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RECYCLING OF INTEGRATED STEEL PLANT SOLID WASTES IN THE SINTERING PROCESS AND CORRESPONDING EFFECTS ON POLLUTANT EMISSIONS

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ABSTRACT

The new practices in sintering technology allows for the use of a wide range of iron-containing materials in charge with obtaining the agglomerate with necessary characteristics for optimal operation of the blast furnace. The essential modifications in the composition of feed materials have an important impact on the nature and the quantity of pollutant emissions from the sintering plant. In this paper is presented an analysis of emissions and of their mechanism formation for the case of the sintering sector from an integrated steel mills, which transformed into agglomerate a variety of materials as iron ore fines, dust collected from blast furnace, ore concentrates and some fractions of metallurgical slag. These are correlated with operation conditions in sinter strand and of other main sections of the process.

KEYWORDS: sinter plant, recycling, metallurgical wastes, pollutant emissions

1. Introduction

In ferrous metallurgy sintering is the thermal preparing process that permits the conversion of fine particles of iron ores under the action of heat into a material suitable for use in blast furnace (Figure 1).

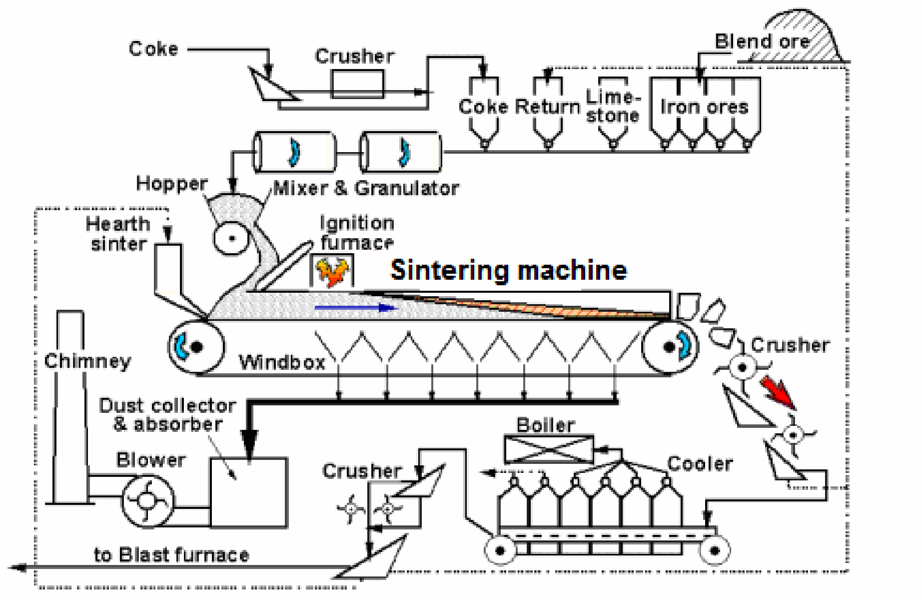

Fig. 1. *Flow sheet of sintering process on Dwight-Lloyd type of sintering machine [1]*

The process is usually carried out by suction of air necessary for solid fuel combustion through a layer composed by a material mixture placed on a sinter band. In the classical sinter plants, iron ore fines, solid fuels (coke fines or coal fine), fine limestone/dolomite are used to compose the feed inputs. Today, in accordance with the new environmental practice for integrated steel mills was developed the sintering technology that allows for the introduction in the charge materials of the various iron-bearing wastes generated in different production steps of iron and steel manufacturing work. Many sinter plants in the world are capable to recycle the wastes up to the extent of 180 - 200 kg/ts [2, 3].

The recycling and utilization of metallurgical wastes (such as oxide dusts, sludge, scales, slag etc.) have as main advantage the reducing of primary raw materials consumption and the recurrent costs of mining/and beneficiation and preserve the environment. Also, the recycling of iron-bearing wastes eliminates their disposal costs, limits the amount of landfilled wastes and their environmental impact.

These materials, as powder or particles with small sizes, are problematic at recycling for their high content of harmful constituents. Are even used only normal feeds that do not contain steel plant wastes, the conventional sintering process is considered as the major source of pollutants within an integrated steel plant.

The sinter plant produces large quantities of pollutant emissions into air. The literature mentions the pollutants: sulphur oxides, nitrogen oxides, carbon monoxide, fluorides dust, heavy metals, alkali-chlorides, hydrocarbons, polychlorinated dibenzo-p-dioxins and furans, polychlorinated bipheyls, organohalogen compounds, polycyclic aromatic hydrocarbons, cooling particulates [4]. At recycling of metallurgical wastes is favoured the generation of emissions and the inadequate operating conditions lead to increasing of their quantity. The recycling the valuable units with reduction of pollutant emissions is one of the most important challenges that require the improving of the operating of sinter plant.

The paper aimes at assessing the impact of recycling of integrated steel plant solid wastes on the sintering process and corresponding pollutant emissions.

2. Solid wastes recycled in the sintering process

In the case of sinter plant analysed the raw materials inputs are typically composed from various sorts of iron ore fines, ore concentrates and undersize sinter returned from process after crushing and screening [5]. Also a variety of recycled process materials in form of small or very small particles are introduced in the materials charge. These are wastes mainly consisting of iron scale from the rolling mills, a wide variety of dusts or sludge separated from waste gas treatment devices, and some fractions rich in iron sorted from metallurgical slag. Thus sinter plants work as a „waste to value” converting unit. The recycling capacity of iron-bearing wastes is determined by their properties (both its chemical composition and its state). The knowledge of their characteristics in accordance with iron ores that are usually used in the feed inputs of sinter plant is imposed. Their recycling makes necessary the change of process parameters and has an influence on the sinter quality and especially on pollutant emissions.

Blast furnace dust and sludge result from air pollution control equipments, dust from dry BOF gas treatment, respectively sludge from wet treatment. According to European Committee Blast Furnace Report, the chemical composition of dust from blast furnaces that operate with iron sinter varies within 38-42% Fe, 0.8-1.2% Mn, 10-12% CaO, 8-10% SiO_2 şi 8-18% C. This is different for the blast furnaces with feeds composed of iron ores and pellets: 44-48% Fe, 0.6-1% Mn, 2-4% CaO, 12-14% SiO_2, 8-18% C. Iron is present as gehlenite ($Ca_2Al_2SiO_7$), magnetite, hematite, wüstite [6]. The recycling is conditioned by the content of Zn, Pb, and alkali. Significant is Zn concentration (mainly as $ZnO{\cdot}Fe_2O_3$) in the BF dust. This is concentrated in fine fractions, where its content varies in the range of 0.01 - 0.5% as against with coarse fractions where the content is 1.4 - 3.4 %. Similar relation is kept for Pb content of the BOF dust (as PbO): 0.01 - 0.04% for fine fractions and 0.2-1.0% for coarse fractions [7]. In some cases the dust contains toxic elements (Cd, Cr and As) [6]. The BF dust has a higher content of K_2O (~ 0.50%). The sulphur is major for BF dust, about 0.50%. It can be explained by its content of unburned coal particles that circumstantial pass nonburned through the stock column of material into blast furnace.

BOF sludge is composed of fine solid particles recovered by wet cleaning of the gas. The moisture content is appreciable (35 - 40%) and it is imposed to be dried before its recycling to the sinter plant. Solid particles from BOF sludge contain C, Fe as oxides, Ca, Mn, Mg, Al, Si, P, alkalis and heavy metals (especially Zn and Pb). The BOF sludge has a high zinc content ranging from 1.8% to 7.8%. The presence of iron is explained by its evaporation during the processes occurring in the converter. The zinc concentration increases in the case of large amounts of galvanized steel scrap used in feeds. Also other metals as Cd, Mn and Pb have origin into scraps recycled. Much of metals emitted from BOF are present in the particles retained in the cleaning equipments (~ 73%) and a small amount of Zn, Pb associated with fine particles unfiltered is released into air [7, 8].

Oil mill scale has a grain size below 10mm. The iron content, mostly in oxide form, is about 70%. The oil content of rolling scale is typically in the range of 0.2 to 2%, but oil contents as high as 10% have been observed. The oil/grease that is bonded to mill scale is the major impediment to the direct recycling [7, 8].

Scrap C is selected from old slag that was historically stored in the dump of the integrated steel plant. Typically BOF slag has the basicity (lime/silica ratio) of 2.5 to 4.0 and higher FeO content approximately 25 to 35%. In this slag is often present the significant content of "free lime". Steelmaking slag is crushed and sized for charging to the sinter plant to utilize the iron and manganese units and also the fluxing compounds CaO, MgO [8].

3. Origin of pollutant emissions

Most important environmental issue associated with sinter manufacturing by using feed with participation of wastes is that of air emissions consisting of particulate matter and gaseous pollutants.

Sinter plants may generate the most significant quantity of ***particulate matter*** as emissions in an integrated steel mill.

The solid emissions as airborne particulate matter arise from materials-handling operations. These are greater at handling of very fine and very dry dusts. The crushing, raw material handling and transport, belt charging and discharging from the crusher and hot screens, involve the generation of considerable amounts of particulate matter. Important dust quantity is released from sintering band.

The grain size distribution of the PM from a sinter strand before reduction consists of two types: coarse PM (with a grain size about of 100 μm) and fine PM (0.1 - 1 μm) [9]. These include the fragments of the raw materials such as iron ores, limestone, and cokes are released from the sintering process and discharged in the gas. Unburned carbon and metallic chlorides are also contained in the dust particles. The main particulate emission sources are collected in the gases of wind-boxes. Some of entrained particulate matter is released to air via the main stack, after passing through the particulate air pollution control equipment.

The fine particles used as raw materials in the sintering process in considerable amounts can lead to increasing of particulate emissions. These potential emissions are normally ducted to a separate dust removal system and discharged through a separate stack. Sometimes some particles may pass from the control system and are vented through the main stack. So the fugitive emissions could be released in air [10].

The air emissions are correlated with the nature of feeding materials and performance of waste gas cleaned solutions. The properties (composition, size, and morphology of particles) of fines and their quantity in the feed are important in the mixing operations (first stage of the sintering process). The mixture of materials is granulated by simultaneous balling and wetting of materials (iron ore fines, coke breeze, flux and wastes) into the mixing drum. The attaching and layering processes of finer particles (< 0.25 mm) onto the surface of coarser particles influence not only the permeability of sinter bed but also the amount of dusty particles entrained by gasses. The dust emitted from bed is formed in the drying/dehydration zone due to the materials and formation of fine particles by granules breakage at decrepitating. Largest amount appears due the extinction of adjacent particles in the combustion zone. Also, the combustion zone favours the formation of the alkali chloride (NaCl, KCl) due to the high temperatures [11]. The wet zone from the strand behaves like a temporary trap for the particles fluidized at upper zones.

Some part of trapped dust must re-stick to granules while the wet zone was drying. So, the wet zone acts as a wet gas scrubber, and therefore there is an accumulation of fine particles immediately downstream of the dry zone. At the same wind-box, the dust emission into exhaust started increasing ast the gas temperature rose, and ceased before the maximum temperature appeared at the melting zone touching the bottom of the sintering bed (i.e., at “the burn through point”) (Figure 2).

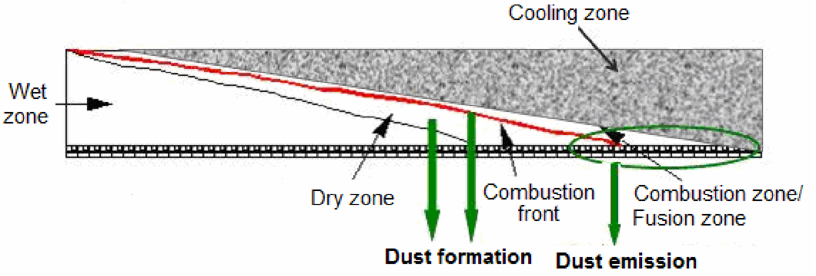

Fig. 2. *Formation and releasing of dust emissions from sinter bed [5]*

The parameters of the process affect the generation of pollutant emissions. The level of dust emissions is influenced by the moisture of the mixture subjected to agglomeration, the temperature of the gas and the basicity of the agglomerate. The increasing of coke content raises the temperature in the sintering bed and as result enhances the dust suppression. More coke, more particles fluidized at combustion zone. Also, the sintering machine operation (start-up/stopping) leads to the generation of dust.

CO and CO_2 emissions result from combustion of fine coke particles and of unburned carbon from BF dust. Also the reduction reactions of iron oxides at high temperature in sintering reaction zone is a source of CO. The combustion of coke begins between 700 and 800°C with hot air from the ignition process. Once the combustion is initiated, its front starts moving downward in the depth of materials bed. With increasing temperature, the CO_2 gas formed reacts with the carbon of coke to produce CO gas. The CO gas reduces hematite to produce magnetite. When further reduction occurs, wüstite is formed. The global rates of CO_2 formation were higher than those of CO formation. So the waste gas emitted at main stack of sinter plant contains more CO_2 (5 - 10%) [12]. The major part of ***sulphur compounds emissions*** is formed during the combustion of coke breeze. Also minor participation has unburned coal particles from BF dust. After formation, just under combustion layer, SO_2 is recombined with CaO or water from wet zone. At advancing of the combustion layer through the sinter bed, the thickness of wet zone decreases and as result its capacity to retain small amounts of SO_2 is reduced. At the end of the sinter bed, the wet zone is saturated with SO_2, and finally this is emitted into the gasses released just before the optimum burning point (Figure 3). The mill role scale present in the sintering charge behaves exothermally during sintering and has an effective contribution in reducing SO_x emission.

Over 90% of ***„nitrogen oxides" or NO_x emissions*** (consisting of NO and NO_2) are originated from the combustion of fuel. The mineralogy of iron ore (the presence of goethite α-FeOOH) has effect on the emissions.

The combustion NO_x formation starts right after ignition, in the combustion layer. These combustion products are no longer recombined. They are not retained in the wet zone, being released regularly during combustion process.

Due to the relatively low temperature of the combustion front of <1300 °C and low localized oxygen concentrations, thermal NO_x is present in a less amount (about 10%) in the wastes gasses emitted from sinter bed (Figure 3) [3].

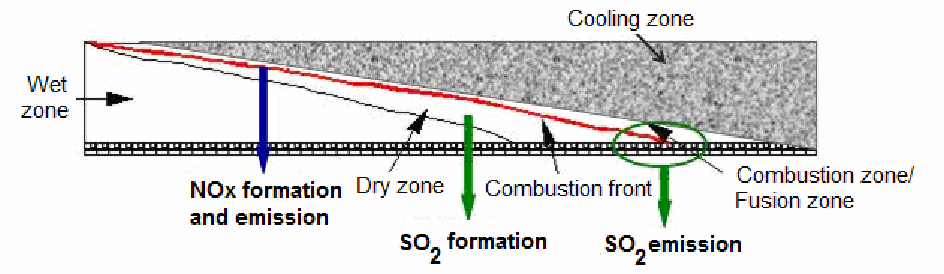

Fig. 3. *Formation and emission of SO_2 and NO_x [5]*

VOCs, hydrocarbons and polyaromatic hydrocarbons are emitted from volatile hydrocarbons in the sinter feed. Coke breeze and oily mill scale are the main source of these emissions.

Heavy metals emissions have the origin into iron ores and some recycled wastes (dusts and sludge) subjected to the sintering process. The BOF sludge has a higher percentage of alkali Zn, Pd, Cd, Cu, Cr, Ni etc. During heating, the heavy metals (especially lead, zinc and tin) contained in these materials may be volatilized and may be adsorbed onto fine solid particles taken by gases emissions. Some fine particles are able to pass through the particulate air pollution control equipment and are emitted in the air. These may have a much higher content of these metals than the raw gas dust or the sinter mixture [2, 3]. Also, during the sintering process, lead reacts with chlorides to form very fine crystals of lead chlorides which are able to pass through most electrostatic precipitators [10].

Emissions of dioxins and furans. Polychlorinated dibenzenoparadioxins (PCDDs) and polychlorinated dibenzenofurans (PCDFs) are formed by thermal and combustion processes in two different areas of sinter installation. Most of dioxins/furans are emitted in the sinter bed during combustion of solid fuel. Appreciatively 10% of the total PCDD/PCDFs are generated in the gas collectors via de novo synthesis [2, 3].

In the sinter bed, PCDD/PCDFs formation starts in the upper regions of the sinter bed shortly after ignition. Then the dioxin/furan and other compounds condense on cooler burden beneath as the sinter layer advances along the sinter strand towards the burn through point (just ahead of the flame front) (Figure 4).

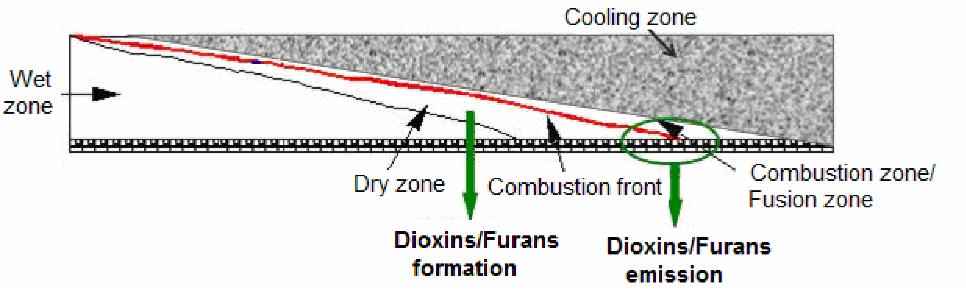

***Fig. 4.** Formation and emission of dioxins and furans [5]*

Near the end of the sinter grate, in the sinter layer there are two temperature intervals favourable for dioxin formation. Though are viable (will be vaporized and emitted from sinter strand) only those formed in the bottom zone. The most likely those generated in the top zone are destroyed at crossing of layers with high temperatures [4].

A small fraction of PCDD/PCDFs is the result of the so-called "de novo" synthesis mechanism. This involves the presence of unburned carbon in the form of soot (and carbonaceous particles derived from hydrocarbon components, chlorine, metallic chlorides and some metals as catalyst [13].

The operating parameters of the sintering process and the composition of the feed mixture have impact on formation of PCDD/PCDFs. The nature of solid combustible and raw materials from sinter bed influences the emissions of chlorine/chlorides, carbon, precursors, metals catalysts, oils etc. Principally the unwanted compounds enter the sinter installation by means of the recycled wastes. Occasionally some components and fine granulation of recycled materials can cause operating unstable conditions for sinter process and as result the flame front propagation is disrupted.

4. Conclusions

The sintering technology allows for the introduction in the charge materials of various iron-bearing wastes generated in different production steps of iron and steel manufacturing work. The recycling of iron-bearing wastes has important benefits: removing of disposal costs; limitation of the landfilled amount of wastes; diminishing of environmental impact for wastes dumped. On the other hand, the essential modifications in the composition of feed materials can have an important impact on the nature and the quantity of pollutant emissions (especially dust, sulphur compounds, heavy metals, dioxins and furans) from sinter plant. Although the flexibility of the sintering process permits recycling of a variety of internal wastes generated from integrated steel plant it is necessary to implement supplementary pollution prevention measures. The primary measures for preventing the use of pollutant emissions refer to the following: the feed materials selection; the removal of the contaminants from the material in accordance with the specification of limits on permissible concentrations of unwanted substances; adequately mixing or blending of materials.

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