The possibility evaluation of zinc sulphate forms extraction from sludge of PJSC EVRAZ NTMK with following metalloflux obtaining

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Abstract. EVRAZ NTMK JSC has significant amount of blast furnace sludges, that accumulated in dumps. Chemical and phase analysis of that sludges was carried out. It has shown significant amount of zinc sulphate, which prevents such sludge utilization in a blast furnace. Moreover, zinc sulphate requires a high temperature unit for recycling by common schemes. The possibility of zinc sulphate conversation into oxidized zinc with simultaneous metallized residue obtaining under the common for Waelz process temperatures was confirmed in laboratory. The obtained during laboratory experiments metallized residue is suitable for using in blast furnace as charge addition. The results of a thermodynamic analysis of the zinc sulphate conversion to oxide and the physicochemical basis for the extraction of such zinc forms are presented. Theoretical calculations and laboratory experiments confirmed that sludges with zinc sulphate could be suitable materials for blast furnace. But, sludges of different processes allow to obtain fired briquettes with different physical properties.

1. Introduction

A significant amount of sludge from the blast furnace shop has been accumulated on the EVRAZ NTMK JSC. Due to the impossibility of processing the open-hearth shop aspiration dust, it was also stored at the plant, despite the fact that the open-hearth production at the plant is closed. The accumulated reserves amount to several million tons. The easiest way to process these sludges is to mix them to raw materials of blast furnace. However, this processing method is not possible, due to zinc containing in these sludges, which leads to the formation of zinc crust in the upper part of the blast furnace. Zinc crust complicate the flow of the blast furnace process and their removal is possible only with overhaul of the blast furnace.

If zinc is removed from the sludge, then it is possible to use it in a blast furnace charge. It is desirable to increase the sludge metallization simultaneously with the zinc removal. However, the zinc removal by traditional methods \cite{1, 2, 3} is difficult, due to zinc in the sludge is in sulfate form.

2. Materials and experimental method

To assess the possibility of removing zinc from the sludge of EVRAZ NTMK JSC, the company provided two samples of sludge: from the blast furnace shop and from the open-hearth furnace dust aspiration system. The chemical analysis is presented in Table 1. Figures 1 and 2 show the phase
analysis of that sludges. Qualitative x-ray phase analysis was carried out on an XRD-7000 diffractometer (Shimadzu).

Table 1. The chemical composition of the provided sludges.

| Sludge                          | CaO  | SiO₂ | Al₂O₃ | MgO  | MnO  | V₂O₅ | Fe₂O₃ | Fe₃O₄ | Zn   | S   | C   |
|--------------------------------|------|------|-------|------|------|------|-------|-------|------|-----|-----|
| Blast furnace shop             | 6.9  | 6.2  | 0.3   | 2.2  | 0.37 | 0.7  | 55.2  |       | 5.1  | 1.1 | 9.8 |
| Open-hearth furnace dust aspiration system | 0.9  | 0.7  | 0.45  | 1.1  | 1.4  | 0.1  | 73.9  |       | 5.5  | 0.4 | 0   |

Figure 1. Phase composition of blast furnace shop sludge.

Figure 2. Phase composition of open-hearth furnace dust aspiration system sludge.
To determine the metallization possibility of the sludge and the removal of zinc according to the developed technology, limestone and coke were mixed with sludges. The raw material mixture was homogenized by co-grinding and pressed. Briquettes were fired according to the proved regime.

3. Thermodynamic calculations and experimental results
According to phase analysis, the sludge is mainly composed of iron oxides. Blast furnace sludge contains carbon in the coke form. Zinc in the sludge is present in complex sulphate form \( \text{ZnO(SO}_4\text{)}_2 \). The extraction of such zinc from sludge is difficult, due to under reducing conditions above 100 °C, sulphate zinc is converted to sulphide zinc by the reaction 1. Reduction of zinc sulphide by carbon is possible by the reaction 2.

\[
\text{ZnO(SO}_4\text{)}_2 + 9\text{C} = \text{ZnS} + 9\text{CO}↑ \quad (1)
\]

\[
2\text{ZnS} + \text{C} = 2\text{Zn}↑ + \text{CS}_2. \quad (2)
\]

The results of thermodynamic calculations indicate that reaction 3 is possible only above 1900 °C. To realize such reaction in practice, the use of special high-temperature units will be required, which is not economically feasible.

To convert zinc from the sulphide form to the oxide form, we proposed adding limestone, magnesite, or dolomite to the raw mix before firing [4, 5]. When using limestone to decompose zinc sulphide and its sublimation, reaction 3 is proceeds.

\[
2\text{ZnS} + 2\text{CaCO}_3 + \text{C} = 2\text{Zn}↑ + 2\text{CaS} + 3\text{CO}_2↑. \quad (3)
\]

The results of thermodynamic calculations indicate that reaction 3 is possible at above 1100 °C.

The composition of the raw mix was adjusted in accordance with the proved methodology and fired. The firing products chemical analysis are shown in table 2.

| Sludge                        | Content, mass. % |
|-------------------------------|------------------|
|                               | CaO  | SiO₂ | Al₂O₃ | MgO  | MnO  | V₂O₅ | Fe₉₇ | Zn   | S    | C    |
| Blast furnace shop            | 19.9 | 20.7 | 4.8   | 5.9  | 0.18 | 0.7  | 50.5 | 0.14 | 2.7  | 0    |
| Open-hearth furnace dust      | 19.3 | 20.3 | 5.4   | 4.2  | 2.6  | 0.3  | 50.9 | 0.78 | 1.1  | 0    |
| aspiration system             |      |      |       |      |      |      |      |      |      |      |

4. Results discussion
According to chemical analysis, the content of silicate materials increased in firing products, while total iron decreased. The zinc content decreased from 5 % to a tenth of a percent. After firing, blast furnace sludge briquettes dispersed, and open-hearth sludge briquettes retain their shape and are well metallized. The phase analysis for the open-hearth sludge briquettes after firing is shown in figure 3.
According to the Figure 3, it can be seen that the firing products contain a significant amount of metallic iron. The degree of metallization was 72%. Zinc in the firing products is absent.

5. Conclusion
The test results indicate that the zinc extraction from the JSC EVRAZ NTMK sludge with subsequent metallization of remains is possible.

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