

The iron-containing electric-furnace steelmaking waste: physical and chemical properties and acidic modification

Svetlana Sverguzova¹, Zhanna Sapronova¹, Ildar Shaihiiev², Anastasia Svyatchenko,^{1*}

¹ Belgorod State Technological University named after V. G. Shukhov, 46 Kostyukova st., 308012, Russia

² Kazan National Research Technological University, 68 Karl Marx st., 420015, Russia

Abstract. The electric furnace steelmaking dust is formed at melting metalized pellets in electric-arc steel-making furnaces and is a large-tonnage waste. It contains such elements as Fe, Mg, Al, C, Si, Zn, Mn, Na. The ferrous and ferric iron compounds in the EFS dust are mostly presented with oxides – the compounds, which are poorly soluble in aqueous media and can't take part in exchange reactions under ordinary conditions. The acid treatment with HCl allows obtaining a coagulating suspension, which can be used for wastewater treatment. Besides, there was detected up to 14 % of CaO, both free and in calcium silicates such as CaSiO₃ and Ca₂SiO₄. So, in the process of treatment with EFS dust the formation of polysilicic acids helps increasing the purification efficiency.

1 Introduction

Over 30% (by some estimates – up to 50%) of the annual global amount of steel is produced by means of electric-furnace steelmaking [1-4]. The steel melting processes take place at high temperatures – over 1600°C, which is accompanied by intensive dust and gas separation [4]. So, taking into account the scale of production, in spite of efforts to minimize the amounts of the generated waste, its accumulation still continues all over the world [5-10].

The electric furnace steelmaking (EFS) dust is formed at melting metalized pellets in electric-arc steel-making furnaces in amount of 25 kg per ton of steel and is concentrated in filters in the course of gas purification [8].

There are works describing research concerning the usage of this waste as an admixture for cement clinker [3] and experiments in dust recycling with the maximum recovery of iron or zinc [11-14]. The dust is recycled by sintering of a composite [15]; it can be also recirculated together with rolling scale to the electric-arc furnace [16].

It is known that after acidic modification the EFS dust can be used as a coagulator for test wastewaters purification [17-19]. At the same time, for the extensive use of this material in producing a reagent for wastewater purification the in-depth research of its

* Corresponding author: sv.anastasiaa@mail.ru

physical and chemical properties and the peculiarities of its chemical transformations is needed.

2 Methods

In the work the standard photolorimetric methods of determining PO_4^{3-} , SO_4^{2-} , Al^{3+} , Fe^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Mn^{2+} were used.

The energy-dispersive analysis was carried out by means of TESCAN MIRA LMU instrument.

The X-ray phase analysis was performed with «ARL9900 Intellipower Workstation» (with the Co-anode tube); the peaks were interpreted by means of using reference literature.

Derivatographic research was carried out with a thermoanalyzer «Simultaneous SDT Q600» with heating rate $10\text{ }^\circ\text{C}/\text{min}$.

The pH of water extract was measured by using a pH-meter (I-500 ionometric converter, Akvilon, Russia)

3 Results and Discussion

At energy-dispersive spectrums (Figure 1) of all the studied sections of EFS dust the following elements were detected: Fe, Mg, Al, C, Si, Zn, Mn, Na.

According to the X-ray phase analysis data, the ferrous and ferric iron compounds in the EFS dust are mostly presented with oxides – compounds, which are poorly soluble in water media and can't take part in exchange reactions under ordinary conditions.

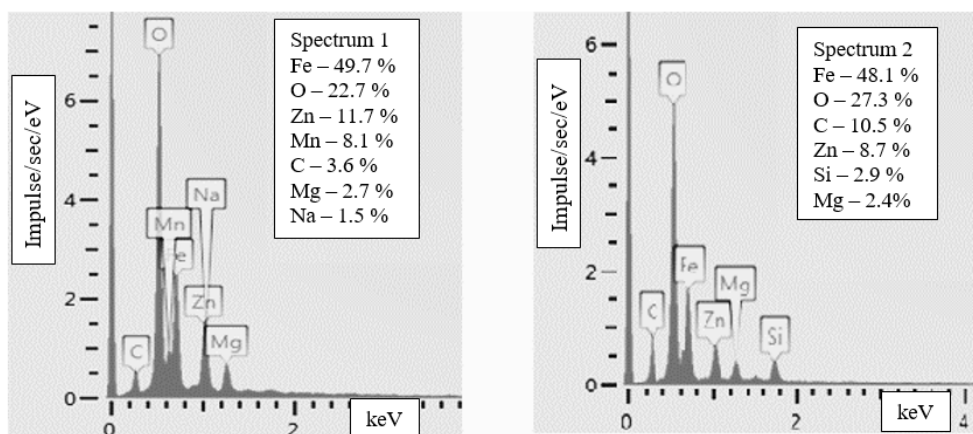
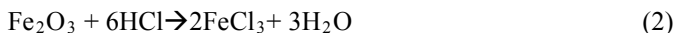


Fig. 1. Energy-dispersive spectrums for sections of EFS dust

The thermal effects were researched by means of a derivatograph Q-1500 with an alundum pot. At that the data about the weight loss of the EFS dust sample in the process of heating, the temperature rise and thermal effects were registered. The total weight loss during the period of heating of the EFS dust sample from 20 to $1000\text{ }^\circ\text{C}$ amounted to 7.703 mg or $3.1\text{ } \%$ wt.

The main endothermic effects correspond to the passing of gamma-iron (Fe_2O_3) to alpha-iron (Fe_2O) at ($474.8\text{ }^\circ\text{C}$); polymorphic transformations of quartz ($585.9\text{ }^\circ\text{C}$); and decomposition of CaCO_3 ($767.6\text{ }^\circ\text{C}$, $876.8\text{ }^\circ\text{C}$).

At treating the EFS dust with hydrochloric acid the following reactions take place:



The resulting ferrous and ferric salts are hydrolyzed in a water medium and can act as reagents for coagulative purification of water media.

A crucial point in obtaining a coagulator from the EFS dust is the completeness of iron (II) and iron (III) passing from the dust under the action of acidic medium.

To 500 ml of HCl solution of the given concentration (in terms of normality) the EFS dust was added (the solid-liquid ratio in all experiments amounted to 1:100), the suspension was boiled, after boiling the contents of the laboratory vessel was filtered, and in the filtrate the concentrations of Fe²⁺ and Fe³⁺ ions were determined by photocolometric method. The dependences of iron ions concentration on the conditions of EFS dust treatment (HCl concentration) are presented in Figure 2.

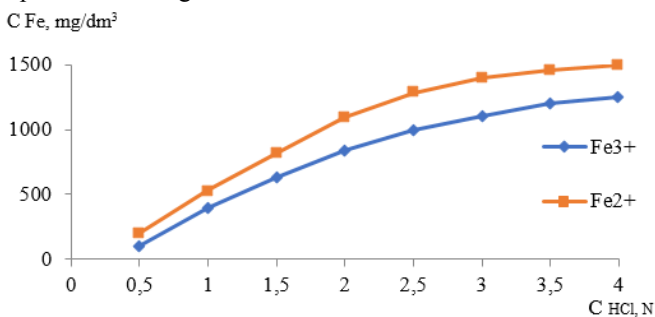
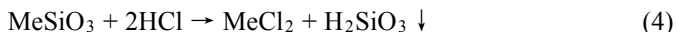


Fig. 2. The dependence of Fe³⁺ and Fe²⁺ ions concentration in the solution from the HCl concentration. The time of acid treatment is 10 min.

According to chemical analysis data of the EFS dust composition, it contains up to 14 % CaO, both free and in calcium silicates such as CaSiO₃ and Ca₂SiO₄. Besides, the EFS dust contains in minute amounts the oxides of Mg, Mn(II), Al, Fe(II), Fe (III), Cu, Sn, Zn, Pb. At adding the solution of HCl (0.1 N) to EFS dust, metal compounds are dissolved by the following schemes:



Thus a suspension is formed, which contains metals in the ionic form.

The similar processes take place in real wastewaters with pH < 7; it should be noted that after CaO is dissolved, the pH value of the medium is increased, which is a favorable factor for the formation of poorly soluble metal hydroxides.

At treating test and real phosphate-containing and metal-containing solutions with this suspension the formation of poorly-soluble compounds is possible.

To check the above-stated hypothesis a test solution was prepared, containing the ions, presented in Table 1 in given concentrations. The pH value of the initial solution amounted to 2.0.

Table 1. Composition of the test solution

Ingredients	PO₄³⁻	SO₄²⁻	CO₃²⁻	Ni²⁺	Al³⁺	Fe²⁺	Fe³⁺	Cu²⁺
Concentrations, mg/dm³	20	700	15	10	10	10	10	10

In the filtrate the concentrations of PO₄³⁻, SO₄²⁻, Al³⁺, Fe²⁺, Fe³⁺, Cu²⁺, Ni²⁺, Mn²⁺ ions were determined. The ions of SO₄²⁻, CO₃²⁻ were studied due to the fact that they are often present in various wastewaters, and the ions of Al³⁺, Fe²⁺, Fe³⁺ and Mn²⁺ were studied because they are contained in the initial EFS dust and in acid medium can pass to the solution. As the EFS dust composition also includes silicates of various metals, at the dissolving of EFS dust the passing of silicate-ions into the solution and the formation of polysilicic acids are likely. As it is known, polysilicic acids have a highly-developed surface, which can adsorb suspended substances and metal ions. So, the formation of polysilicic acids in the process of wastewater treatment with the EFS dust increases the purification efficiency.

The analysis data of the filtrate after purification are presented in Table 2. As it can be seen from the results, presented in the table, in experimental conditions the test solutions are efficiently purified from all the ingredients, and a certain content of silicate-ions passes into the solution due to dissolving of metal silicates.

Table 2. Composition of the filtrate after purification

Ingredients	PO₄³⁻	SO₄²⁻	Fe²⁺	Fe³⁺	Al³⁺	Ni²⁺	Cu²⁺	Mn²⁺	Si
Concentrations, mg/dm³	0.23	403.83	<0.05	0.44	0.43	0.07	0.06	0.081	17.8
Purification efficiency, %	98.9	42.3	-	-	95.7	99.3	99.4	-	-

In the course of the research it was also determined that the lower is the pH of the initial solution, the higher is the content of silicate-ions in the solution (expressed as Si): at pH=2 the amount of C_{Si2+} = 1.8 mg/dm³, at pH=4 C_{Si2+} = 1.3 mg/dm³, at pH=7 C_{Si2+} = 0.7 mg/dm³.

So, the presence of silicate-ions in water medium after adding the EFS dust to it has been confirmed, which proves the possibility of polysilicic acids formation and the adsorption of polluting substances on their surface. It has been also confirmed that the EFS dust could be used for purification of phosphate-containing and metal-containing water media.

4 Summary

The available data about the mineral composition, physical and chemical properties of the electric-furnace steelmaking waste have been expanded.

According to X-ray phase analysis data, ferrous and ferric iron compounds in the EFS dust are mostly presented with oxides. The acid treatment of the material results in the formation of hydrolysable ferrous and ferric salts.

According to chemical analysis data of the EFS dust composition, it contains up to 14 % CaO, both free and in calcium silicates such as CaSiO₃ and Ca₂SiO₄. Besides, the EFS dust contains in minute amounts the oxides of Mg, Mn(II), Al, Fe(II), Fe (III), Cu, Sn, Zn, Pb.

In the course of the research the presence of silicate-ions in water medium after adding the EFS dust was confirmed, which proves the possibility of polysilicic acids formation and the adsorption of polluting substances on their surface.

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