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Experimental analysis on the use of BF-sludge for the reduction of BOF-powders to direct reduced iron (DRI) production


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ABSTRACT

Approximately 25 Mt/year of sludge and dust are obtained from the treatment of the exhaust gases produced during the manufacturing of cast iron and steel from blast furnace, converter and continuous casting machines. This waste contains a large amount of valuable elements that could be recycled in the steelmaking process itself. Unfortunately, sludge and dust are difficult to recycle and so most of them are disposed in landfills. In this work, a feasibility study on the use of blast furnace sludge as a reducing agent to produce direct reduced iron from BOF-dust is presented. Self-reducing briquettes containing a mixture of BOF-dust, BOF-sludge and BF-sludge were produced. Thermo-gravimetric and roasting tests were performed in non-isotherm conditions from room temperature to 1170 °C in both argon and air atmospheres. The XRD and SEM analysis performed highlighted the metallization ratio of about 50–60% for air reduced briquette and 60–80% for argon reduced briquette. These results foster the technical feasibility of the use of BF sludge as a reducing agent to produce direct reduced iron (DRI). The use of BF-sludge as C-source for BOF dusts reduction lead to a cost saving estimated to 1500 M€/year worldwide.

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1. Introduction

During steel production by integrated cycle 25–30 Mt/year of dust and sludge are abated by wet filters (cyclones) and electrostatic precipitators (ESP), which treat the exhaust gases. Due to the residual heavy metal content (Zn, Pb, As) as well as alkaline oxides, halides and hydrocarbons, both the recycling and final depositions of fine fractions are problematic, even because these materials are classified as hazardous waste ([European Waste Catalogue, 2002](#)). The cost of landfill and the loss of iron units represent two important concerns ([Kelebek et al., 2004](#)). In particular, landfilling costs are estimated to be 80–100 €/t for non-hazardous waste, and this price could increase if the disposal occurs in hazardous waste landfills ([Bazzucchi, 2005](#)). Hazardous waste must be disposed in

dedicated landfills, which are associated with higher disposal costs due to their low number and limited size ([D.LGS 36, 2003](#)). The possibility to stock a hazardous waste in a non-hazardous waste landfill depends upon the leachability of specific substances, i.e. Zn, Cd, As, Pb. Italian regulation ([D.M. 27/09, 2010](#)) fixes the maximum admissible limits for such polluting elements. Often, to respect these limits, a stabilization treatment is required (e.g. by the addition of lime; [BREFs, 2014](#)) leading to an increase of volume to be disposed of and, consequently, an increase of treatment and disposal costs.

Blast furnace (BF) gases are usually treated in two stages: coarse dust separation, i.e. by dust-catchers or cyclones, followed by fine dust separation in a wet ESP or scrubber. The amount of coarse dust and fine sludge fractions of BF-powders varies from 3.5 kg/t to 18 kg/t and 2 kg/t to 22 kg/t of hot metal,

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respectively, in European blast furnaces (BREFs, 2013). This implies between 0.2 and 2.2 Mt/year of BF-powder residual, because of a plausible yearly estimated average iron-making output of 100 Mt (BREFs, 2013; EUROFER, 2013; WSA, 2014). The coarse dust is normally brought back to the sinter strand. This is much more difficult for the sludge, because its Zn and Pb contents are 10–30 times higher (BREFs, 2013). Despite the 50% of carbon and the 20–30% of iron oxide still present, the BF sludge cannot be directly reused in the steel-plant because of their significant content of harmful materials (1–10% Zn, 1–2% Pb and 1% alkali), which could induce several difficulties in the production process or in a high consumption of the refractories (Kryachko et al., 2005; Yang et al., 2009; Besta et al., 2012). In addition, direct reuse of sludge in the blast furnace is not recommended, because it would increase the concentration of heavy metals, exacerbating the above-mentioned criticalities. The chemical composition of the BF sludge is highly variable due to the differing chemical compositions of the materials fed in the blast furnace and the stratification between ore and coke inside the furnace itself (Koen et al., 1995; Babich et al., 2008). Today, only limited industrial applications exploit the BF-sludge as raw material. Most of them can be considered as depuration processes, aimed at recovering the heavy metal fraction still present in the sludge for producing residues which could be further recycled within the steel-plants or safely disposed of, without generating environmental problems (Das et al., 2007). Some attempts to leach Zn from BF-sludge were carried out by hydro-metallurgical processes based both on acidic or alkaline solutions (Zeydabadi et al., 1997; Xiangfu, 1999; Van Herck et al., 2000; Huang et al., 2007; Vereš et al., 2011; Steer and Griffiths, 2013). Other attempts (Lopez et al., 1995; Lopez-Delgado et al., 1998; Das et al., 2002) tried to recover valuable products from the BF-powders. For example, coke fines, with a carbon content of 80% (with a yield of approximately 30%) can be recovered by the technique of column flotation (Xiangfu, 1999). Additional studies have investigated the use of BF sludge as a cation adsorbent (especially for Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , and Cr^{3+}) for treating industrial waste and cleaning water (Lopez et al., 1995; Lopez-Delgado et al., 1998).

Basic oxygen furnace (BOF) coarse dust comes from the first de-dusting step and the fine dust from the second. There are different systems for separating coarse and fine dust. This operation can be performed along the process itself, e.g. by individual capture and separation of dust in the consecutive de-dusting steps or by subsequent treatment of the dust/sludge, e.g. the coarse sludge can be recovered in a pre-settling tank and the fine sludge in a second settling tank. The primary de-dusting is usually performed by the Venturi-type scrubbers or by ESP, which can be featured by dry or wet configuration. Before the inlet section of the Venturi-scrubbers or of the ESP, the coarse particulates are usually removed by means of a deflector. The secondary de-dusting system captures and filters the fumes produced during charging or tapping in the surrounding areas of converters, and from the other steelmaking plants (i.e. pre-refining, treatment plants, casting areas). The coarse and fine dusts from BOF are produced with a specific rate from 0.75 up to 24 kg/t of liquid steel (BREFs, 2013). Thus, it is possible to estimate that each year, from approximately 75 kt to 2.4 Mt of BOF powder residues are generated in the EU and 25 Mt worldwide (EUROFER, 2013; WSA, 2014). The coarse dust is usually returned to the oxygen steelmaking process (after the pelletizing or briquetting process) or it is recycled to the sinter strand or to cold bonded briquettes for

use in blast furnaces. The fine dust contains larger amounts of lead and zinc than the coarse dust. The main source of these heavy metals is usually scrap charged to the BOF. In some cases it is possible to control the lead and particularly the zinc input by a correct check of the scrap (ITP steel, 2001). However, the availability of scrap featured by less than 1% of zinc has decreased continuously during the recent years, thus a consistent part of the fine dust cannot be recycled is usually landfilled. In addition, the sludge generated during hydrocyclonage and/or the sedimentation of the suspended solids in the scrubbing water circuit can be totally recycled within the iron and steelmaking process only if the zinc input via the scrap is strictly limited, i.e. back to the sintering plant or to the BOF after cold briquetting. At several other steelmaking plants worldwide, the sludge cannot be used and is either externally used in the cement making industry or stored or disposed of (BREFs, 2013).

The dust and sludge from converter (BOF) are featured by 60–65% of iron oxides, 9–10% of lime and low carbon content (1–5%). However, carbon content from the secondary filtering line could change in a wide range, due to the different plants enslaved. Besides the extraction of Zn and other leachable metals (Pb, Fe, etc.) by hydro-metallurgical processes (Hoang-Trung et al., 2001, 2011; Kelebek et al., 2004; Cantarino et al., 2012), the BOF sludge can be used as feeding material for blast furnace (Kurunov et al., 2003) or as raw material for the directly reduced iron production in Rotary Heart Furnaces (RHF) or Radust processes (Jalkanen et al., 2005; Oda et al., 2006). In any case, the proposed techniques always require the addition of coal or coke to make sure that after the roasting operation, the obtained sponge iron can be exploited in a steel shop.

The goal of this work is to evaluate the use of BF-sludge as a carbon source to produce self-reducing briquettes for direct reduced iron production. BOF dusts and sludge were mixed with BF-sludge and then hot briquetted. The briquettes were then subjected to different thermal cycles in different atmospheres (air or argon) to evaluate the performance of the oxide reduction route.

The resulting products were characterized from chemical and morphological perspectives by means of energy dispersive X-ray fluorescence (ED-XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The reduced briquettes indicate the correct features for use as raw material in direct reduction processes for DRI production.

2. Experimental procedure

Self-reducing briquettes were prepared mixing BOF dust, BOF sludge and BF sludge in different blends. Table 1 indicates the chemical composition of the different wastes used whereas Table 2 summarizes the briquettes composition. BOF sludge and BOF dust 1 come from the secondary de-dusting lines, whereas BOF dust 2 is taken from primary filtering line. The powders were cold-bonded using hydrated lime and organic molasses as a binder before being compressed. After drying, the powders mix was hot briquetted at 700 °C through a hot pressing briquetting machine set-up at 100 kgf/cm² to obtain pillow-shape 40 mm × 30 mm × 20 mm briquettes. The process takes approximately 5 s/briquette. Five briquettes for each blend were prepared. The different blends were designed to have a C/FeO_x weight ratio of about 1.5 in order to exceed the stoichiometric value for Fe₂O₃ reduction to metallic iron.

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