

Study of Siderurgy Slags for the Reuse of Iron Oxides for Biotechnology Application [†]

Diogo T. Moreira ¹, Arno H. Oliveira ¹ and Adriana S. M. Batista ^{2,*}

¹ Departamento de Engenharia Nuclear, Universidade Federal de Minas Gerais, Belo Horizonte 31270-901, Brazil; teixeira.diogo100@gmail.com (D.T.M.); heeren@nuclear.ufmg.br (A.H.O.)

² Departamento de Anatomia e Imagem, Universidade Federal de Minas Gerais, Belo Horizonte 30130-100, Brazil

* Correspondence: adriananuclear@yahoo.com.br; Tel.: +55-031-3165-6779

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Abstract: The reuse of slag for the extraction of iron oxides, besides allowing the use of potentially polluting material, allows its strategic use in biotechnological applications. For this it is necessary a characterization of the slag as the proportion of iron oxides to study the feasibility of extraction and reuse. For this work siderurgy slag was collected in the steel mill slag yards, as a remnant of the transformation of pig iron into steel and study for identify the presence of magnetite in the samples. Results were discussed in the context of reuse possibility in biotechnological application, for example, in implants of the magnetic materials. The siderurgy slag studied presents iron oxides in a proportion that encourages future work of extraction for use in the composition of magnetic materials for biotechnological applications.

Keywords: siderurgy slag; Fe₃O₄; re-utilization

1. Introduction

Siderurgy slags are now considered as a by-product of the iron and steel industries, due to its constituents. Throughout the world, studies have been developed with the objective of concentrating value materials present in the slag, by gravimetric or pyrometallurgical processes, for example [1]. During the production of steel, 2–4 t of wastes are being generated per tonne of steel produced in the form of slags and sludges that are emerged from steel plants are blast furnace slag, blast furnace flue dust, etc. It is desirable to recover the valuables and utilize these wastes, but detailed scientific investigation is necessary for the proposed utilizations are being carefully evaluated [2]. One the past 100 years, slag has been used for many industrial purposes, especially as raw material in cement production, landfill cover material, and the numerous construction and agricultural applications [3]. These applications mainly involve their mineral composition, but some slag contains a notable amount of heavy metals and release of them to earth may cause some environmental problems [2]. On the other hand, iron oxides may be of interest for biotechnological applications, not only for show interesting size-dependent magnetic properties and can be functionalized with both organic and inorganic compounds, but also they are thought to be biocompatible and non-toxic, which makes them excellent candidates for biomedical applications and in-vivo experiments [4].

In recent years, novel size-dependent physicochemical properties have led to metallic iron nanoparticles of great potential in a wide range of applications, including storage media, ferrofluids, biosensors, catalysts, separation process, and environmental remediation [5]. Specially, magnetite is a common magnetic iron oxide having a cubic inverse spinel structure. The compound exhibits

unique electric and magnetic properties based upon the transfer of electrons between Fe^{2+} and Fe^{3+} in octahedral sites [4]. Whereas other heavy metals have been extracted from slag quite efficiently as the extraction of vanadium and titanium [6], in this work it is evaluated the possibility of iron ore slag magnetite extraction, of samples collected in the slag yard of a siderurgy located in the Ferriferous Quadrilateral of Minas Gerais, Brazil. A small proportion of magnetite as a constituent of the slag would already be encouraging, as biotech applications involve a small amount of material for use in vivo, in cancer treatments by magnetic resonance induced hyperthermia, for example, or as drug carriers, among others. In this case the magnetic separation process would be an attractive way of extracting of Fe_3O_4 , associated to a later characterization process for differentiation of other metallic materials extracted by this same technique.

2. Materials and Methods

The test has been conducted on steel slag created during the product of Oxygen Furnace Process (BOF) by Linz-Donawitz (LD) process in the siderurgy localized in Ferriferous Quadrilateral of Minas Gerais, southeastern Brazil. Five samples were collected in the steel mill slag yards, as a remnant of the transformation of pig iron into steel. The material was prepared for granulometric reduction with 0.210 mm sieve opening using a sieve Granutest® and a sixth sample was prepared by mixing the others. Scanning Electron Microscope (SEM) and energy dispersive x-ray spectrometer (EDS) was performed at a SIGMA VP field emission scanning electron microscope ZEISS. For XRD diffractogram of the samples, we used the diffractometer Rigaku, model and system D/MAX ULTIMA automatic, with theta-theta goniometer (θ - θ) and $2\theta/\theta$ scan with 2θ detector and copper anode, with X-ray energy beams of 8.04 keV. Samples were being homogenously dispersed with KBr powder for prepared of the disks for Fourier Transform Infrared Spectroscopy (FTIR). FTIR analyses was performed with a BOMEM spectrometer, each collected with 32 scans each, for wavenumbers ranging from 300 to 4000 cm^{-1} .

3. Results and Discussion

The diffraction analyzes shows the higher proportion of calcium in the sample composition, with characteristic diffraction peaks of calcite (CaCO_3), portlandite ($\text{Ca}(\text{OH})_2$), larnite (Ca_2SiO_4), mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) and jasmundite ($\text{Ca}_{11}(\text{SiO}_4)_4\text{O}_2\text{S}$) (Figure 1).

We observed in Figure 1 that the samples contain a good proportion of graphite. Considering the purpose of the present work it is interesting to observe that the only iron compound identified by diffraction was magnetite, and only in half of the samples, being that samples 4, 5 and 6 did not show peaks characteristic of Fe_3O_4 . Table 1 shows the percentage of magnetite calculated through the diffractograms.

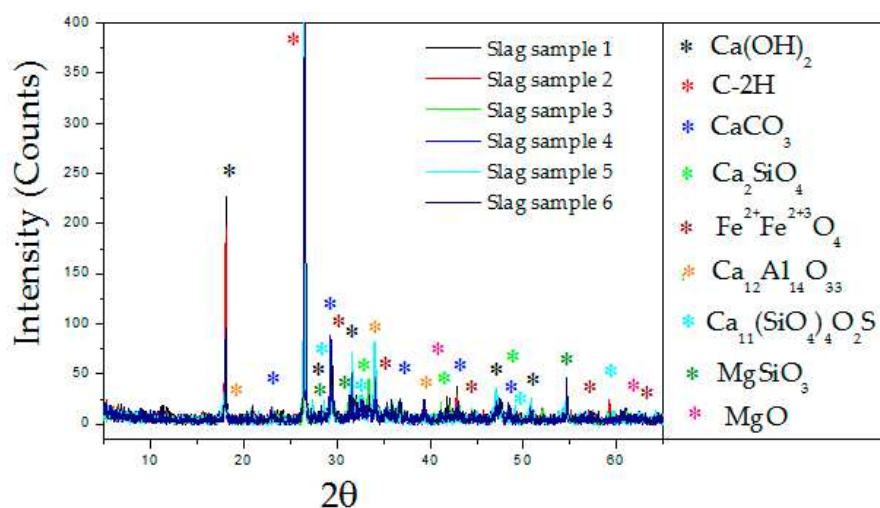


Figure 1. XRD diffractogram of the slag samples with signaling of the characteristic peaks of the minerals identified.

Table 1. Quantification in percentage of slags composition using the technique of X-ray diffraction.

Composition	Slag Sample 1	Slag Sample 2	Slag Sample 3
Ca(OH) ₂	12.3%	15.4%	9.5%
2H-C	10.1%	15.5%	26.1%
CaCO ₃	55.6%	54.2%	42.5%
Ca ₂ SiO ₄	8%	4.1%	13.3%
Fe ₃ O ₄	2.3%	3.3%	1.7%
MgO	8.3%	2.8%	-
Ca ₁₂ Al ₁₄ O ₃₃	3.3%	4.7%	-
MgSiO ₃	-	-	6.9%

SEM is used in the characterization of siderurgy slag because it allows the elementary identification, bringing important information in the definition of reuse. An analysis of the composition made with EDS indicates the majority presence of oxygen that makes up the oxides (68.5%) and calcium (21.1%). Minor proportions of silicon (3.6%), iron (2.2%), magnesium (1.3%), manganese (0.55%), sulfur (0.72%), phosphorus (0.1%) are present in all samples but sodium (0.05%), titanium (0.08%) and aluminum (1.8%) only in some of them. To confirm the presence of magnetite and to identify the presence of other iron oxides, FTIR analysis was performed, where characteristic absorption peaks can differentiate magnetite (Fe₃O₄), hematite (α-Fe₂O₃) and maghemite (γ-Fe₂O₃) that are three of the most common and important iron oxide polymorphs. The results are shown in Figure 2a,b.

The peaks observed in the FTIR spectrogram bring similar information to the diffractograms, since it is possible to identify absorption peaks characteristic of calcite, portlandite, clinoenstatite, periclase and graphite (Figure 2a). In detail of the region between 300 cm⁻¹ and 700 cm⁻¹, shown in Figure 2b, we see peaks characteristic of iron oxides. Black, red and blue dotted lines differentiate the position of peaks related to magnetite, maghemite and hematite, respectively [7].

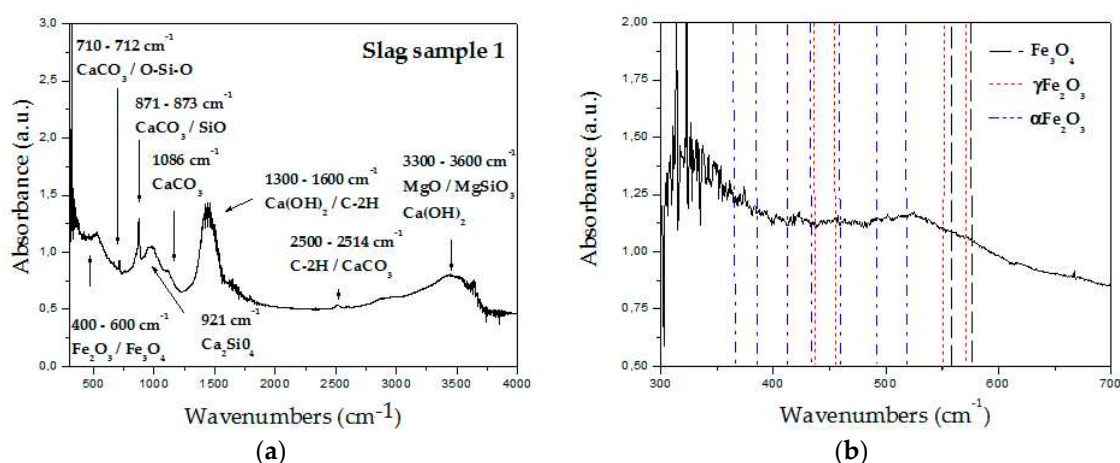


Figure 2. FTIR spectra of the: (a) slag sample 1 for wavenumbers ranging from 300 to 4000 cm⁻¹; (b) slag sample 1 for wavenumbers ranging from 300 to 700 cm⁻¹.

4. Conclusions

For the reuse is necessary in principle a careful characterization, since the composition of the slag varies greatly from one steel plant to another, depending on the origin of the precursor material. In the analysis performed in this work the presence of magnetite in the slag was identified, a material of great interest for use in applications associated with recent technological advances, focused on biotechnological use. The results obtained reinforce the idea of reuse of magnetite for technological purposes, instead of its return to steelworks, as scrap, considering that for this use small proportions of materials are used to obtain significant results in the production of biocomposites.

Author Contributions: A.S.M.B. and A.H.O. conceived and designed the experiments; D.T.M. performed the experiments; A.S.M.B. analyzed the data; D.T.M. contributed reagents/materials/analysis tools; A.S.M.B. wrote the paper.

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References

1. Chand, S.; Paul, B.; Kumar, M. Sustainable Approaches for LD Slag Waste Management in Steel Industries: A Review. *Metallurgist* **2016**, *60*, 116–128, doi:10.1007/s11015-016-0261-3. Available online: <https://link-springer-com/article/10.1007/s11015-016-0261-3> (accessed on 26 May 2018).
2. Das, B.; Prakash, S.; Reddy, P.S.R.; Misra, V.N. An Overview of Utilization of Slag and Sludge from Steel Industries. *Resour. Conserv. Recycl.* **2007**, *50*, 40–57, doi:10.1016/j.resconrec.2006.05.008. Available online: <https://www.sciencedirect.com/science/article/pii/S0921344906001297> (accessed on 26 May 2018).
3. Branca, T.; Pistocchi, C.; Colla, V.; Ragaglini, G.; Amato, A.; Tozzini, C.; Mudersbach, D.; Morillon, A.; Rex, M.; Romaniello, L. Investigation of (BOF) Converter Slag Use for Agriculture in Europe. *Metal. Res. Technol.* **2014**, *111*, 155–167, doi:10.1051/metal/2014022. Available online: <https://www.metallurgical-research.org/articles/metal/abs/2014/03/metal140009/metal140009.html> (accessed on 26 May 2018).
4. Wu, W.; He, Q.; Jiang, C. Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies. *Nano Res. Lett.* **2008**, *3*, 397–415, doi:10.1007/s11671-008-9174-9. Available online: <https://nanoscalereslett.springeropen.com/articles/10.1007/s11671-008-9174-9> (accessed on 26 May 2018).
5. Sun, S.H.; Murray, C.B.; Weller, D.; Folks, L.; Moser, A. Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices. *Science* **2000**, *287*, 1989–1992, doi:10.1126/science.287.5460.1989. Available online: <http://science.sciencemag.org/content/287/5460/1989.long> (accessed on 26 May 2018).
6. Jena, B.C.; Dresler, W.; Reilly, I.G. Extraction of Titanium, Vanadium and Iron from Titanomagnetite Deposits at Pipestone Lake, Manitoba, Canada. *Miner. Eng.* **1995**, *8*, 159–168, doi:10.1016/0892-6875(94)00110-X.
7. Aaron, M.J.; Heather, C.A. Vibrational Spectroscopic Characterization of Hematite, Maghemite, and Magnetite Thin Films Produced by Vapor Deposition. *Appl. Mater. Interfaces* **2010**, *2*, 2804–2812, doi:10.1021/am1004943. Available online: <https://pubs.acs.org/doi/abs/10.1021/am1004943> (accessed on 26 May 2018).



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