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The Recycling of Materials Containing Iron and Zinc in the OxyCup Process

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Abstract

Environmentally friendly and economically profitable technologies, enabling utilisation of wastes from metallurgical processes and regeneration of Fe and Zn contained in them, are looked for. This allows also saving of natural resources such as ores.
Several techniques have been developed and introduced for recycling sludge and dust that contain iron and zinc. Currently, there are three major ways to treat zinc -bearing dust:

- rotary hearth furnaces method (the FASTMET process);
- rotary kiln method (the Waelza process);
- shaft furnace method (the OXYCUP method).

This technology can be used to fully recycle metallurgical wastes such as slag crusts or metal-bearing fractions of desulfurization slags without the need for additional preparation of these materials, dust, sludge and scale generated in different stages of iron and steelmaking. The OXYCUP process described in paper combines the function of melting in traditional cupola furnaces (CF) with function of reduction in blast furnaces (BF).

Keywords : Recycling of iron and zinc, Cupola, Modern technologies, Wastes

1. Introduction

The growth in the steel production worldwide has focused experts attention on the increasing effect of the ferrous metallurgy industry on the environment in connection with its emissions of greenhouse gases and the formation of hard-to-recycle waste products [1, 2].
The production of 1 Mg of steel requires the expenditure of almost 20 GJ energy and is accompanied by the release of 1,7 Mg CO_2 into the atmosphere. This accounts for 6-7% of the emissions of anthropogenic CO_2 in the world [3]. Large amounts of sludge and dust are produced in iron and steel making process, mainly including sintering process (SP), blast furnaces (BF) and convertor or electric arc furnace (EAF). Steel production forms 20-25 kg of slag and dust with an iron-oxide content up to 60% iron. Usually, the zinc content in dust from EAF is up to 20% [4] and it may exceed 30% if the dust is recycled to the EAF [5]. The traditional sintering process to treat zinc – bearing dust cannot remove zinc, lead and other harmful elements. During the circulate in BF dust will be enriched in zinc, which will reduce the lining life, destroy the reaction stability in the furnace and affect the performance of BF and circulate in BF. The presence of iron oxides and zinc in steel prevents it from being recycled in blast furnaces. A similar situation exist in regard to blast furnace slag, which contains not only iron and carbon (25-30%) but also 1,5% zinc.
Thus developing economical and environmentally sound technologies for recycling hard-to-recycle sludge and dust is a

problem that is important for integrated metallurgical plants from both and ecological standpoint and an economic standpoint.
Therefore environmentally friendly and economically profitable technologies, enabling utilisation of wastes from metallurgical processes and regeneration of Fe and Zn contained in them, are looked for. This allows also saving of natural resources such as ores.
Several techniques have been developed and introduced for recycling sludge and dust that contain iron and zinc. Currently, there are three major ways to treat zinc -bearing dust:

- rotary hearth furnaces method (the FASTMET process);
- rotary kiln method (the Waelza process);
- shaft furnace method (the OXYCUP method).

2. The OXYCUP process

The OXYCUP process, developed by the company Kuttner GmbH& Co., was realized on an industrial scale in 2004 by the company Thyssen-Krupp Steel. Dusts from dedusting of oxygen converters operating in this steelworks contain approximately 65% of iron, it means only 10% less than the best grade ores. This installation corresponds very well with the concept ‘Zero wastes’.
This technology triggered a lot of interest in the metallurgical industry, since it enables obtaining liquid iron from dusts and sludge originated from metallurgical processes. Apart from iron of the pig iron quality, slag and gases rich in CO are formed as side products.

This technology can be used to fully recycle metallurgical wastes such as slag crusts or metal-bearing fractions of desulfurization slags without the need for additional preparation of these materials, dust, sludge and scale generated in different stages of iron and steelmaking. The OXYCUP process combines the function of melting in traditional cupola furnaces (CF) with function of reduction in BF [3, 6, 7]. In contrast to EAF and BF operation cupolas can easily process high amounts of zinc in the burden which may either originate from steel plant residuals or from automotive scrap (Fig 1).

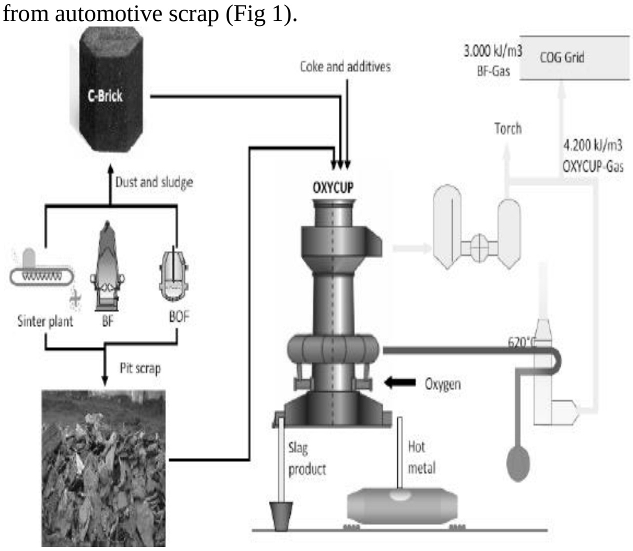

Fig. 1. Schemat procesu OXYCUP [8,12]

Self-reducing briquettes obtained from sludge or other iron-bearing wastes on a cement binder are melted in a cupola operated with an oxygen-enriched blast (5 -15% of oxygen enrichment). In addition to briquettes, the charge contains fluxes and large (up to 1 m) pieces of scrap. The resulting pig iron is used in a convertor shop, the slag is granulated, the cleaned top gas is used as a fuel, and the top dust is recycled into briquettes. When the zinc content of the top dust rises to the level that makes the dust a commercially viable product, it is periodically removed from the process and sold as zinc concentrate. In contrast to BF smelting, in the OXYCUP process most of the iron is reduced at 900-1400^{o}C over a short period of time 20-30 minutes. Most of the iron is reduced by carbon in the briquettes [3].
This process is environmentally friendly and emissions of such substances as: SO_x, NO_x, dioxins and furans are below the allowable values.

3. OXYCUP furnace

The OXYCUP furnace is a unique miniature replica of a blast furnace in terms of both its use and its principle of operations (Fig. 2). The upper part of the furnace contains the charge receiving hopper positioned above the chamber of the gas flue. The middle parts serves for preheating the charge and finally for melting the iron and slag bearing constituents. The lower part contains the cupola hearth and the iron-slag separator. In contrast to common BF operation, the metal and slag are discharged continuously from OXYCUP furnace.
The lower part is filled with coke , the coke bed. Hot blast at 500 to 620^{o}C and oxygen are blown through water-cooled tuyeres and lances into the coke bed to yield high temperatures of approximately 1900 to 2500^{o}C (Fig 2).

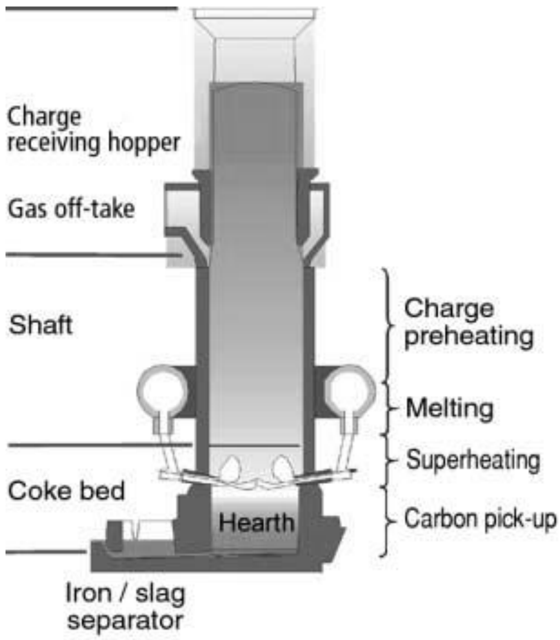

Fig. 2. Section view of a OXYCUP furnace showing the zones for operation and its components [7, 9]

At these temperatures superheating and carburizing of liquid metal droplets occur sufficiently rapidly when in contact with the coke. The hot gas leaving the coke bed provides the necessary heat for reducing the iron oxides inside the bricks, melting the metallic charge and preheating the metallic charge in the gas counter – flow. The coke is burned to a mixture of CO and CO_2.

4. Raw materials

High amounts of iron oxides can be processed in OXICUP shaft furnace in the form of self-reducing bricks. These bricks may contain residuals from steel plants or even iron ore fines [10]. In all cases, the carbon necessary for the reduction of the oxides must be present inside brick (Fig. 3). Briquettes, apart iron-bearing wastes (sludge, dusts, rolling scale, fine-grained ore) contain carbon as a reducer (12 -14%) and cement (10 - 12%) as a binding material.

In a normal cupola process, due to a low reducing ability of gases (low CO content) and a short contact time of the metal charge with coke (approximately 1 hour), it is not possible to perform reduction of iron oxides. Iron oxides present in the charge enter slag in unchanged form (for comparison: contact time of the charge, containing iron oxides, with coke in a blast furnace equals 4 – 5 hours). Whereas, when iron oxides are in a form of briquettes together with carbon the reduction process occurs much faster (20-30 minutes) and at a higher temperature (900-1400°C). E.g. at a temperature of 1430°C after 10 minutes 95% of iron oxide is reduced to metallic iron.

A reduction of iron oxides within a briquette does not proceed according to the direct reaction: FeO + C = Fe + CO, but via intermediate stages containing oxidation of carbon:

C + CO_2 = 2CO (Boudouard reaction) and in its result carbon oxide necessary for the reduction process is formed. In the reduction process of iron oxide CO_2 is formed and it can oxidise subsequent carbon portions to CO. Therefore the reduction of iron oxides to metallic iron within briquettes containing carbon requires supplying a reducing gas from the outside. Moreover the reaction of oxidation of carbon occurs only after heating briquettes to high temperatures [13,14]. Briquette components such as silica, CaO contained in wastes together with cement decide on slag alkalinity. Furthermore gaseous components, CO and CO_2 are present in briquette pores.

Rate of iron oxide reduction is controlled primarily by the rate of oxidation of carbon in the CO_2/CO mixture which prevails within the inter-particle pores. An oxidation rate of carbon with CO_2 is noticeable only above 1000°C but becomes high at 1400°C. (Fig. 4).

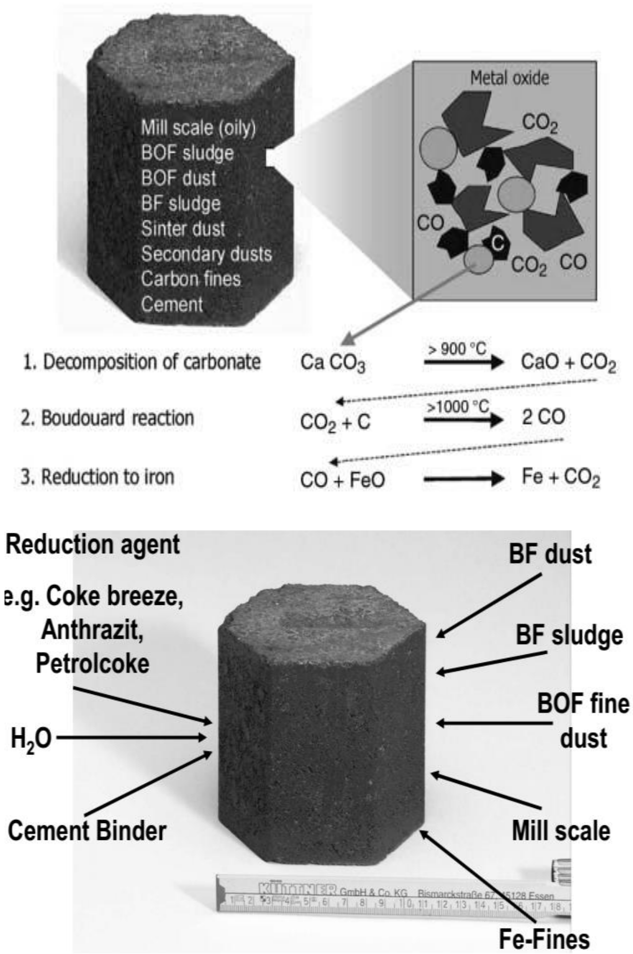

Fig. 3. Composition and self-redcing reactions in the C-brick [7,12]

The pattern of the OXYCUP process occurring in a shaft furnace is presented in Fig. 4. At the first stage briquettes are heated to a temperature of 500°C in a stream of the furnace waste gases. The first portions of metallic iron are formed on the external surface of briquettes. This coating is growing and protects briquette against decomposition at a temperature above 1000°C, when cement decomposes and the direct reduction by carbon contained in briquettes starts. At a temperature above 1450°C briquettes pass - as a whole - into spongy iron, which are melted together with the metallic charge loaded to the furnace. Metal tapping of a temperature of 1500°C and 4% carbon content occurs continuously. The reduction process of oxides contained in briquettes can last not longer than 20 minutes. The most often metal from the OXYCUP process is mixed with pig iron and after desulphurising the mixture is transported to a converter or electric arc furnace.

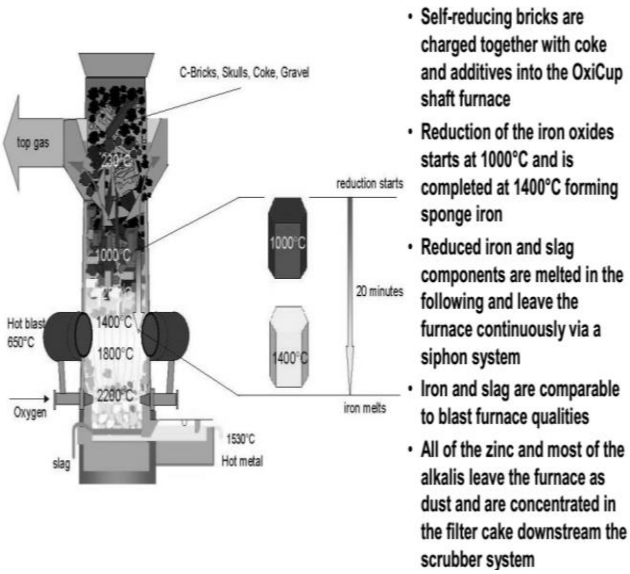

Fig. 4. Temperature and time range for FeO reductionin C-brick [7]

Inside the furnace zinc travels together with the charge through zones having different temperatures and gaseous atmospheres of different compositions from the cold region (in the upper part of the furnace) to the hot tuyere zone. Pure zinc already evaporates above its melting point of 420^{o}C. However, in an oxidizing atmosphere evaporation becomes sluggish because of the formation of ZnO or other zinc compounds that remain solid or liquid up to very high temperatures. The zinc compounds particles formed during the oxidation are carried out of the furnace by the dust in the flue gases. The zinc content of the top dust is above 30%, which is sufficient to consider the dust for further processing.

4.1. Manufacturing of briquettes

Briquettes, being cupola charge, are manufactured in the concrete blocks technology. These briquettes must have suitable properties ensuring their stability at high temperatures (e.g. compression strength at a room temperature, minimum 5 N/mm^2).

4.2. Energy consumption in the OXYCUP process

For reduction and melting of 1 Mg of briquettes containing carbon the same amount of energy is needed (252 MJ/Mg briquette) as for melting 1 Mg of scrap (250 MJ/Mg scrap). However, from 1 Mg of briquettes 400 to 500 kg of iron can be obtained (depending on the Fe content in scraps used for making briquettes - it was assumed that the iron [as Fe_2O_3] content in briquettes equals to 40%). The energy amount - in case of briquettes treatments - consists of: energy needed for the Fe_2O_3 reduction, energy used for melting the formed iron and energy needed for melting slag components.

Most of carbon is burnt in front of tuyeres to provide energy for the reaction and heating charge material. Only 33,11% of carbon is used to reduce ferrous and non-ferrous oxides (Fig. 5) [9]. Compared with BF top gas, OXYCUP top gas has a relatively high caloric value. The heat taken away by slag and hot metal is relatively modest. The rest of heat is used for heating and melting the scrap, and take away by top gas.

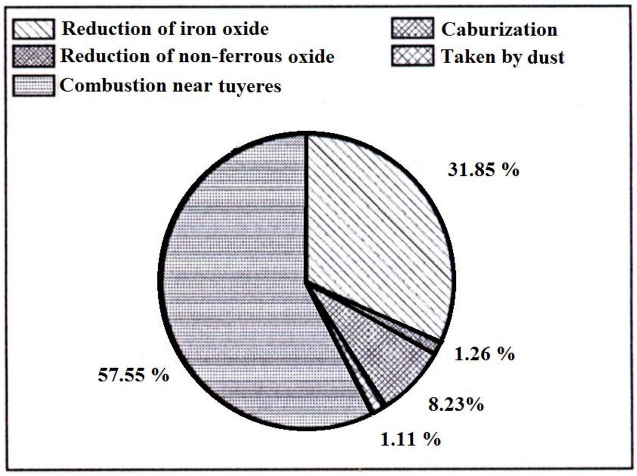

Fig. 5. The role of carbon in the OXYCUP furnace [9]

Currently working installations where OXYCUP process is performed:

- ThyssenKrupp Steel, Germany OXYCUP® for recycling of 500 t/day of ferrous dust and sludge material
- Sicartsa, Mexico Shaft furnace producing 2.000 thm/day from scrap
- Nippon Steel, Japan Shuttle furnace producing 1.350 thm/day from scrap
- JFE, Japan Scrap melting shaft furnace plant 2.400 thm/day
- Taiyuan Iron and Steel Company in China (2011)

5. Conclusions

The OXYCUP process produces hot metal, slag and top gas. All kinds of metallic revert metals, such as skulls, desulphurisation metals and metals from slag processing can be treated. OXYCUP process adopts two kinds of fuels: coke and carbon fines. Coke provides most of the energy source for the furnace with its partly complete combustion and stock column skeleton and guarantees the permeability of stock column. The OXYCUP process not only solves the problem of making use of by-products at plant, but also provide the metallurgical industry with additional amounts of liquid pig iron.
Some of advantageous features are as:

– hot metal cost from OXYCUP process lower than hot metal from BF;
– use of cheaper Zn - coated scrap steel plant;
– optimization of sinter plant by taking out fine materials;

– Zn - enriched sludge (30% Zn) can be sold for further Zn recovery;

Due to the OXYCUP technology the idea "zero waste" becomes real in metallurgical processes.

By-products and wastes are turned into hot metal and slag in a single step. The OXYCUP in turn finally delivers hot metal of precisely known quality to the steel plant.

Acknowledgements

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