Analysis of Steel Slag Composition and Properties to Facilitate the Search for Rational Slag Recycling Methods

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Abstract. This paper is devoted to the challenging problem of steel slag recycling. This study considers the composition and properties of steel slag, namely, slag of electric and pneumatic steelmaking. Slag of the pneumatic and electric steelmaking was found to be composed of calcium silicate Ca$_2$SiO$_4$, while phosphorus is represented by a complex calcium silicophosphate. Iron is in oxidized forms of FeO, Fe$_2$O$_3$ and Fe$_3$O$_4$ with the following ratios to the total mass of iron oxides, %: 51.51:37.16:11.33 for pneumatic steelmaking slag, and 75.92:20.90:3.18 for electric steelmaking slag, respectively. Chemical composition study showed the following content of the main elements for electric steelmaking slag, mass %: 31.6–33.2 Fe; 0.330–0.383 P; 19.15–19.2 Ca; 4.62–5.39 Si; for pneumatic steelmaking slag, mass %: 18.7–20.5 Fe; 0.630–0.710 P; 27.8–28.0 Ca; 4.73–5.04 Si. Electron microprobe analysis of slag samples showed the presence of Fe, C, O, P, Ca, Si, Mn, Ti, Cr, and Mg heterogeneously distributed over the sample crosscut surface. Samples had low content of phosphorus, however, this element was found to be accumulated in clusters together with Si and Ca.

1. Introduction

Ferrous metallurgy enterprises generate a significant amount of iron-containing waste [1–8], e.g., several thousand tons per month, which is unsuitable for reuse due to impurities, which significantly reduces the technical and economic performance of the metallurgical processing. The development of steelmaking is directly linked to innovative technologies for recycling secondary resources and industrial waste. Efficient recycling of non-reclaimable waste and intermediate products will increase the competitiveness and environmental safety of the production.

Due to both internal and external reasons, one of the main strategic goals of the ferrous metallurgy development in the Russian Federation for 2014–2020 and in the long term until 2030 is resource and energy saving, as well as reduction of negative environmental impact [9]. Therefore, recently, increasing attention is paid to research related to ferrous slag waste recycling technologies development.

Nowadays, up to 190 kg/t and 280 kg/t of slag is created in the pneumatic and electric steelmaking processes, respectively [1, 9]. The resulting solid and liquid slag is reused in steelmaking process to purify metal of unfavourable impurities (desulfurization and dephosphorization), to partially replace certain materials (e.g., lime and limestone, fluor spar), to increase the product yield via aluminothermic reduction processes of metal from oxides, as well as to reduce the metal product rejection rate. Also, the resulting slag is used in other industries: in
general construction [10–18], road construction [14, 17, 19], railway construction, and agriculture [10]. Fine slag fractions are used as adsorbents. Slag is also recycled in blast furnaces to extract additional metal [20]. Blast furnace slag is used as backfill mixture in mines. However, high volumes of waste can not be recycled in full yet.

One of the main constraints on the reuse of slag from electric and pneumatic steelmaking processes for metal purification is phosphorus accumulation in the slag, which, if reused, returns back to the metal, thereby polluting the final product. Therefore, phosphorus shall be extracted into a separate product to enable slag to be used to purify metal from unfavourable impurities (desulfurization and dephosphorylation). However, rational technology can be selected only after the preliminary study of slag’s chemical composition allowing to determine the phase and elemental composition.

2. Study of the chemical composition of the research subject

The subject under research were samples of slag from electric and pneumatic steelmaking – dark grey agglomerates of various sizes up to 300–400 mm. Slag samples contain clusters of metallic iron, which is most specific for electric steelmaking samples.

To study the elemental and phase composition, slag samples were preliminarily crushed to obtain a particle size of 3 mm. To assess the particle size distribution in samples, particle sizes were determined by a sieve method and laser diffraction measurement using the Analysette 22 NanoTec plus particle size analyzer (Fritsch, Germany).

The phase composition of samples was determined by X-ray diffraction analysis (XRD) using the XRD-7000 X-ray diffractometer (Shimadzu, Japan) with a vertical θ–θ goniometer. Metallic iron was removed from the samples prior to analysis. Filming was performed in a step mode for 2θ angle range from 3 to 80° using Cu-α radiation. The experimental conditions for the analysis were as follows: 40 kV, 50 mA, exposure – 6 s, step size – 0.05º 2θ. X-ray diffraction patterns were calculated using diffractometer software. PDF-2 powder diffractogram base was used to identify the phases. The analysis results are presented in Table 1.

Table 1. Qualitative and quantitative composition of samples (XRD data).

| Slag sample                | Content, mass % |
|----------------------------|-----------------|
|                            | Ca₂SiO₄ | FeO | Ca₂(SiO₄)₆(Ca₃PO₄)₂ | Fe₂O₃ | Fe₃O₄ | Total |
| Pneumatic steelmaking      | 53.58     | 11.77 | 23.57              | 8.49  | 2.59  | 100   |
| Electric steelmaking       | 45.52     | 28.63 | 16.77              | 7.88  | 1.20  | 100   |

XRD results for an average sample show that slag samples from pneumatic and electric steelmaking processes consist ~50% of calcium silicate Ca₂SiO₄, while phosphorus is represented by a complex calcium silicophosphate. Iron is in oxidized forms of FeO, Fe₂O₃ and Fe₃O₄ with the following ratios to the total mass of iron oxides, %: 51.51:37.16:11.33 for pneumatic steelmaking slag, and 75.92:20.90:3.18 for electric steelmaking slag, respectively.

To study the elemental composition of slag samples, chemical analysis was performed using atomic absorption spectrometry (AAS) and optical emission spectrometry (OES) utilizing the VARIAN AA 240, VARIAN AA 240 FS, and VARIAN 730-ES spectrometers, as well as methods of x-ray fluorescence spectrometry (XRD) and inductively coupled plasma optical emission spectrometry (ICP-AES) (Table 2).

Spectrometry showed that the samples contain up to 34% iron and 30% calcium. The average phosphorus content was 0.35% in electric steelmaking slag and 0.63% in pneumatic steelmaking slag.

After particle size analysis, the content of basic elements was also determined for slag samples. Element distribution is shown in the diagram (Figure 1), which shows that the content of phosphorus and other elements varies slightly for different particle sizes.
Table 2. Chemical composition of steel slag.

| Element                  | Content, mass % |
|--------------------------|-----------------|
|                          | Fe  | Ca   | P    | Si  | Mn  | Mg  | Al  | Ti  | Cr  | Cu  | Other |
| Electric steelmaking slag| AAS and OES | 33.2 | 19.15 | 0.33 | 5.39 | 4.68 | 2.11 | 1.68 | 0.38 | 0.8 | 0.0125 | 0.1093 |
|                          | XRD and ICP-AES | 31.6 | 19.2 | 0.383 | 4.62 | n/a* | n/a | n/a | n/a | n/a | n/a |
| Pneumatic steelmaking slag| AAS and OES | 20.5 | 27.8 | 0.63 | 4.73 | 5.29 | 1.26 | 0.61 | 0.32 | 0.0028 | 0.06 |
|                          | XRD and ICP-AES | 18.7 | 28.0 | 0.71 | 5.04 | n/a | n/a | n/a | n/a | n/a | n/a |

Figure 1. Element content depending on size electric steelmaking (a) and pneumatic steelmaking (b) slag.

3. Slag microstructural analysis

To study the structure of electric and pneumatic steelmaking slag samples, samples were prepared for electron microprobe analysis (EMPA) by sputtering a thin gold film (of nanometer thickness) on their surface with accelerated gold ions in an Ar medium to create a conductive layer. The film was sputtered using SPI Module Sputter/Carbon Coater (Structure Probe Inc., USA). The prepared samples were analysed using JIB-Z4500 scanning electron microscope (JEOL, Japan).

Fe, C, O, P, Ca, Si, Mn, Ti, Cr, and Mg were found in the studied sample of electric steelmaking slag and were heterogeneously distributed over the crosscut surface of the sample (Figure 2a, Table 3). Region 4 corresponds to carbidizable metallic iron (84.89% Fe, 15.11% C). X-ray diffraction results show that iron oxide, mainly FeO, is concentrated in the region 5 (38.29% Fe, 40.09% O), which also contains insignificant amounts of Mn, Mg, Ca, Cr, and C. Region 6 is mainly composed of carbon (62.61%) and a smaller amount of iron oxide. Region 7 is represented mainly by calcium and silicon oxides, and to a lesser extent by phosphates of these elements, which also confirms the XRD results.

EMPA results of pneumatic steelmaking slag element distribution (Figure 2b, Table 4) show that the material has almost the same elemental composition as the electric steelmaking slag. Five microstructure regions (spectrums) of the sample were investigated. Region 2 is mainly represented by calcium and silicon oxides, and also most likely by phosphates of these elements (mainly calcium phosphate). Region 3 corresponds to carbidizable metallic iron (79.81% Fe, 20.19% C). Iron oxide is concentrated in region 4. This region has an increased content of magnesium (11.66%), as well as a small amount of Mn, Ca and C. Region 5 has a heterogeneous composition, mainly represented by calcium oxide (17.40% Ca) and a smaller amount of Fe, Al, C, Ti, Cr, and Mg. Region 6 has a carbon inclusion.
Figure 2. EMPA results for the electric steelmaking (a) and pneumatic steelmaking (b) slag samples by regions.

Table 3. EMPA results for the electric steelmaking slag sample by regions.

| Region | Content, mass % | C   | O   | Mg  | Al  | Si  | P   | Ca  | Ti  | Cr  | Mn  | Fe  | Total |
|--------|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------|
| Region 4 |                 | 15.11 |     |     |     |     |     |     |     |     |     |     | 84.89 |
| Region 5 |                 | 7.99 | 40.09 | 3.18 |     |     |     |     |     |     |     |     | 38.29 |
| Region 6 |                 | 62.61 | 18.44 | 0.83 | 0.16 |     |     |     |     |     |     |     | 13.74 |
| Region 7 |                 | 7.82 |     |     |     |     |     |     |     |     |     |     | 94.89 |
| Total   |                 | 12.52 | 40.13 | 1.03 | 1.62 | 2.41 | 0.14 | 7.11 | 0.18 | 0.56 | 2.98 | 31.32 | 100   |
| Max     |                 | 62.61 | 49.33 | 3.18 | 1.62 | 12.01 | 1.67 | 29.22 | 0.18 | 1.05 | 7.90 | 84.89 | 100   |
| Min     |                 | 7.82 | 18.44 | 0.24 | 0.16 | 2.41 | 0.14 | 0.59 | 0.18 | 0.55 | 0.43 | 0.94 | 100   |

Table 4. EMPA results for the pneumatic steelmaking slag sample by regions.

| Region | Content, mass % | C   | O   | Mg  | Al  | Si  | P   | Ca  | Ti  | V   | Cr  | Mn  | Fe  | Total |
|--------|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------|
| Region 2 |                 | 16.6 | 43.74 | 0.86 | 8.57 | 1.27 | 27.80 | 0.18 | 0.58 |     | 0.85 |     | 100   |
| Region 3 |                 | 20.19 |     |     |     |     |     |     |     |     |     |     |     | 79.81 |
| Region 4 |                 | 12.04 | 38.57 | 11.66 |     |     |     |     |     |     |     |     |     | 29.50 |
| Region 5 |                 | 13.25 | 50.41 | 0.71 | 5.37 | 0.34 | 17.40 | 2.039 | 0.44 | 1.55 | 0.42 |     | 7.73 |
| Region 6 |                 | 46.39 | 44.49 | 0.17 | 1.99 |     |     |     |     |     |     |     | 0.82 | 100   |
| Total   |                 | 19.13 | 38.61 | 2.01 | 5.13 | 0.52 | 16.57 | 0.34 | 0.19 | 1.38 |     | 15.08 | 100   |
| Max     |                 | 46.39 | 50.41 | 11.66 | 5.37 | 8.57 | 1.27 | 27.80 | 2.39 | 0.58 | 1.55 | 6.13 | 79.81 | 100   |
| Min     |                 | 12.04 | 38.57 | 0.71 | 0.17 | 0.34 | 0.52 | 2.09 | 0.18 | 0.44 | 0.19 | 0.42 | 0.82 | 100   |

The sample surface microstructure of electric and pneumatic steelmaking slag was also studied using Olympus GX-51 inverted metallurgical microscope (Japan). Electric and pneumatic steelmaking slag surface microstructure has a heterogeneous composition. Thus, electric steelmaking slag samples have a finer-grained structure (Figure 3a) in comparison with the microstructure of the pneumatic steelmaking
slag (Figure 3b), which has needle-shaped grains. Presumably, bright regions of the samples have mainly iron oxide (FeO, Fe₂O₃, Fe₃O₄) and insignificant amounts of Mn, Mg, Cr, which is also confirmed by XRD and EMPA results. Dark regions have high calcium silicate content and a lesser amount of calcium silicophosphate. Also, samples have pores and metallic iron inclusions.

Figure 3. Slag surface microstructure (50x magnification): a – electric steelmaking; b – pneumatic steelmaking.

4. Conclusions

Phosphorus content has negative effects on steel, and reducing its content is an important task. Phosphorus comes into furnaces with minerals of agglomerate and ore rock, and also with fluxes. The main component for binding phosphorus transferring it into slag is lime. To prevent phosphorus reduction from slag to metal (repeated phosphorization), the necessary slag alkalinity and oxidation shall be maintained. The following optimal ratios shall be considered for the slag: (CaO)/(SiO₂) = 2.8÷3.1 and (CaO)/(FeO) = 4.5÷5.

Phase composition study of the samples by X-ray diffraction spectrometry showed that electric and pneumatic steelmaking slag is composed 50% of calcium silicate Ca₂SiO₄, while phosphorus is represented by a complex calcium silicophosphate. Iron is in oxidized forms of FeO, Fe₂O₃ and Fe₃O₄ with the following ratios to the total mass of iron oxides, %: 51.51:37.16:11.33 for pneumatic steelmaking slag, and 75.92:20.90:3.18 for electric steelmaking slag, respectively. Chemical composition study using atomic absorption spectrometry, optical emission spectrometry, X-ray fluorescence spectrometry, as well as inductively coupled plasma optical emission spectrometry showed the following content of the main elements for electric steelmaking slag, mass %: 31.6–33.2 Fe; 0.330–0.383 P; 19.15–19.2 Ca; 4.62–5.39 Si; for pneumatic steelmaking slag, mass %: 18.7–20.5 Fe; 0.630–0.710 P; 27.8–28.0 Ca; 4.73–5.04 Si.

EMPA and microscopic metallography results for showed the presence of Fe, C, O, P, Ca, Si, Mn, Ti, Cr, and Mg heterogeneously distributed over the sample crosscut surface. The samples have regions with metallic iron and its oxide. In addition to iron oxide, magnesium and manganese are also detected in this region. Samples had low content of phosphorus, however, this element was found to be accumulated in clusters together with Si and Ca. Also, inclusions of elemental carbon and small amounts of Al, Cr, V, and Ti were detected in the studied samples. Electric steelmaking slag samples have a finer-grained structure in comparison with the microstructure of the pneumatic steelmaking slag, which has needle-shaped grains.

To reincorporate slag into metal purification (desulfurization and dephosphorization), the phosphorus content in the slag shall be reduced. Based on the concluded research, technological
solutions for the extraction of fluorine using physical, pyro- and hydrometallurgical methods shall be considered.

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