Study of the characteristics of iron-containing waste from steelmaking and rolling production

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Abstract. A study of the physicochemical characteristics of mill scale and dehydrated sludge from gas purification of oxygen-converter production was made. Their chemical, phase, particle size distribution and density are determined. It was established that the total iron content in the scale is 73.3%, in the sludge – 41.2%. The technological expediency of their use in metallization processes is determined. In this case, preliminary briquetting in a mixture with a carbon reducing agent is necessary.

1. Conclusion

Currently, the following technological options for metallization of various raw materials are known [1-4]:

1) Production of partially metallized materials for blast furnaces.
2) Production of metallized product (sponge iron) in solid form for melting in steelmaking units (temperature 500-1000 °C).
3) Production of metallized product in a plastic state (production of critical iron) for various purposes, including as an option of pyrometallurgical enrichment of refractory, poor and complex ores (temperature 1100-1400 °C).
4) Obtaining of liquid metal (cast iron or intermediate) for remelting in steelmaking furnaces (temperature above 1200-1400 °C).

The main solid-phase metallization processes are Midrex, HyL, Danarex, Finmet, etc. [5-9], and the main liquid-phase iron reduction processes are Corex, Finex, Romelt, Ausmelt, Hismelt, TECHNORED, etc. [2 - 4].

Metallization of fine-grained and powdery oxy-iron-containing wastes is an important area in metallurgy. According to the World Steel Association [10], the production of direct reduction iron over the past 10 years has grown in the world by 18%, in Russia – by 66%, which indicates an extremely dynamic development of this area. Metallization is especially important for mini-factories due to the lack of sinter production in their structure, which allows metallurgical enterprises to process rolling mill scale, sludge from blast furnace and steelmaking and other iron oxide-containing wastes.

The urgency of the problem is due to a significant number of mini-factories in the world – about one thousand [11], and, accordingly, a significant amount of generation of oxy-iron-containing waste. According to forecasts, in 2020 more than 50% of global steel production will be provided by mini-factories. In the territory of the former USSR, 7 mini-factories have already been built: in Russia...
(Komsomolsk-on-Amur, Kaluga, Saratov, Rostov and Tyumen regions), in Belarus (Zhlobin) and in Moldova (Chisinau) [11, 12].

To study the metallization processes of iron-oxide-containing technogenic raw materials, their physicochemical certification is necessary. As an object of study, mill scale and gas treatment sludge from the oxygen-converter shop No. 1 of EVRAZ ZSMK JSC (BOF sludge) were selected. These materials were also studied previously by a number of authors [13–16], but the data presented are either contradictory or insufficiently complete.

2. The purpose of the research
The aim of the present work is to study the physicochemical characteristics of mill scale and dehydrated sludge from a gas purifier of basic oxygen steelmaking (chemical, particle size and phase composition, density) – a promising technogenic oxide-iron-containing raw material for producing metallized briquettes demanded in steel production.

3. General characteristics of materials and methods for their research
Rolling scale is formed as a result of secondary oxidation of the surface layer of the metal when heated before rolling. When heating 1 tonne of steel, approximately 25-30 kg of scale (2.5-3.0%) is formed [8]. According to the World Steel Association [5], up to 50 million tonnes of mill scale are formed annually in the world, and up to 1.5 million tonnes in Russia.

At the construction site of EVRAZ ZSMK JSC, approximately 200 thousand tonnes of mill scale are formed per year. According to [6], on average, 1.0-1.5 million tonnes of rolled steel are produced at one metallurgical mini-plant; therefore, approximately 25-45 thousand tonnes of mill scale are formed. Scale in sinter production is widely used as an iron-containing component of sinter charge.

Sludges from basic oxygen steelmaking are formed during wet gas treatment of converter gases. Sludge refers to rich ($Fe_{tot}=55÷67\%$) or relatively rich iron ($Fe_{tot}=40÷55\%$). With wet gas cleaning, 10-30 kg of sludge is formed per 1 tonne of smelted steel (1-3%) [9]. Consequently, approximately 14.0–38.0 million tonnes of BOF sludge is generated in the world, and 0.5–1.5 million tonnes in Russia. Dehydrated sludge is most widely used in sintering as an iron-containing component of sinter charge. The specific consumption of sludge can reach 200 kg/t of sinter. However, a significant drawback of this technology is the fact that the content of zinc and lead increases in the resulting agglomerate, which is unacceptable due to the significant influence of these impurities on the masonry of blast furnaces.

In this regard, a number of alternative technologies are proposed, such as a scheme for heat treatment of sludge in a rotary furnace, a scheme for treating sludge with spent nitric acid pickling solution at a neutralization station, and a combined two-stage scheme with solid-phase metallization and zinc removal from the sludge and further liquid phase recovery of partially metallized intermediate. But some metallurgical plants, in particular EVRAZ ZSMK JSC, dump some of the sludge into the sludge storage facilities. So, about 2.7 million tonnes of iron in the composition of iron-containing sludge is accumulated in the sludge storage facility of EVRAZ ZSMK JSC.

It should be noted that the gas treatment sludge from different BOFs varies significantly in properties due to the fact that different smelting technologies are used, and there are three technologies for removing and purifying exhaust converter gases:

1) systems working with air suction through the gap between the converter and the boiler-cooler and the complete combustion of carbon monoxide in the latter, i.e. with air flow coefficient $\alpha>1$;

2) systems operating without access of air to the gas path and without afterburning of carbon monoxide, i.e. when $\alpha<0.15$;

3) systems operating with partial afterburning of carbon monoxide in a converter gas cooler, i.e. for $1>\alpha>0$.

When choosing between sludges of BOF-1 and BOF-2, EVRAZ ZSMK JSC settled on sludge BOF-1 due to the higher content of total iron in it. When analyzing the physicochemical properties of
the above materials, the following characteristics were determined: chemical, particle size and phase compositions, as well as density.

The chemical composition was determined according to GOST R 52939-2008. The mass fraction of total iron was determined according to GOST 23581.18-81 (1987 Edition, amendment No. 1 of May 1987), the mass fraction of iron (II) oxide was determined according to GOST 23581.3-79 (1986 edition, amendment No. 1 dated July 1982 and No. 2 dated January 1986), metallic iron – according to GOST 23581.11-79 (1986 edition with amendment No. 1 dated January 1986), arsenic – according to GOST 23581.19-91, phosphorus by GOST 23581.19-91, sulfur by GOST 23581.20-81 (1987 edition as amended by No. 1 of May 1987), copper – in accordance with GOST 23581.6-79 (1986 edition with amendment No. 1 of January 1984 and No. 2 of January 1986).

The particle size distribution was determined according to GOST-27562-87, the phase composition was determined by x-ray analysis. Density determination was carried out according to GOST 26732-88.

4. Results and discussion
The results of determining the chemical composition of mill scale and sludge are shown in table 1. From table 1 it can be seen that mill scale has a higher total iron content (73.3%) than BOF-1 sludge (41.18%). It should be noted that the total iron content in the BOF-2 sludge is about 35%. The following picture is observed in the distribution of iron over oxides: in mill scale, FeO accounts for 75.5%, and Fe₂O₃ – 20.86%; in the sludge, on the contrary, FeO accounts for 4.69%, and Fe₂O₃ – 53.67%.

![Image](https://example.com/image.png)

**Table 1.** The chemical composition of mill scale and sludge.

| Chemical composition, % | Scale   | Sludge  |
|-------------------------|---------|---------|
| Fe₂O₃       | 73.30   | 41.18   |
| FeO         | 75.50   | 4.69    |
| SiO₂        | 2.24    | 1.47    |
| Al₂O₃       | 0.20    | 0.12    |
| CaO         | 0.24    | 20.59   |
| MgO         | 0.24    | 0.36    |
| K₂O         | Not def.| 0.13    |
| Na₂O        | The same| 0.10    |
| TiO₂        | »       | 0.04    |
| Mn          | »       | 0.74    |
| MnO         | 0.66    | Not def.|
| P           | 0.019   | 0.15    |
| Cr₂O₃       | Not def.| 0.016   |
| V₂O₅        | The same| 0.04    |
| S₄O₆        | 0.036   | 0.21    |
| SO₃         | Not def.| 0.07    |
| S₄Sulfide   | The same| 0.18    |
| BaO         | »       | < 0.01  |
| Ni          | »       | 0.012   |
| Cu          | »       | 0.03    |
| Zn          | »       | 0.28    |
| Pb          | »       | 0.09    |
| As          | »       | 0.0025  |
| C₄O        | »       | 4.32    |
| C₄sol      | »       | 0.82    |
| LOI         | »       | 16.57   |

*a* Was not defined
Thus, mill scale is less oxidized than sludge. The low content in mill scale (less than 3%) of iron-free compounds should also be noted. In the sludge, on the contrary, the CaO content reaches 20.59%. In addition, in mill scale, the sulfur and phosphorus contents are 0.036% and 0.019%, respectively, against 0.21% and 0.15% in sludge. However, the slurry contains elements and compounds that are alloying in the production of steel. These are compounds of manganese, nickel, vanadium, chromium. The sludge also contains up to 4.32% of total carbon, including up to 0.82% of solid carbon. Thus, both mill scale and sludge are of interest as oxide-iron raw materials for the metallization process.

The study results of the particle size distribution of scale and sludge are shown in table 2. From table 2 it is seen that the sludge is a finer dispersed material than mill scale.

The predominant mineral of sludge is magnetite. Hematite, wustite, calcite, feldspar are also present. The data obtained are in good agreement with the data of chemical analysis. The true density of mill scale was from 4.6 to 4.9 g/cm³, converter sludge from 3.5 to 5.0 g/cm³. Thus, the density of mill scale and sludge CCC is comparable.

The analysis of the properties of the specified oxide-iron raw materials allows the feasibility of its use in the metallization process to be concluded. Moreover, the use of mill scale is more preferable due to the higher content of total iron in it.

Table 2. Granulometric composition of mill scale and sludge.

| Size class content, % | Scale | Sludge |
|-----------------------|-------|--------|
| > 2.5 mm              | 24.7  | 7.4    |
| 1.6-2.5 mm            | 18.3  | 3.6    |
| 1.0-1.6 mm            | 20.3  | 3.8    |
| 0.63-1.0 mm           | 6.1   | 5.6    |
| 0.315-0.63 mm         | 12.3  | 8.5    |
| 0.16-0.315 mm         | 11.5  | 6.9    |
| 0.10-0.16 mm          | 3.7   | 4.0    |
| 0.063-0.10 mm         | 1.5   | 4.8    |
| 0.05-0.063 mm         | 1.4   | 1.9    |
| 0.032-0.05 mm         | 0.2   | 9.0    |
| 0.016-0.032 mm        | –     | 22.3   |
| 0.008-0.016 mm        | –     | 10.3   |
| < 0.008 mm            | –     | 11.9   |
| Total                 | 100.0 | 100.0  |

5. Conclusion
The chemical, phase, granulometric compositions and density of mill scale and dehydrated sludge for gas treatment of BOF No. 1 of EVRAZ ZSMK JSC were investigated. The total iron content in the scale is 73.3%, in the sludge – 41.2%. The content of FeO and Fe₂O₃ in the scale is 75.5% and 20.9%, in the sludge 4.7% and 53.7%. It was established that sulfur and phosphorus content is lower in the scale – 0.036% and 0.019%, respectively, against 0.21% and 0.15% in the sludge. Sludge also contains 20.6% CaO, 4.3% of total carbon. The granulometric compositions of scale and sludge are significantly different: the content of the particle size of classes +1.0 mm and -0.016 mm in the scale is 63.3% and 0%, in the sludge – 14.8% and 44.5%. The true density of the scale is 4.6 - 4.9 g/cm³, sludge – 3.5 -5.0 g/cm³. The obtained results confirm the technological feasibility of using fine-grained scale and powdery sludge in metallization processes, including their preliminary briquetting in a mixture with a carbon reducing agent, for example, brown coal semi-coke, supplied in the form of a fine-grained product of class 0 – 3 mm.

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