Chapter 12
Dioxin Emission Reduction in Electric Arc Furnaces for Steel Production

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Abstract Steel production through electric arc furnaces has strongly increased in the past decade. Dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are the main type of greenhouse emissions in such kind of plants. The main factors influencing the emissions levels are the composition of raw materials, the processing conditions employed during melting, and the adsorbent effects of additional compounds added before filtering. Many techniques have been experienced in the recent past to improve the abatement of emissions levels. In the present chapter, the greenhouse emissions belonging to an industrial steel electric arc furnace are monitored in different processing condition setups. The effect of lignite and CuCl addition on the dangerous emission levels have been deeply investigated.

12.1 Introduction

Electric arc furnaces (EAFs) are employed in the steel industry to melt scraps at very high temperatures by using electric arcs (normally divided into high-pressure and low-pressure arcs). Graphite electrodes are the main sources of electrical energy; the electric arc leading to the material melting burns between the electrodes and the metal; those arcs are normally divided into high current and ultrahigh current (if the current exceeds 10 kA). Normally, oxygen is blown into the furnace using an oxygen lance; such oxygen, combined with the carbon, leads to the formation of a foam slag that works as a protective agent. Many studies focus on the efficiency of reducing the chemical energy loss by increasing the oxygen content in the furnace. During refining, the removal of carbon and further inorganic impurities, such as phosphorus, sulfur, silicon, manganese, aluminum, chromium, etc., is carried out by the oxygen lances. The oxidized elements are risen and enter the slag phase, which coats on the surface of the molten steel. This phase consists of the oxides of the impurities and slag former materials (CaO, MgO). Once the impurities

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are removed from the steel, their separation is carried out during the deslagging phase, when the furnace is tilted and the slag is poured out through the slag door. Apparently, during each phase of normal EAF operation, emission of fumes and gases is presented and can be divided into primary and secondary emissions. Generally, if carbon monoxide content in the exiting gases diminish below the flammability limit and the rest cannot be burned at the combustion gap, if the temperature remains high, the generated carbon dioxide could dissociate to carbon monoxide and oxygen, which would form dioxins in the downstream of the off-gas system. Consequently, the carbon monoxide and dioxin content of the off-gases are very high. The homogenous temperature is achieved through the employment of oil burners. Electric arc furnace and sintering plants (Cavaliere and Perrone 2013) represent the main sources of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) during steel production processes. Even if sinter plants are considered the main sources of dangerous dioxin emissions, the use of EAF for steel production is strongly increased, and this fact leads to a strong attention in their use and management. The high energy consumption of the EAF motivates the development of control and optimization strategies that would reduce production costs, while maintaining targeted steel quality (steel grade) and meeting environmental standards. The knowledge about optimized melting conditions of various types of scraps is limited to results belonging to statistical analyses, and the description of the relationships between the system efficiency and the greenhouse emission levels is very poor. Both PCDDs and PCDFs are persistent stable organic pollutants formed in all those high-temperature processes with an abundance of organic material in the presence of chlorine and copper. Dioxins and furans are chlorinated tricyclic organic compounds resulting from the combination of organic compounds impregnated with halogens (i.e., fluorine, chlorine, bromine, or iodine) with a specific molecular heterocyclic structure. A deep and complete thermodynamic description of the PCDD/F formation has been presented (Tan et al. 2001). These compounds are commonly grouped under the name “dioxins,” but their chemical structures and their properties can be very different. Dioxins are a class of heterocyclic organic compounds whose basic structure consists of rings with four carbon and two oxygen atoms. On the other hand, furans have only one oxygen atom, and the two outer benzene rings are linked by a pentagonal structure. Among the 200 types of known dioxins, the most famous are certainly the PCDDs, characterized by the presence of chlorine atoms that will complement the aromatic rings. The chemical stability of such compounds derives from the presence of these rings. The most dangerous of dioxins, for serious problems of bioaccumulation and environmental contamination, is certainly TCDD. A detailed description of their formation is presented in the literature (Kulkarni et al. 2008; Raghunatan and Gullet 1996; Suzuki et al. 2004). The PCDDs are generally measured in terms of TEQ relative to TCDD as a reference, being the most polluting and dangerous. The polydibenzo-dioxins have different toxicities in relation to their structure. The TEQ expresses the quantity of a “toxic” substance as the concentration of the reference substance that can generate the same toxic effects of TCDD. It is also possible to obtain the concentration of a

PCDD with its toxic equivalency through the use of the TEF. The TEF for TCDD is assigned equal to 1, while the other dioxins have a factor of <1. This dimensionless parameter, multiplied by the actual concentration, results in the TEQ. Many studies presented in literature report the effect of processing factors and off-gases filtering on dioxin emissions (Prüm et al. 2004; Öberg 2004; Chang et al. 2006). The main factors influencing the emissions levels are the composition of row materials, the processing conditions employed during melting, and the adsorbent effects of additional compounds added before filtering. Many techniques have been investigated in order to improve the abatement of dioxin levels. The techniques converge on the activated carbon adsorption or catalytic oxidation (Everaert and Baeyen 2004). From these studies, the employment of activated carbon results in the best available technique to reduce the dioxin levels from EAF. Anyway, these techniques require a very precise control of gas temperature in order to result efficient. Another efficient solution is the Cu chloride addition; in presence of urea, the addition leads to a strong reduction in PCDD/F formation (Li et al. 2008). Normally, dioxin compounds are destroyed at higher temperatures, but dioxins reform in the off-gas at lower temperatures. Such parameter is fundamental in monitoring the dioxin behavior and in the setting of optimal plant parameters in order to reduce dangerous emissions. In the present paper, both the process parameter tuning and the additive addition, all finalized to the PCDD/F reduction, are analyzed and the results presented. It is demonstrated how the optimal management of processing parameters and the precise utilization of additives lead to a strong reduction in dangerous emissions from EAFs.

12.2 Electric Arc Furnace Operations

The electric arc furnace investigated in the present study is a 100 t furnace designed for a maximum flow rate of 1500 Nm^3/h. The stack off-gases are emitted in the atmosphere through a 32 m height stack. In EAF, graphite electrodes carry the current through the furnace roof into the charge of metal. The electric arc formed melts the charge at very high temperatures. The melting sequence for the electric arc furnace comprises the different stages: charging, melting, oxidization, and tapping. The waste gases produced in the furnace are extracted through an aperture in the furnace roof and the dust from various sources in the housing. The waste gas is cooled to recover heating as steam, hot water, or electric energy and is then dedusted by cloth filters. In some operating conditions, the dust from the electric furnace can contain considerable quantities of heavy metals, such as zinc and lead, and so it is worth recovering them. After filtering, the examinations of the off-gases were performed according to EN 1948 parts 2 and 3, EN 1948SS (Sampling Standards, Wellington Laboratories), EN 1948ES (Extraction Standards, Wellington Laboratories), and EN 1948IS (Injection Standards, Wellington Laboratories), by employing a high-resolution gas chromatograph and a high-resolution selective

Table 12.1 Electric arc furnace processing parameters

Parameters	Value
Flow rate (Nm^3/h)	300–1100
Coke (t/h)	0.2–1.2
Gas temperature (°C)	60–350
Lignite (kg/h)	0–100

mass detector. The emission levels of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans are determined through a 12 h monitoring per each experimental condition in a time range of 4 years. Many experimental conditions belonging to different plant setup were monitored. These conditions are summarized in Table 12.1 in terms of plant processing parameters. Flow rate, coke, and gas temperature were considered as processing parameters of the electric arc furnace. In all the conditions, different quantities of lignite were added in order to monitor the effect on dioxin emissions. For selected experiments, 5 mmol of CuCl were added to the charge.

12.3 Greenhouse Emission Reduction

The main results of this study can be summarized as follows. Dioxin emissions decrease as flow rate increases (Fig. 12.1); very low rates of coke lead to an increase in dioxin emissions for low flow rate.

In correspondence of high flow rates, dioxin emissions decrease in correspondence of intermediate values of coke rate. Such behavior is a good indicator of plant efficiency; a high flow rate corresponding to a high plant efficiency leads to emission lowering. Also for high efficiency, coke rate should remain from low to intermediate values. Dioxin emissions decrease as the gas temperature and the flow rate increase (Fig. 12.2).

Dioxin compounds form in a temperature range of 200–600 °C with a maximum in the range 250–400 °C. The maximum levels of dangerous emission concentration are recorded at intermediate values of temperature and flow rate. Such behavior is time dependent; in this way, the more time off-gases remain at a stable temperature, the more dioxin formation is allowed. In this way, it is easy to demonstrate that, as increasing the gas flow and tuning the gas temperature far from the dangerous range, the emission levels are strongly reduced. In this way, it is not only the temperature that plays a role in the reaction kinetic but also the reaction rate due to the gas flow. The rapid cooling of off-gases coupled with high flow rate represents an optimal solution in reducing dioxin formation and improving the plant efficiency. Such a process control system can be used to regulate the furnace stability by working at operating parameters that reduce dioxin production in the plant. As a matter of fact,

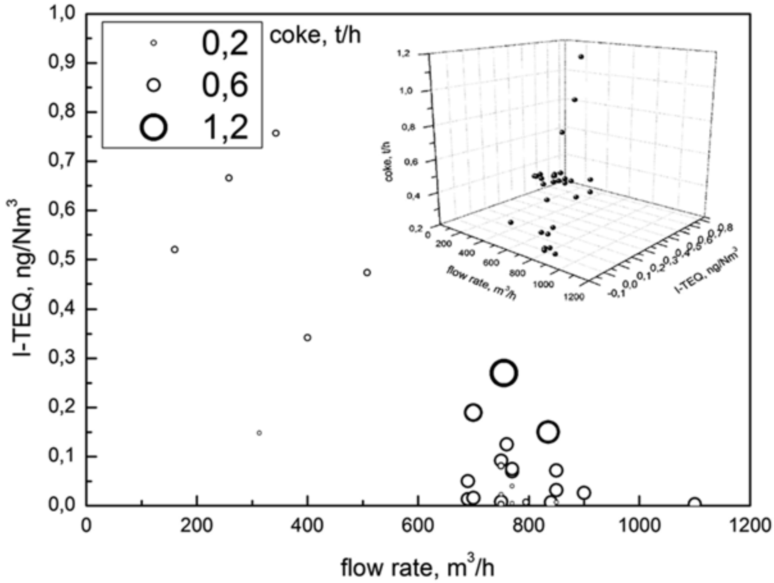

Fig. 12.1 Dioxin emissions as a function of flow and coke rates showing a decrease in dioxins level by increasing the flow rate and by fixing the coke rate to intermediate values

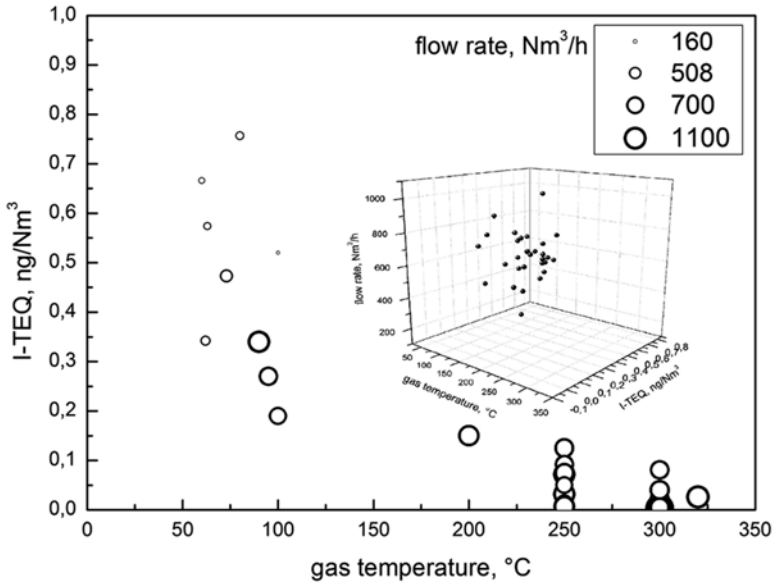

Fig. 12.2 Dioxin emissions as a function of temperature and flow rate showing the abatement of emissions by increasing both gas temperature and flow rate

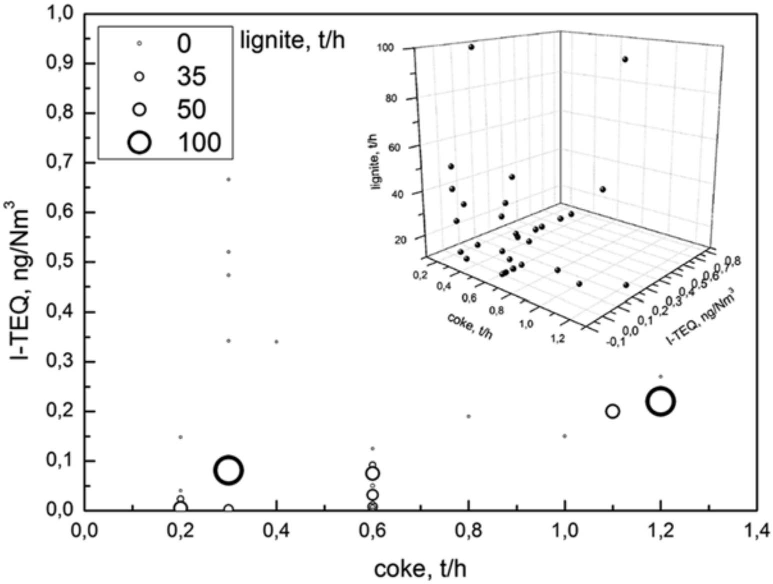

Fig. 12.3 Dioxin emissions as a function of coke rate and lignite addition, lignite injection contributes to the emissions reduction at fixed values of coke rate

many plant layouts employ off-gas post-combustion to destroy PCDD/Fs, but such system does not eliminate dangerous product formation.

Dioxin emissions decrease from low to intermediate values of coke rate; such reduction is amplified by lignite injection (Fig. 12.3).

Lignite coke can be employed to reduce dioxin/furan concentration when it is used as an adsorbent to the waste gas flow. PCDD/Fs are strongly reduced thanks to the lignite addition because of its strong bonding irreversible action on dangerous emissions and the further decomposition during heat treatment phase. Lignite is injected into the gas flow acting as a strong redactor of dioxin and furan emissions. Normally, the lignite injection is operated in different points of the gas flow pattern with various percentages; in the present study, the global addition of lignite to the exhaust gases is considered. For high coke rate levels, dioxin emission increases also with lignite injection. By taking a look to the dioxin evolution as a function of gas temperature and lignite injection, a strong decrease of emissions as temperature and lignite increase can be underlined (Fig. 12.4) even if lignite injection is still active at high gas flow temperatures.

A strong effect on the reduction of dioxin emissions is noted for the addition of CuCl. In Fig. 12.5, a strong reduction of emission level for the same lignite addition is due to the presence of CuCl.

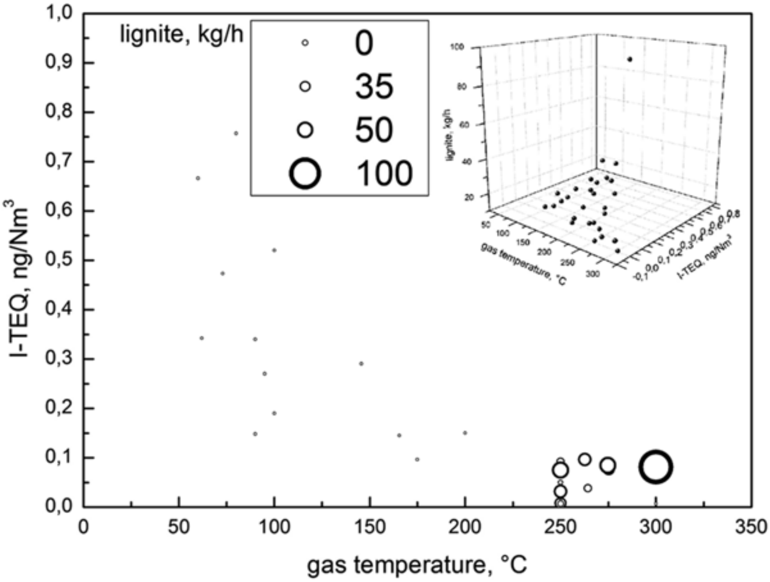

Fig. 12.4 Dioxin emissions as a function of gas temperature and lignite addition, high efficiency in emissions reduction is achieved by increasing temperature and lignite injection

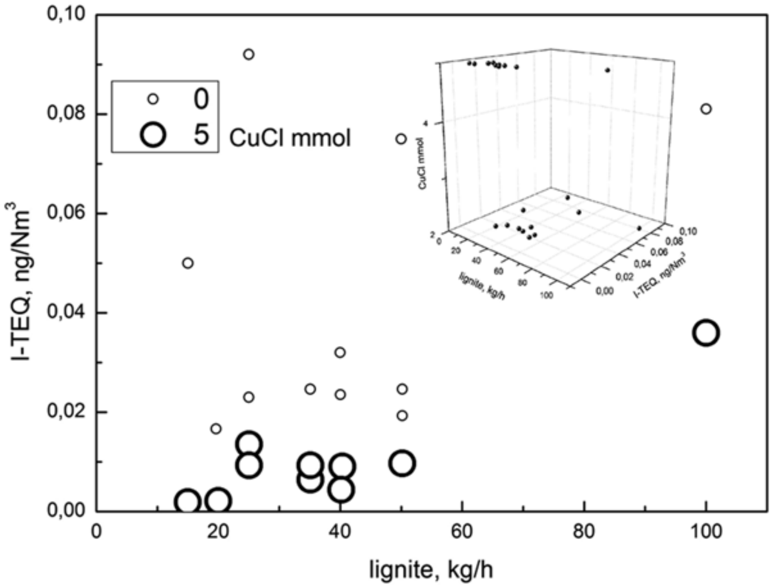

Fig. 12.5 Dioxin emissions as a function of lignite and CuCl, addition of CuCl is very efficient in reducing emissions levels

12.4 Conclusions

An electric gas furnace designed for a maximum flow rate of 1500 Nm^3/h was monitored in the present study. Different processing parameters were employed in order to measure the variation of dioxin and furan emissions to atmosphere. The results of the experimental analyses conduced to the main following conclusions:

- Dioxin emissions reach low levels at high flow rate and intermediate coke rates. Such result has been identified as a good instrument to control the PCDD/Fs control during the process.
- Also the temperature increase has a beneficial influence on dioxin and furan reduction.
- Lignite injection leads to a reduction in greenhouse emissions.
- An important effect on emission reduction is due to the addition of CuCl during processing.

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