Study of the possibility of iron extraction from waste coal by magnetizing roasting

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Abstract. The efficiency of magnetizing roasting of waste coal in converting iron, contained in the mineral part, from weak-magnetic and non-magnetic minerals (siderite, pyrite, marcasite) into high-magnetic ones (magnetite, maghemite) is shown. Products of magnetizing roasting are used as raw material for the subsequent magnetic separation.

1. Introduction

Wastes from mining and processing of mineral recourses are the most widespread types of solid wastes. Thus, in Russia total generation of wastes in 2014 was 5.15 billion tonnes including mining wastes – 4.7 billion tonnes, or 91.2 % [1]. In Kemerovo region in 2014 2.64 billion tonnes of wastes were generated, among them are mainly overburden and host rock from open pit coal mining which is 99.33% or 2.62 billion tonnes of the total amount [2]. In recent years the coal processing has rapidly increased. In 2010 in Kuzbass at the processing plants 127.1 million tonnes of coal were processed and 49.8 million tonnes of coal concentrate were produced [3], which resulted in 77.3 million tonnes of waste coal from the mineral rock processing.

Over a long period of operation coal processing enterprises located in various regions of the country accumulated more than 20 billion tonnes of waste coal. During designing new centers of coal mining a mandatory construction of modern processing plants is required. In general, in Russia it is planned to increase the level of coal enrichment from 40 % to 60%. Annually as a result of operation of coal processing enterprises about 240 million tonnes of waste coal will be generated. [4]

Currently, the main method of coal mining wastes disposal is their use for stowing and waste coal – for production of construction materials: bricks, porous aggregates (aggloporite, lightweight expanded clay aggregate), crushed aggregate [5, 6]. New directions for utilization of coal rocks are still insufficiently developed. The waste dumps have accumulated huge reserves of some metals comparable to the volumes of natural mineral deposits. Therefore, mining wastes can be considered as an alternative way for replenishing natural resources. One of the promising areas of processing coal rocks is the iron extraction from them.

It is known that waste coal in Kuznetsk Basin are characterized by relatively stable mineral composition, dominated by silicon oxides, aluminum and iron. The content of iron oxide in the mineral part of coal averages 5-15 %, reaching in some cases up to 25 % [7].
2. Experimental research and results

Complex studies of coal tailings in Kuzbass, stored in the tailings reservoir of JSC “EVRAZ ZSMK”, conducted by the authors [8-10] showed that they contain iron mostly as a component of siderite, as well as pyrite and marcasite. Thus, iron containing minerals are attached to carbonaceous particles. In [10] it is noted that for iron extraction from waste coal it is advisable to use the method of magnetic separation with preliminary magnetizing roasting in the weak oxidizing medium, in the process of which the burn-out of carbonaceous particles, destruction of attachments, decomposition of carbonates and iron sulfides with formation of magnetite will take place.

Samples of waste coal with sizes 0-1 and 1-3 mm were subjected to roasting in the laboratory muffle furnace at 600 °C under conditions of air access restriction for 1.5 hour until constant mass was achieved. The results of chemical and X-ray phase analysis of the initial and roasted samples given in Tables 1 and 2 prove the full siderite decomposition with formation of magnetite in both samples. In the small fraction of size 0-1 mm a small amount of hematite was detected, that indicates its increased oxidation. Thus, the thermal treatment of samples in the laboratory conditions can be characterized as magnetizing roasting.

Table 1. Content of iron and iron-containing phases in the waste coal of various sizes.

| Particles size, mm | \(\text{Fe}_{\text{tot}}\) | \(\text{Fe}_{\text{met}}\) (fraction from \(\text{Fe}_{\text{tot}}\), % rel.) | \(\text{Fe}^{2+}\) (fraction from \(\text{Fe}_{\text{tot}}\), % rel.) | \(\text{Fe}^{3+}\) (fraction from \(\text{Fe}_{\text{tot}}\), % rel.) |
|-------------------|----------------|-----------------|-----------------|-----------------|
| Initial 0-40      | 14.0           | 0.98 (7.0)      | 12.92 (92.3)    | 0.10 (0.7)      |
| 0-1               | 13.5           | 0.23 (1.7)      | 13.5 (78)       | 3.91 (20.3)     |
| 1-3               | 14.6           | 1.37 (9.4)      | 13.71 (73.2)    | 3.62 (17.4)     |

Table 2. Results of X-ray phase analysis of waste coal.

| Name of the sample | Particles size, mm | Dominant mineral | Other minerals | Impurities |
|--------------------|--------------------|------------------|----------------|------------|
| initial            | 0-40               | Hydromuscovite   | Hydromica, montmorillonite, X-ray amorphous materials (AM) | Calcite, feldspar, kaolinite or chlorite, dolomite, graphite (carbon) |
| initial            | 0-1                | Siderite FeCO\textsubscript{3}, quartz | AM, hydromica, montmorillonite | Calcite, kaolinite or chlorite, dolomite |
| initial            | 1-3                | Siderite FeCO\textsubscript{3}, quartz | AM, hydromica, montmorillonite | Calcite, kaolinite or chlorite, dolomite |
| after roasting     | 0-1                | Magnetite Fe\textsubscript{3}O\textsubscript{4} | Hematite \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}, silica, AM, hydromuscovite | Calcite, feldspar and other impurities |
| after roasting     | 1-3                | Magnetite Fe\textsubscript{3}O\textsubscript{4} | Quartz, AM, hydromuscovite | Calcite, feldspar and other impurities |

Mossbauer spectra, their parameters and interpretation of the initial and roasted samples with sizes 1-3 mm (PK34-1 and PK-34-3) and 0-1 mm (PK34-2 and PK34-4) are provided in Figure 1 and in Table 3.
Figure 1. Mossbauer spectra of waste coal before and after roasting (a and b – initial samples of sizes 0-1 mm and 1-3; c and d – roasted samples with sizes 0-1 and 1-3 mm).

Table 3. Mossbauer spectra parameters of waste coal before and after the magnetizing roasting and their interpretation.

| Name of the sample | Spectrum component | Isomer shift $\delta$, mm/s | Quadrupole splitting $\Delta$, mm/s | Magnetic fields on nuclei $Fe^{3+}$, H, kOe | Component area $S$, % | Interpretation |
|--------------------|-------------------|-----------------------------|---------------------------------|--------------------------------------|-----------------|---------------|
| Initial 1-3 mm     | D1($Fe^{2+}$)     | 1.23                        | 0.18                            | 0                                    | 87.5            | Siderite      |
| Initial 0-1 mm     | D2($Fe^{2+}$)     | 0.29                        | 0.61                            | 0                                    | 12.5            | Pyrite        |
| Roasted 1-3 mm     | C2($Fe^{2+}$)     | 0.58                        | -0.04                           | 452                                  | 36.0            | Magnetite-maghemite |
| Roasted 0-1 mm     | C3($Fe^{2+}$)     | 0.32                        | -0.03                           | 369                                  | 7.6             | Siderite      |
|                    | D1($Fe^{3+}$)     | 0.22                        | 1.00                            | 0                                    | 6.8             | Hydromica     |
|                    | D2($Fe^{3+}$)     | 1.16                        | 1.73                            | 0                                    | 6.2             | Siderite      |
|                    | C1($Fe^{3+}$)     | 0.31                        | -0.01                           | 489                                  | 43.6            | Hydromica     |
|                    | C2($Fe^{3+}$)     | 0.42                        | -0.16                           | 462                                  | 20.7            | Siderite      |
|                    | C3($Fe^{2+}$)     | 0.69                        | -0.12                           | 451                                  | 22.2            | Siderite      |
|                    | D1($Fe^{3+}$)     | 0.34                        | 1.07                            | 0                                    | 6.8             | Hydromica     |
|                    | D2($Fe^{3+}$)     | 1.27                        | 2.28                            | 0                                    | 6.7             | Siderite      |

The obtained results showed high efficiency of magnetizing roasting in converting iron from non-magnetic (pyrite) and weak-magnetic (siderite) forms into high-magnetic ones (magnetite and maghemite $\gamma$-$Fe_{3}O_{5}$). In the roasted products non-stoichiometry of magnetite is revealed, $Fe^{3+}$ ions of tetrahedral position form two non-equivalent positions, which indicates the possible isomorphic
substitutions leading to their formation. Doublet D1 of Fe$^{3+}$ ions has a tetrahedral coordination, perhaps it is related to hydromicas. Doublet D2 is related to siderite.

Mossbauer spectra of the roasted samples of various sizes, as well as of the initial ones, differed slightly, mainly, in cationic distribution in magnetite. In the roasted sample with size 1-3 mm in comparison to the sample with size 0-1 mm there is no additional non-equivalent tetrahedral position of Fe$^{3+}$ ions, it appears in octahedral coordination. The total fraction of iron in the composition of high-magnetic phases (magnetite and maghemite) depended little on the particle size of the initial samples and was 87 % rel. for the sample with size 1-3 mm, and 86.5 % for sample with size 0-1 mm. As it follows from Figure 1, as a result of roasting the bulk of iron transformed from divalent into trivalent state, part of the iron ions is represented by the ions Fe$^{3+}$ and Fe$^{2+}$ of octahedral position, which are connected by electron exchange. The roasted sample of fine fraction 0-1 mm was characterized by a higher content of ferric iron, which indicates a greater degree of its oxidation. However, the oxidized ferric iron was present in the composition of high magnetic phases (magnetite and maghemite).

The initial and roasted samples of waste coal were studied by the method of combined thermal analysis (CTA), which included a differential scanning calorimetry (DSC) and the definition of weight loss (TG). The measurements were performed in the argon atmosphere at a heating rate of 20 deg/min to 1000 °C. DSC and TG curves are given in Figure 2. Comparison of the thermogravimetric curves of the initial and roasted samples (Figure 2 a and b) shows that these samples are completely different in mineral composition.

![Figure 2. Curves of differential scanning calorimetry (DSC) and thermogravimetry (TG), waste coal before (a) and after (b) magnetizing roasting.](image-url)
While on DSC curve of the initial sample three distinct endothermic peaks with maxima at temperatures 508.2 °C (siderite decomposition), 759.5 °C and 860.5 °C (reduction of iron to wustite and metal) are observed, on DSC curve of the roasted sample two endothermic effects – flat in the range of 400 – 500 °C are observed, which is probably due to the dissociation of residual siderite and other low temperature impurities, for example, calcite and dolomite, and the peak with a maximum at 737.8 °C indicating the wustite formation.

Thus, unlike the initial sample the roasted sample is characterized by the exothermic peak at 806.3 °C most likely associated with the emission of heat during the oxidation of carbonaceous argillite, and in the range 850 – 975 °C by the endothermic effect due to iron reduction to α-Fe and γ-Fe. Mossbauer spectra of the sample after heating under conditions of CTA confirmed the presence of these iron phases.

Figure 3 shows the diagram of the calculated phase composition of iron-containing components of the examined samples with the distinct high-magnetic (magnetite, maghemite) and weak-magnetic (siderite) phases.

As Figure 3 shows, even with during heating under laboratory conditions at a rather low for magnetizing roasting temperature (600 °C) from the waste coal was obtained a product, in which approx. 90 % of iron-containing phases were high-magnetic. It is expected that in industrial conditions complying with the technological regime as a result of magnetizing roasting all iron contained in this material would convert from weak-magnetic (siderite) and non-magnetic (pyrite) minerals into high-magnetic minerals (magnetite, maghemite), which conditions the feasibility of their extraction by magnetic method. It is appropriate to carry out magnetizing roasting in a low-oxidizing atmosphere in order to oxidize carbon of carbonaceous particles, which would provide formation of CO and destruction of their attachments to iron-containing minerals.

3. Conclusions

Thus, the received results confirm the usefulness of the magnetizing roasting of waste coal for conversion of iron, contained in the mineral part, from weak-magnetic siderite into high-magnetic magnetite and maghemite. At the same time the contained in waste coal carbon would provide the roasting process with its own heat, which would help to reduce the costs of the product. The products of magnetizing roasting, enriched by high-magnetic minerals, are the raw material for the subsequent magnetic separation.

4. References

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