | 6.4     |
| - 20                    | 2.0         | 72.4                 | 2.2      | 13.6              | 1.6     |
| Initial magnetic concentrate | 100,0      | 66.56                | 100.0    | 17.42             | 100.0   |

The magnetic concentrate obtained from Kashirskaya GRES coal fly ash differs from the ordinary iron concentrate so that iron in it presents in the magnetic spheres and the glassy phase (figure 2).
Figure 2. The SEM image of magnetic concentrate obtained from Kashirskaya GRES coal fly ash.

It should be mentioned that a large size magnetic spheres have a higher amount of iron compares to magnetic spheres with a small size. Besides, the magnetic spheres with a small size have the correct shape, but the magnetic spheres with a large size have incorrect shape and often present in fragments. Usually, the magnetic spheres represent almost the pure magnetite, but magnetic spheres also represent intergrown between magnetite, hematite and aluminosilicate glass. The magnetic spheres have sizes from 0.5 μm up to 250 μm.

The X-Ray diffraction analysis of magnetic concentrate showed that the main iron phases are Fe₃O₄ (magnetite), Fe₂O₃ (hematite) and FeO (wustite). These phases' relative content was estimated as Fe₃O₄ :Fe₂O₃ :FeO = 3,3 :1,5 :1 proportion. The magnetic concentrate also contains glaucophane (Na₂Mg₃Al₂(OH)₆), quartz (SiO₂) and probably anorthoclase ((Na,K)AlSi₃O₈). The part of the sample present in an amorphous phase. The same phases are found in the composition of initial CFA, magnetic concentrate and tailings of magnetic separation, and the difference between them lies only in the quantitative ratio of phases.

The table 1 shows that CFA also contains more than 14% of C, extracted into the carbon concentrate by the flotation method. Figure 3 illustrates a flow-sheet extraction of carbon from CFA by the flotation method.

Figure 3. The flow sheet of carbon extraction.
According to figure 3, the final concentrate with the content of 37.78% C obtained. A mixture of kerosene with heavy vacuum gas oil (1: 1.5 kg/t) was used as collecting agent; the frothing reagent was pine oil (0.33 kg/t), duration process 5 minutes. The aluminosilicate product was treatment by magnetic separation according to the flow-sheet shown in figure 1. Table 4 shows two samples' chemical compositions, final magnetic concentrates and carbon concentrate obtained after treatment initial CFA by flotation and magnetic separation methods.

### Table 4. The chemical compositions of magnetic concentrates and carbon concentrate.

| Component        | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | TiO$_2$ | MnO | Na$_2$O | K$_2$O | P$_2$O$_5$ | S | MgO | CaO | C  |
|------------------|---------|-------------|-------------|---------|-----|---------|-------|------------|---|-----|-----|----|
| Magnetic concentrate No 1 (MC-1) | 17.88   | 7.26        | 61.53       | 0.34    | 1.22| 0.18    | 0.44  | 0.23       | 0.02| 1.42| -/-| -/- |
| Magnetic concentrate No 2 (MC-2) | 25.42   | 9.60        | 48.96       | 0.45    | 0.8 | 0.26    | 0.71  | 0.24       | 0.02| 1.52| -/-| -/- |
| Carbon concentrate (CC) | 32.85   | 16.69       | 5.78        | 0.57    | 0.12| 0.85    | 0.96  | 0.37       | 0.48| 0.96| 2.60| 37.78 |

The magnetic concentrates contain a high amount of Fe$_2$O$_3$ and significantly differs in SiO$_2$ content. The carbon concentrate contains more than 37% of C and can be used to reduce iron oxides of magnetic concentrates. The obtained concentrates contain low P and S and can be used to obtain cast iron by reduction smelting.

For producing cast iron from magnetic concentrates, several experiments performed. The magnetic concentrate mixed with carbon concentrate or graphite and flux, then placed into carbon crucible and smelting in a vertical resistance tube furnace. Reduction smelting was carried out at $1380 - 1500$ °C during 1 hour. To reduce the oxygen potential in the gas phase and to avoid erosion of the carbon heater due to burning, Ar gas was introduced into the tube with a 0.5 L/min flow rate through a gas inlet in the lower part of the furnace. For lower slag melting point, the CaO as the fluxing agent was used in some experiences. The amount of reducing agent was calculated based on the complete reduction of iron oxides. The elemental composition of the smelting products was determined by inductively coupled plasma atomic emission spectrometry and infrared absorption method. The components of mixtures and conditions for different experiments represents in table 5.

### Table 5. The components of mixtures and experimental conditions.

| Experiment number | Mixtures            | Temperature, °C |
|-------------------|---------------------|-----------------|
| 1                 | MC-1, graphite      | 1500            |
| 2                 | MC-1, CC            |                 |
| 3                 | MC-1, graphite, 15 % CaO |         |
| 4                 | MC-2, graphite      |                 |
| 5                 | MC-2, graphite, 20 % CaO | 1500 |
| 6                 | MC-2, MC-2          |                 |
| 7                 | MC-1, CC            |                 |
| 8                 | MC-2, MC-2          | 1400            |
| 9                 | MC-1, graphite      |                 |
| 10                | MC-2, graphite      | 1380            |

The experiments showed that at 1380 °C and using graphite as a reducing agent (No 9 and No 10 in table 5), fully separation on alloy and slag for both concentrates not occurred. After experimental, the alloy particles mixed with slag observed. An increase of temperature up to 1500 °C (No 1 and No 4 in
(Table 5) lead to alloy particles' growth, but entirely separate slag from alloy not occurred. The image of products obtained after reduction smelting of mixtures 1, 4, and 9 depict in figure 4.

![Figure 4](image-url)

**Figure 4.** The reduction smelting products (№9 (a), №4 (b) and №1 (c)). The alloy place from above and slag from below.

It is well known [4] that with an increase of SiO₂ content in the slag, its viscosity increases that causes difficulties in the separation of alloy and slag and leads to losses of metal with slag. The experiments with CaO additives (No 3 and No 5 in Table 5) were performed to slag viscosity reduce. It is shown that CaO adding have a positive effect on alloy particles growth, but fully separation of alloy and slag is not occurring. It should be noted that additives can change the colour of slags, and slags of different colours from dark green to purple can be obtained. The image of products obtaining after reduction smelting mixtures 3 and 5 with CaO additive depict in figure 5.

![Figure 5](image-url)

**Figure 5.** The products of reduction smelting №3 (top) and №5 (bottom).

The best results in separating alloy and slag were obtained by using CC as reductant. Even at 1400 °C, the separation was with ease for smelting both MC-1 and MC-2. Nevertheless, the number of metal losses with slag during smelting MC-2 was higher and increased with increasing temperature, probably associated with the slag's intense boiling. The image of products obtaining after reduction smelting mixtures 2, 6, 7 and 8 depict in figure 6.
**Figure 6.** The reduction smelting products (№ 7 (a), № 2 (b), № 8 (c) and № 6 (d)). The alloy placed from below and slag from above.

Table 6 and 7 represent alloys’ and slags’ chemical compositions obtained after reduction smelting of different mixtures, accordingly.

### Table 6. The chemical composition of obtained alloys, %.

| Experiment number | Element | S  | C  | P  | Si  | Mn  |
|-------------------|---------|----|----|----|-----|-----|
| 1                 |         | 0.03 | 4.46 | 0.32 | 1.72 | 0.80 |
| 2                 |         | 0.01 | 7.68 | 0.32 | 0.58 | 0.30 |
| 3                 |         | <0.01 | 5.46 | 0.19 | 1.71 | 1.49 |
| 4                 |         | 0.03 | 4.73 | 0.30 | 1.55 | 0.39 |
| 5                 |         | 0.01 | 5.49 | 0.29 | 2.94 | 0.86 |
| 6                 |         | 0.05 | 4.45 | 0.31 | 0.96 | 0.26 |
| 7                 |         | 0.06 | 3.87 | 0.24 | 0.094 | 0.074 |
| 8                 |         | 0.08 | 4.55 | 0.34 | 0.23 | 0.052 |
| 9                 |         | 0.02 | 7.18 | 0.24 | 0.33 | 0.20 |
| 10                |         | 0.02 | 4.33 | 0.29 | 0.045 | 0.026 |

### Table 7. The chemical composition of obtained slags, %.

| Experiment number | Component | CaO | SiO₂ | Al₂O₃ | FeO | P₂O₅ | MgO |
|-------------------|-----------|-----|------|-------|-----|------|-----|
| 1                 |           | 10.96 | 46.25 | 19.37 | 0.41 | 0.002 | 6.73 |
| 2                 |           | 6.75 | 49.20 | 19.67 | 1.95 | 0.018 | 4.93 |
| 3                 |           | 25.77 | 41.22 | 15.86 | 0.81 | 0.023 | 5.26 |
| 4                 |           | 6.58 | 52.34 | 19.90 | 1.82 | 0.007 | 4.58 |
| 5                 |           | 25.00 | 43.59 | 16.39 | 0.88 | 0.023 | 3.71 |
| 6                 |           | 7.34 | 52.22 | 19.47 | 2.79 | 0.002 | 3.88 |
As can be seen, obtained alloys correspond to steelmaking pig iron [5] with the low content of S and P. It should be noted significant fluctuations in Mn and Si in alloys samples in different conditions. High carbon contents in the alloy’s samples of No 2 и No 9 are associated with the incomplete separation of alloy and slag and graphite ingress into the pig iron. The optimal mixtures were MC-1 with CC and after reduction, smelting of its the best results of alloy and slag separation, iron recovery and obtained of high-quality steelmaking pig iron. Nevertheless, despite the higher iron recovery at 1500 °C compared to reduction smelting at 1400 °C (see table 6), the optimal temperature of reduction smelting for this mixture was 1400 °C, because obtained at this temperature pig iron more suitable for the steelmaking process. The CaO additives lead to an increase in iron recovery and decrease in P content in the alloy. FeO content in slags obtained with CaO additives was lower than 1%, that lower than the content of it in the slags obtained without CaO addition. The lower P content (table 6) was obtained after reduction smelting of MC-1 and 15% CaO mixture (No 3) using graphite as reductant.

The obtained slags content of a large amount of Al₂O₃ can be used for its extraction [6]. Also, these slags can be used for produced construction materials [7].

Conclusions
The experiments showed that the high-quality magnetic and carbon concentrates could be obtained by flotation and magnetic separation methods from Kashirskaya GRES coal fly ash. The steelmaking pig iron with a low content of hindering impurities and the slag with a high amount of alumina can be obtained by reduction smelting of the magnetic and carbon concentrates.

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