

WET MAGNETIC SEPARATION OF IRON FROM FINE-GRAINED STEELMAKING SLAGS

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<https://doi.org/10.37904/metal.2022.4448>

Abstract

Large volumes of slags are formed as by-products during the refinement of pig iron and steel manufacturing. Generally, the steel slag (steel furnace and ladle furnace slags) contains an appreciable amount of magnetic substances such as metallic iron and magnetic iron oxide, and thus, they can be recycled by wet magnetic separation. This work presented here investigates the effect of fine grinding for maximum recovery of iron from the steel furnace slags. Three kinds of slags, namely furnace steel slag (FS) containing 30 wt. % of Fe₂O₃, ladle slag (LS) containing approx. 16 wt. % and slag from desulfurization process (DeS) containing approx. 35 wt. % of Fe₂O₃, were crushed, grounded and sieved under 0.045 mm for wet magnetic separation experiments. Results showed that the proposed magnetic separation process allowed to isolate 24, 18 and 42 wt. % of magnetic fractions for FS, LS and DeS, respectively. The content of Fe₂O₃ in magnetic fractions increased from 30 to 48 wt. %, from 16 to 46 wt. %, and from 35 to 44 wt. % of Fe₂O₃ in the case of the FS, LS and DeS, respectively. The fractions obtained by wet magnetic separation process were subjected to the chemical and phase analysis, the morphology of the particles was studied using scanning electron microscopy.

Keywords: Metallurgical slags, wet magnetic separation, iron recovery, Fine-grained slags

1. INTRODUCTION

During the steel making process the furnace steel (FS) and ladle steel (LS) slags originate as by-products. Contrary to blast furnace slags (BFS), to find the application of the steel slags is more difficult mainly due to higher variability of the chemical and thus also phase composition of these slags. In general, steel slags include some valuable elements such as iron, silica, phosphorous and calcium, however can contain also the elements which are harmful to living environment, such as copper, zinc, lead, chromium, and cadmium. For this reason, the steel slag, especially LS, is often considered as solid waste emitted from the steel making process. FS slags include the slags from electric furnace, converter, and open-hearth furnace [1]. These by-products cause large volumes of waste streams. As a result, steelmaking slags are either being disposed of at landfills or being stored on the ground in large quantities, not only adding a considerably heavy financial burden to steelmaking plants, but also causing enormous losses of potentially valuable resources and causing potential environmental liabilities [2].

The recycling of steel slag not only protects the environment, but also promotes utilization ratio of resources. Hence, effective recycling of iron from steel slag, would not only alleviate environment pressures and improve economic efficiency, but would also reduce the industrial demand for iron ore [3]. The technique used for efficient recycling of iron mainly include dry magnetic separation of bulk slag, wet stage grinding and magnetic separation, wet magnetic separation for full grain level, fine-grained level flotation, and gravity separation.

Usually, the wet magnetic separation method is used to separate the metallic iron particles from the slag powder [4].

The magnetic process, in principle, separates the magnetic part (mostly metallic material connected with other non-magnetic impurities) from the slag mixture. The total amount of metallic part associated with the slags is around 3 – 8 % of the weight of the slag depending on the used production process [5]. The crushing and grinding efficiency and strength of the magnetic field that is employed in the process determines the amount of slag being carried along with the metal [6]. Development of technology for efficient recycling of iron resources from fine-grained steel is, therefore, of utmost importance [7].

In this work we studied the wet magnetic separation on a very fine FS, LS and DeS slag fraction (<0.045 mm). The chemical composition of the obtained magnetic and non-magnetic fractions was characterized using X-ray fluorescence spectroscopy, phase composition was studied using X-ray diffraction method. Scanning electron microscopy was used for the observation of the particles morphology.

2. MATERIALS AND METHODS

2.1. Studied materials

Three slags, FS, LS and DeS originated during steel making processes were studied and their chemical composition is shown in **Table 1**. Calcium oxide is the dominant component of FS and LS and iron oxide, sulphur trioxide in case of DeS slag as evident from **Table 1**. All three FS, LS as well as DeS consist of significant amount of iron, in **Table 1** expressed as Fe_2O_3 .

Table 1 Chemical compositions of original slags (wt. %)

Samples	Components						
	MgO	Al ₂ O ₃	SiO ₂	CaO	SO ₃	MnO	Fe ₂ O ₃
FS	3.36	1.65	10.00	47.98	0.16	4.38	30.17
LS	3.57	6.15	10.03	47.18	1.40	2.55	15.70
DeS	11.40	2.15	10.21	13.67	24.13	2.19	34.89

In order to liberate the metallic iron from the slags, each of the received slag was stepwise crushed by a jaw crusher (Brio s.r.o., Czech Republic) followed by the vibration milling (Testchem, Poland). A jaw crusher with a feeding size smaller than 80 mm and discharging size smaller than 15 mm was employed in the primary crushing of both slags in order to adjust the particle size of slags prior the milling with vibration mill. The vibration mill with a feeding size smaller than 5 mm and discharging size of >0.020 mm, was employed in the further crushing. The mild slags were then classified by a sieve with aperture size 45 µm.

2.2. Wet magnetic separation experiments

Experiments were carried out using a glass beaker on which a belt with neodymium magnets was placed on the outside wall. Typically, about 5 g of the slag was put into the glass beaker and mixed with 300 mL of water. The obtained suspension was then stirred 5 min using mechanical overhead stirrer (Heidolph Model RZR 2041) operated at 250 RPM in order to homogenise the suspension. A belt of neodymium magnets was then placed on the outer wall of the glass vessel and the suspension was next stirred for 10 minutes. During this process, most of the strong magnetic particles presented in slag adhered to the glass wall, and the nonmagnetic materials fell to the bottom part of the beaker. Subsequently, the non-magnetic fraction was separated by the filtration. Finally, after removing of the magnets, the magnetic fraction fell to the bottom of the beaker and small amount of the water was added. After that, the magnetic fraction was separated by filtration. Both, magnetic and non-magnetic fractions were dried at 70 °C and weighed.

2.3. Characterization of the slags

Chemical composition of the original slags and individual fraction of the slags obtained during magnetic separation was performed on wave dispersive X-ray fluorescence spectrometer Supermini 200 (Rigaku, Japan) equipped with Pd tube (200W) and scintillation counter and F-PC detector.

Phase composition of the samples was studied using Theta/2Theta X-ray diffractometer MiniFlex600 (Rigaku, Japan) equipped with Co tube (600W) and D/teX Ultra detector. Samples pressed in rotational holders were analysed in reflection mode.

Scanning electron microscope Aspex Explorer (ThermoFisher Scientific, USA) equipped with thermionic emission source CeB₆, secondary electron and back scattered electron detector was used for the characterization of the slag particles. Energy dispersive detector was used for local chemical analysis.

3. RESULTS AND DISCUSSION

The yield of the magnetic fractions obtained by wet procedure for FS, LS and DeS slags is shown in **Table 2**.

Table 2 Yield of magnetic fractions for wet separation procedure

Samples	Magnetic fraction (wt. %)
FS	24
LS	18
DeS	42

The magnetic separation procedure divides the slags matter into two fractions: magnetic (M) and non-magnetic (NM). Wet magnetic separation procedure made it possible to obtain magnetic fraction yields for FS, LS and DeS to 24, 18 and 42 wt. %, respectively (**Table 2**). These results indicate the efficiency of the wet separation of magnetic fractions to reduce the total volume of FS, LS and DeS slags. Subsequently, for both M and NM fractions, the chemical and phase analysis was performed. The chemical composition of the magnetic (M) and non-magnetic (NM) fractions for both slags is shown in **Table 3**.

Table 3 Chemical compositions of magnetic (M) and non-magnetic (NM) part for wet magnetic separation (wt. %)

Samples	Fraction	Components						
		MgO	Al ₂ O ₃	SiO ₂	CaO	SO ₃	MnO	Fe ₂ O ₃
FS	M	4.2	0.97	5.58	32.3	0.13	7.24	47.7
	NM	3.46	1.51	9.53	46.56	0.26	4.10	27.50
LS	M	6.62	3.21	6.88	29.43	0.53	6.60	45.57
	NM	4.20	6.83	12.25	51.58	1.13	2.21	12.12
DeS	M	11.20	2.00	9.68	6.59	21.99	2.90	44.19
	NM	13.17	2.38	11.28	9.46	26.82	2.66	25.32

Comparing the data in **Table 3** with the chemical composition of the original slags (**Table 2**) the enrichment of the magnetic fraction by Fe₂O₃ to approximately 48 wt. % in the case of FS slag, for LS and DeS slags to approximately 45 wt. %, was achieved. The presence of Fe₂O₃ in non-magnetic fractions of all three slags signalize there is still reasonable amount of iron containing phases which should be separated.

Comparison of the phase composition for samples FS, LS and DeS is shown in **Figures 1a)-c)**. The phases relevant to separation of iron and non-stable phases are indicated in these images.

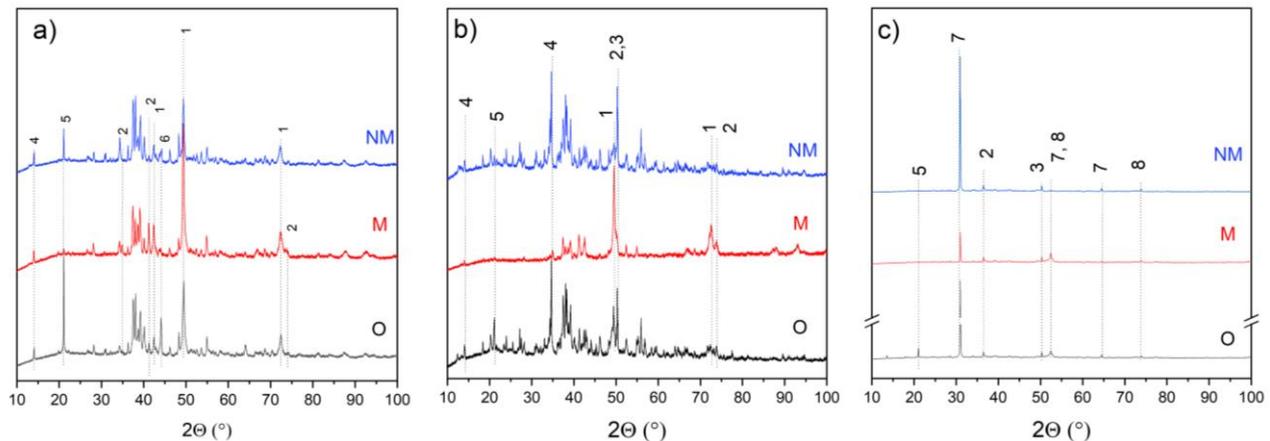


Figure 1 XRD patterns of samples FS (a), LS (b) and DeS (c). (1 ... FeO, 2 ... Fe₃O₄, 3 ... MgO, 4 ... Ca₂Fe₂O₅, 5 ... Ca₁₂Al₁₄O₃₃, 6 ... CaO, 7 ... graphite, 8 ... α-Fe)

The diffraction patterns of the samples FS (**Figure 1a**) and LS (**Figure 1b**) show the typical composition of these kind of the slags. Besides the identified phases, these slags contain also dicalcium silicate – calcio-olivine and larnite, and manganese magnesium oxide. The enrichment of these slags with iron oxides is clearly visible. Magnetic fraction (M) of slag FS and LS was significantly enriched with FeO and Fe₃O₄. On the other hand, the M fraction of both FS and LS was visibly depleted with Ca₁₂Al₁₄O₃₃, and the intensity of the diffraction lines of this phase was also decreased in the case of NM fraction what indicates this phase as a water soluble. Other iron rich phase present in original FS and LS slags was identified as Ca₂Fe₂O₅ and the (**Figure 1a**) revealed homogenous distribution of this phase between M and NM fractions, in the case of LS sample the diffraction lines intensities of this phase was decreased in the case of M fraction. The comparison of the phase composition of M and NM fractions of sample DeS indicate the alpha iron as the phase which enriched the M fraction due to the magnetic separation process.

The example of SEM images of the original, M and NM fractions of FS sample is shown in **Figure 2**. Comparing the images, the differences in morphology of the particles of the original FS milled below 45 μm (O) and the individual fractions (M, and NM) are visible. The prevailing part of the particles of M fraction (**Figure 2b**) appears as bigger, while the portion of finer particles is significantly higher in the case of NM fraction.

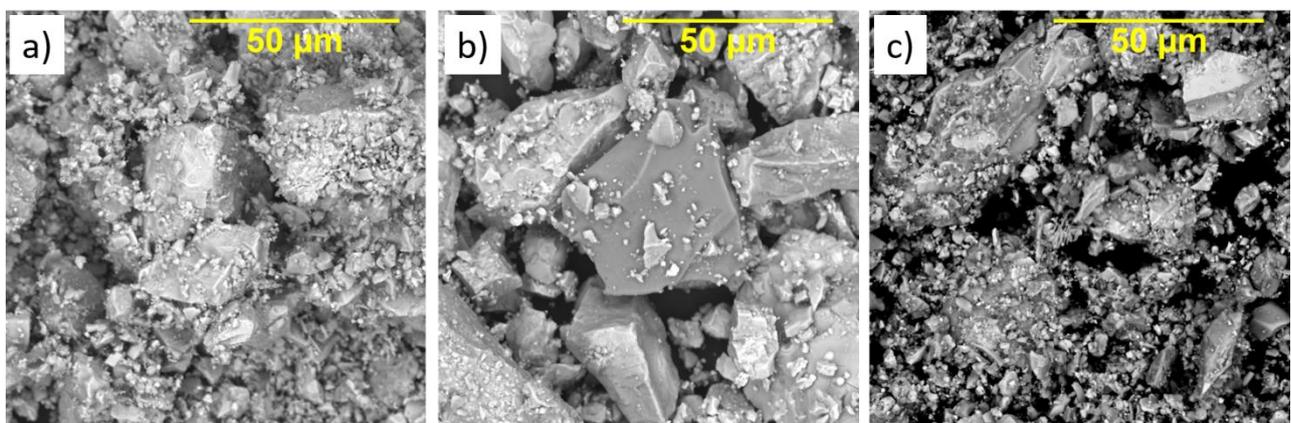


Figure 2 SEM image of samples O (a), M (b) and NM (c)

The complex character of the particles in magnetic fraction is documented in **Figure 3**. The white areas of the particle represent iron based oxides encapsulated in a matrix presented by calcium rich phase.

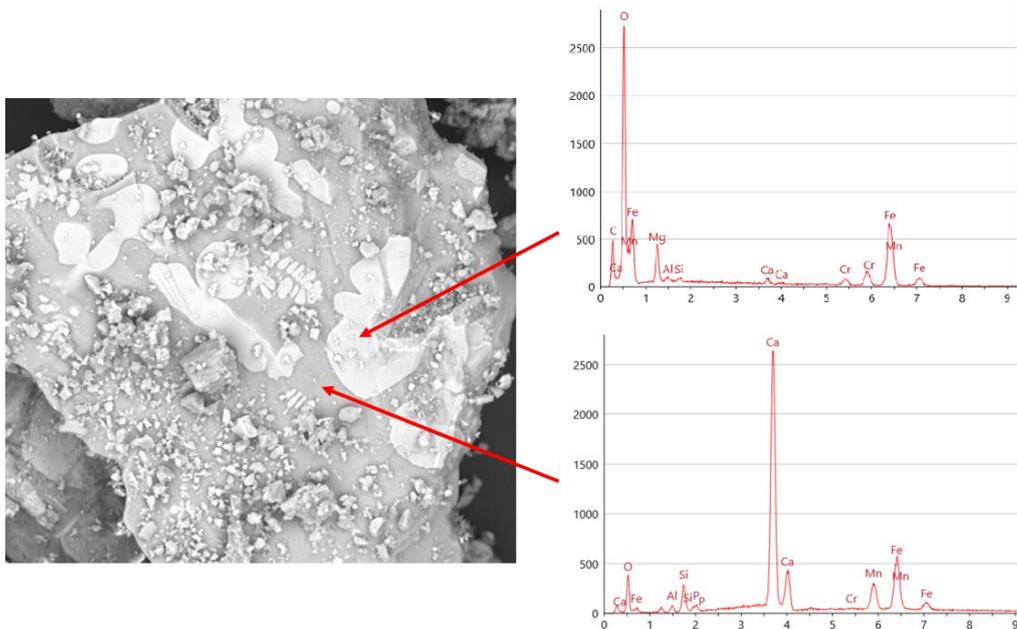


Figure 3 Detail of the selected particle in M fraction

4. CONCLUSIONS

The wet separation technique was used for the isolation of the magnetic fraction presented in very fine fractions of FS, LS and DeS slags. In the light of the results presented above, it could be concluded that very fine slag grinding and the use of wet separation led to the isolation of 24, 18 and 42 wt. % of magnetic fractions for FS, LS and DeS, respectively.

These magnetic fractions were enriched by 17, 30 and 10 wt. % of Fe_2O_3 for FS, LS and DeS samples if compared with the Fe_2O_3 content analysed in pristine FS, LS and DeS samples. The observation of the particles presented in magnetic fraction with SEM revealed the fact, that small particles of iron-bearing phases are firmly encapsulated in the complex matrix, most probably represented by calcium phase. This observation highlights the necessity for the searching of the separation technique, which enables to liberate the particles of these small iron containing phases.

ACKNOWLEDGEMENT

This work was supported by projects "Research on the management of waste, materials and other products of metallurgy and related sectors" (CZ.02.1.01/0.0/0.0/17_049/0008426).

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