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Study of the Processes of Obtaining Iron-Free Raw Materials from Ash and Slag Waste from the Combustion of Brown Coal of KAFEC

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Abstract

The processes involved in obtaining iron-free X-ray amorphous aluminosilicate raw material of the required composition from the ash and slag waste (ASW) from the combustion of brown coal of KAFEC are investigated. Carbon thermal reduction during ASW melting is used to extract iron and its compounds. The distribution of elements – iron (Fe^{2+} , Fe^{3+} , Fe^{0} , Fe^{tot}), sulphur (S) and carbon (C) – in the metal (magnetic) and silicate (nonmagnetic) fractions at different temperatures of ASW heating is shown. The equations describing the temperature dependence of the standard change of Gibbs energy for the reactions of the reduction of iron oxides are presented. The effect of silicon carbide, formed in the silicate fraction of the melt, on the recovery of iron oxides to metal iron and the resistance of foam formed due to the reducing gases are discussed. The introduction of the melt into water changes the morphology and leads to the formation of foamed heat-insulating material. Normalization of the charge during melting allows obtaining foamed materials of the required composition.

Keywords: ash and slag wastes, reducing melting, magnetic and non-magnetic fractions, fluidised bed, brown coal, silicon carbide, iron silicide, melt foaming, carbon thermal reduction

INTRODUCTION

A traditional area of the use of ash and slag wastes (ASW) both in Russia and abroad is the construction industry [1–12]. A unique component of flue ash exhibiting because the diversity of practical application is aluminosilicate hollow microspheres [13–18], however, the content of these microspheres is insignificant. The use of the accumulated enormous resources of ASW in the production of materials does not exceed 10 %. Limitations of a broad application of ASW with the major components CaO, SiO₂, Al₂O₃, MgO, Fe₂O₃, K₂O, Na₂O is due to their variable chemical and phase composition. The presence of admixtures of transition metals (iron, manganese, chromium, titanium in different valence states, etc.), free calcium oxide also hinders their application. In order to use this raw material in the industry to obtain a broad range of ceramic, glass-ceramic, heat-insulating, optically transparent materials of the required composition, it is necessary to stabilize its chemical composition and neutralize free calcium oxide with the isolation of colouring oxides of transition metals. In this connection, the search for the methods of integrated waste-free use of ASW with obtaining stabilized raw material is especially urgent. Reductive melting of ASW with the normalization of melt composition meets these requirements. Unlike for the classical method of pyrometallurgical processing of iron-containing ores, this method provides the required composition of ash melt during melting with the accompanying metal extraction. Similarly to the metallurgical operation of iron ore processing, iron is reduced as a result of chemical interaction of gaseous carbon (II) oxide with metal oxide according to the scheme known as a two-stage adsorption autocatalytic scheme of carbon thermal recovery of iron [19–23].

The goal of the work was to study the process of obtaining iron-free silicate melt suitable for the production of ceramic materials based on ASW, by means of reductive melting, and accompanying metal extraction.

EXPERIMENTAL

Experiments were carried out with ash from the Heat Station No. 1 (Krasnoyarsk) having the following composition, mass %: SiO₂ 50.2, CaO 25.3, Al₂O₃ 9.0, Fe₂O₃ 8.31, MgO 4.31, TiO₂ 0.39, C 0.1, S 0.39, Na₂O 0.19, K₂O 0.41.

Ash was fused in Tamman furnace in graphite crucibles with the addition of brown coal for the reduction of metal oxides. The temperature was recorded with the help of the tungsten-rhenium thermocouple. Crucibles with a thoroughly mixed sample composed of 500 g of ash and 14 g of brown coal were placed in the furnace and heated to the required temperatures 700, 900, 1100, 1200, 1250, 1300, 1500 °C. After cooling, the sample mass was measured using laboratory balance VLKT-500M. Weighting error was 0.1 g.

The samples were ground in a disc attritor of LDI-3 type to the particle size of 80 mm and subjected to magnetic separation. The mass of the magnetic (metal) fraction was determined using the same balance. The mass of non-magnetic (silicate) fraction was calculated as the difference between the mass of the whole sample and the mass of the magnetic fraction.

A sample 50 g in mass was taken by quartering from the non-magnetic fraction to measure the content of carbon, sulphur, total iron (Fe^{tot}), metal iron (Fe⁰), di- (Fe²⁺) and trivalent iron (Fe³⁺). The magnetic fraction was used completely for chemical analysis for the components under investigation. Sample analysis was carried out from two parallel weighted portions. Chemical analysis of ash and the obtained materials was mainly carried out according to the standard procedure of cement analysis (GOST 5382-91). Silicon dioxide content was determined using he gravimetric hydrochloric method; the oxides of aluminium, calcium, magnesium were determined by means of volumetric trilonometry; titanium dioxide was determined by means of photocolorimetry with diantipyrylmethane; potassium and sodium oxides were determined by means flame photometry.

Total iron content in the magnetic fraction was established with the help of dichromate method using tin dichloride as a reducing agent. Total iron content in the non-magnetic fraction was determined by means of photocolorimetry with 2,2-dipyridyl through the decomposition of the sample by fusing in platinum crucibles with a mixture of soda and sodium tetraborate. Metal iron both in the magnetic fraction and in non-magnetic one was determined using the copper sulphate method [24]. The sum of divalent and metal iron was determined using the bichromate method after the dissolution of the weighted portion in hydrochloric acid with a density of $1.19 \text{ cm}^3/\text{g}$ in the atmosphere of carbon dioxide. Trivalent iron was determined as the difference of total iron and the sum of divalent and metal iron. Divalent iron was calculated as the difference between the sum of divalent and metal iron and metal iron alone.

Carbon content was measured using the method based on burning a weighted portion in the flow of oxygen with the potentiometric ending of the analysis with an AN-7529 gas analyser (Russia) (GOST 23881.9-79). Sulphur was determined by burning the weighted portion in oxygen flow with the iodometric ending of the analysis (GOST 18262.13-88). For the determination of carbon and sulphur, copper (II) oxide was used as a flux.

Electron microscopic and X-ray phase analysis of the samples obtained from foamed silicate was carried out with a Hitachi TM 3000 scanning electron microscope (Japan) in the shared equipment centre at the Federal Research Centre of the Krasnoyarsk Scientific Centre SB RAS.

RESULTS AND DISCUSSION

According to the results of chemical analysis and the masses of samples, the masses of components were calculated using the equation: $m = (C \cdot M)/100$, where *m* is the mass of the component in the sample; *C* is the content of the com-



Fig. 1. Dependence of the amount of Fe^{0} , Fe^{2+} , Fe^{3+} in magnitic (*a*) and non-magnetic (*b*) fractions on the temperature of ASF heating.



Fig. 2. Dependence of the amount of carbon and sulfur in magnetic and non-magnetic fractions on the temperature of ASF heating.

ponent in the sample, mass %; M is sample mass. The dependences of the amount of components in

the magnetic and non-magnetic fractions on the temperature of ASW heating are shown in Fig. 1, 2.

TABLE 1

Compound	Reducing agent		
	С	СО	-
FeO	$\Delta_{\rm r} G_{1273}^0 (6) = -0.1543 \ T + 153.46$	$\Delta_{\rm r} G^0_{1273} \ (4) = \ 0.0212 \ T \ - \ 18.023$	
$\mathrm{Fe}_{3}\mathrm{O}_{4}$	$\Delta_{\rm r} G^0_{1273} (5) = -0.6595 \ T + \ 654.91$	$\Delta_{\rm r} G^0_{1273} (2) = 0.041 \ T - 30.065$	

Equations for the temperature dependence of the change of Gibbs energy $\Delta_r G_T^0$ of reactions of iron reduction from FeO and Fe₃O₄ by carbon (reactions (5), (6)) and carbon monoxide (II) (reactions (2), (4)) at T = 1273 K

One can see that iron in the initial samples is present mainly in the trivalent state both in the magnetic fraction and in non-magnetic one (see Fig. 1). This is due to the fact that coal combustion proceeds in the presence of an excess of oxygen, so iron is present in the highest oxidation degree +3 in the form of oxides in the magnetic fraction and iron salts in the non-magnetic fraction.

During fusion in graphite crucibles, at first, the added brown coal necessary for iron reduction burns out. Coal is distributed uniformly during mixing over the whole mixture volume, so inside the sample in the crucible it burns with the formation of carbon (II) oxide due to the lack of oxygen, while on the surface of the sample it burns with the formation of carbon (IV) oxide.

Carbon (II) oxide rises up and reduces iron (III) oxide. Initially, iron (II, III) oxide (Fe_3O_4) is formed in agreement with the principle formulated by A. A. Baykov:

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$$
 (1)

This reaction is possible within a broad temperature range (see Fig. 1).

An increase in the amount of metal iron in the region of low temperatures (see Fig. 1) occurs in agreement with reaction

$$Fe_{3}O_{4} + 4CO = 3Fe + 4CO_{2}$$
 (2)

and simultaneously the reduction of iron (III) incorporated in iron (II, III) oxide proceeds, at first into iron (II) oxide

$$Fe_2O_3 + CO = 2FeO + CO_2$$
 (3)
and then from iron (II) oxide to metal iron (1)

$$FeO + CO = Fe + CO_2$$
(4)

The formation of metal iron from iron (II, III) oxide at temperatures T > 800 °C in agreement with the standard Gibbs energy change is possible only in the interaction with solid carbon:

 $Fe_{3}O_{4} + 4C = 3Fe + 4CO$ (5) FeO + C = Fe + CO(6)

The kinetic conditions for reactions (5) and (6) during the reductive melting of ash from the combustion of brown coal are the fine state of flue ash and the gas flow formed by the reductive gases. Due to the excess of the force of dynamic pressure (*P*) of gases over the force of gravity (*F*) exerted on ash particles ($P \ge F$), the fluidised bed effect is created. The gaseous product of reactions will be carbon (II) oxide because the equilibrium of carbon gasification reaction at $T \ge 800$ °C is shifted to its formation. The equations of the temperature dependence of the standard change of Gibbs energy ($\Delta_r G_T^0$)) for iron reduction are shown in Table 1.

One can see that the highest development at high temperature is exhibited by reaction (5) of iron reduction from Fe_3O_4 by carbon. The obtained results do not contradict the data reported in [25] for the investigation of thermodynamics of iron reduction from oxygenated and sulphide compounds.

Sulphur is present in the initial samples, similarly to iron, in the highest oxidation degree +6 in the form of sulphates. At a temperature about 500 °C, iron (III) sulphate present in the non-magnetic fraction starts to decompose into sulphur (VI) oxide, which is decomposed into sulphur (IV) oxide with an increase in temperature. The latter compound rises up and contacts carbon to get reduced to elemental sulphur: $SO_2 + C = S + CO_2$. At this stage, violent gas evolution occurs (CO, CO₂, SO₂) from the inner layers of the mixture, which promotes the formation of a fluidised bed in the crucible. During melting the ash of brown coal. with further temperature rise to 900 °C, the decomposition of sulphates, carbonates and calcium hydroxide present in ash proceeds. For example, calcium carbonate is decomposed at a temperature of 800 °C. Carbon (IV) oxide, which is formed both in carbonate decomposition and in carbothermal reduction of iron, rises up and contacts the walls of the graphite crucible transforming into carbon (II) oxide, which participates in the subsequent reduction of iron according to the reactions indicated above. A part of carbon (II) oxide at a temperature of 1100 °C dissociates into carbon and carbon (IV). Soot carbon released during the decomposition is deposited on the reduced iron particles and reacts with it with an increase in temperature, which is confirmed by an increase in carbon content in the



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Fig. 3. Shape of metal particles released on the surface of sintered ash particles within the sample volume at ASW heating temperature 1100 $^{\circ}$ C according to the data of scanning electron microscopy.

magnetic phase (see Fig. 2). This provides a decrease in the melting point of carbonized iron and promotes its spread over the surface of ash particles (Fig. 3).

Metal particles have rounded fritted shapes. One can see in Fig. 4, that at this stage of reductive melting ash sintering with the formation of the porous structure occurs.A similar release of the metal phase in porous iron-containing ore was observed by the authors of [26], who considered the probability of the electrochemical nature of metal reduction. A decrease in sulphur and iron (II) content in the magnetic fraction of ash from the Heat Station No. 1 at a temperature of 1250 °C and an increase in sulphur content in the nonmagnetic fraction at this temperature may be explained by the formation of non-magnetic pyrite: $Fe + 2S = FeS_{2}$. Pyrite is unstable and readily decomposes during the further temperature rise into pyrrhotine and sulphur: $FeS_{2} = FeS + S$, which is confirmed by analysis data (see Fig. 1, 2). The formation of pyrite can be detected not in all the cases during rapid temperature rise. Iron (II) sulphide - pyrrhotine is mixed with iron melt in any relation. This causes some increase in sulphur content in the magnetic fraction at the temperature of ASW heating 1300 °C and therefore this leads to a decrease in the relative fraction of metal iron in comparison with its level at 1200 °C.

With an increase in temperature, spreading particles of carbonized metal over the surface of sintered ash are drawn into submicron particles located within the melt volume. The reduction of iron (II) oxide by carbon from the metal transfers this reaction into the melt volume causing its foaming with reducing gases, according to reaction FeO + C = Fe + CO. As a result of gas formation, convection flows bubble through the slag layer and carry the reduced iron particles into the upper layers where they are kept by the surface tension forces in the melt [27]. The collapse of gas bubbles with metal particles leads to their coagulation into larger drops with the shift to crucible wall and draining to the crucible bottom along the graphite - melt boundary with the capture of released sulphur and carbon, and with the formation of the liquid metal phase. Metal sulphides in the upper layers of the melt are captured by metal iron particles, that determines the increased sulphur content in the magnetic fraction (see Fig. 2).

The appearance of the liquid metal phase creates thermodynamic prerequisites for the reduction of silicon from the slag melt and the formation of iron silicides (FeSi), which provides an increase in the mass of Fe^{2+} and Fe^{3+} in the magnetic fraction (see Fig. 1, a). With temperature rise above 1500 °C, carbides of calcium, magnesium, aluminium, silicon are formed in the nonmagnetic fraction of the melt according to reactions similar to $SiO_2 + 3C = SiC + 2CO$. These carbides are held by the surface tension forces of the foamed melt and are uniformly distributed over its volume participating in the additional reduction of FeO in the melt according to the reaction FeO(liq) + SiC(sol) = [FeSi(liq)] + CO(gas).The formation of carbon (II) oxide in this reaction at this stage of metal reduction promotes an additional increase in the lifetime of the foamed state of the melt [28, 29], which affects the heat and mass exchange in the reactions of reductive melting. The stability of the foam due to the reaction of CO (gas) formation and the dependence on silicon carbide in the melt and its temperature is conserved till complete reduction of iron. The melt of the required aluminosilicate composition is stabilized by additional burdening during the reductive melting process. The absence of iron in the melt is the start of the formation of the silicate (non-magnetic) fraction of the melt into water with the formation of foamed X-ray amorphous material (foam silicate). Heating of thus obtained foam silicate of the composition, mass %: SiO_2 48.03, Al_2O_3 3.27, Fe_2O_3 not detected, CaO 45.8, MgO 2.3, SO₃ 0.47, ZrO₂ 0.02, K₂O 0.09, P₂O₅ 0.02, leads to the crystallization of wollastonite structure. The magnetic fraction of the composition, mass %: Fe 73.7, Si 24.5, Al 0.59, Cr 0.29, Mn 0.39, C not detected, P 0.54 occurs in the casting form. The obtained compound is almost correspondent in its composition to ferrosilicium – doped iron alloy of FS25 grade (GOST 1415-93).

CONCLUSION

Temperature regions of the distribution of elements – iron Fe^{2+} , Fe^{3+} , Fe^{0} , Fe^{tot} , sulphur and carbon in the metal (magnetic) and silicate (nonmagnetic) fractions during reductive melting were established, which allowed us to determine the sequence of physicochemical processes taking place during the formation of iron-free melt.

The required composition of foam silicate is determined by additional burdening, temperature modes and the type of reducing agent.

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