

Reducing dioxin emissions in electric steel mills

During steel production in electric arc furnaces dioxins and furans are produced. These emissions depend on the scrap quality and can require additional waste gas cleaning. Adsorptive waste gas cleaning using activated lignite (HOK) in an entrained phase process constitutes one of the most simple and at the same time lowest-cost cleaning methods successfully applied in five European electric steel mills. Reliable pollutant reduction to dioxin and furan concentrations below 0.1 ngTE/m^3 are achieved.

Introduction

The increasing use of scrap significantly contaminated with organic substances leads to a deterioration in the quality of waste gases from EAF plants that process metallic scrap. The dimension of the waste gas flow to be treated in electric steel plants calls for waste gas cleaning processes that permit technically efficient and economically justifiable environmental protection.

Dioxin emission reduction plays a significant role here, all the more so since waste gas flows of sometimes more than 1 million m^3/h can result in considerable pollutant loads. During the thermal treatment of scrap contaminated with paints, oils or other organic substances, dioxins and furans are released or produced during waste gas treatment and emitted into the

evaporated off but not thermally destroyed; one result here being the formation of volatile organic chlorinated hydrocarbon compounds and the precursor compounds of dioxins and furans.

The requirement to decrease dioxin and furan emissions into the atmosphere calls for effective reduction facilities to be installed on the waste gas side. The reduction in PCDD/F emissions is also of particular importance as the EU Council of Ministers set the goal to achieve by 2005 a 90% reduction in dioxin emissions in the EU, as compared to the reference year 1985 [3]. Independent of this target, some countries have already established emission limit values for the operation of electric steel mills in the last few years, most of which are even more stringent.

Luxembourg taking the lead in emission limits

The authorities in Luxembourg were the first worldwide to stipulate an emission limit value of 0.1 ngTE/m^3 for dioxins and furans applicable as of January 1, 1997. The Arcelor subsidiaries Profilarbed and Ares, which operate several electric arc furnaces at various locations in Luxembourg, were thus the first electric steel mill operators to be forced to install a reduction facility ensuring both compliance with the limit value and maintenance of the steel mill's economic efficiency.

For the specific conditions prevailing in this sector of industry, RWE Power AG (formerly Rheinbraun AG), together with Ares, developed and started operation of an entrained-phase process in the **Schifflingen plant** in 1997. In this particular application, the process enables effective dioxin and furan reduction through simple injection of activated lignite into the waste gas flow upstream of the dust separator.

As a result of the positive dioxin reduction experience gained in the Schifflingen electric steel mill, the two **Esch-Belval** and **Differdingen** mills

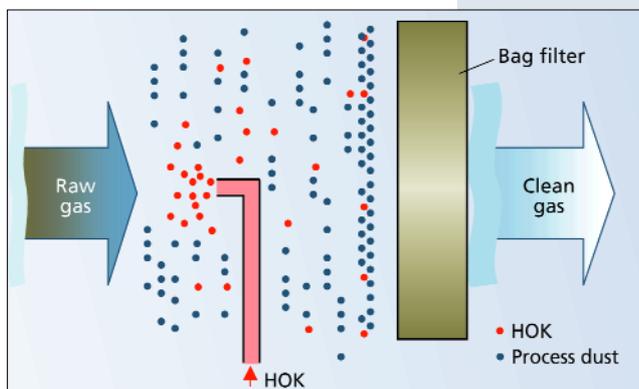


Figure 1. Pollution separation in the filter-bed process

atmosphere along with the furnace fumes. Comprehensive measurement programmes revealed that electric arc furnaces can emit polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) in concentrations between 0.02 and 9.2 ngTE/m^3 [1, 2].

The highest PCDD/F emissions with TE contents of up to 9.2 ngTE/m^3 were observed with electric arc furnace processes that include scrap preheating. Due to the process-specific low temperature in the scrap column, the organic constituents adhering to the scrap, such as oils and greases, are only

Charles Prüm, Plant Director Differdingen; Charles Werner, Head Environmental Protection Department, **Profilarbed S.A.** (Arcelor Group), Luxembourg; Jürgen Wirling, Head of Waste Gas and Waste Water Cleaning Group, **Rheinbraun Brennstoff GmbH**, Cologne, Germany

Contact: www.rheinbraun-brennstoff.de
E-mail: juergen.wirling@rwe.com

were also retrofitted in 2001 to include the waste gas cleaning technology. In addition, the electric steel mills at **Stahl Gerlafingen**, Switzerland, and **ALZ**, Genk, Belgium, decided to implement dioxin reduction by applying the activated lignite technology. At Stahl Gerlafingen, the entrained-phase system was commissioned in 1998, while the newly built ALZ Genk steel mill successfully started up its system in 2003.

Comprehensive measurements have confirmed that the activated lignite based plant meets the emission reduction demands placed on innovative environmental technology. Activated

time is required to have dioxins and furans adsorbed on activated lignite. This is the principle on which entrained-phase adsorption is based (figure 1).

In the entrained-phase process, the pulverized carbon-containing sorbent, usually activated lignite, is injected into the waste gas flow upstream of an existing dust separation unit; for example, a fabric filter or an electrostatic precipitator. An important precondition for achieving optimum separation efficiency is the presence of a homogeneous and at the same time turbulent mixture already at the injection

favourable pore structure present in the HOK lignite featuring high mesopore and macropore portions (1 to > 50 nm) permits easy access to the inner surface area which is decisive, among other things, for the adsorption of macromolecular compounds such as those of dioxins and furans.

The micro- and submicropore range (< 1 nm) which is more pronounced for many, and often expensive, activated carbons is frequently not, or only to a limited extent, useful for this application. The cleaning efficiency of HOK is favoured by the high pore volume of about 50 %.

The separation efficiency depends considerably on the probability of contact between the sorbent and the pollutant molecule. The distribution of the adsorbent in the waste gas flow plays a major role here and can be improved significantly by the milling rate.

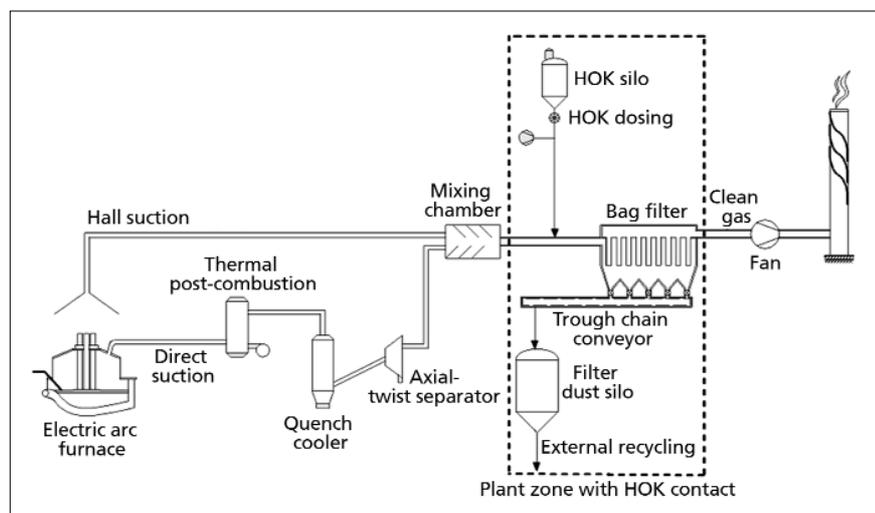


Figure 2. Dust separation system at the Esch-Belval electric steel mill

lignite based entrained-phase adsorption was included in the European Union's "Best Available Techniques Reference Document on the Production of Iron and Steel". The process thus is among the best technologies currently available in Europe for emission reduction in this field.

General process concept

Various adsorption processes are available, in particular the moving-bed and filter-bed processes known from waste incineration. In addition to their application in independent adsorption devices, the use of sorbents is increasingly integrated into existing dust separation processes. This allows investment costs to be significantly reduced without any major losses in separation efficiency.

Comprehensive investigations have shown that only a very short contact

tion point where the first pollutant separation step takes place.

A significant factor in selecting the adsorbents is an optimum pore radii distribution for pollutant molecule adsorption. Activated lignite which – as a mass sorbent – continues to be available at a much lower price level than most other activated carbons, features this property.

Activated HOK lignite differs considerably from most activated carbons both in terms of production and properties. Carbon activation of the lignite extracted in the opencast mines of RWE Power AG located near Cologne, Germany, is done according to the so-called rotary-hearth furnace process which gave this product its brand name HOK (German abbreviation for rotary-hearth furnace coke). The activated lignite thus produced has a characteristic pore structure which results in the high adsorption efficiency for a multitude of pollutants. The

Application at Esch-Belval

At the Esch-Belval plant, ProfilArbed operates an electric arc furnace with a tap weight of 155 t. Figure 2 shows the general layout of the electric furnace system with the subsequently installed entrained-phase adsorption facility for dioxin reduction. The waste gases produced during the melting process are exhausted immediately at the suction pipe of the electric furnace and, following post-combustion, supplied to an evaporation cooler via water-cooled pipes. Following waste gas cooling to about 250 °C, the coarse particles contained in the waste gas are separated in an axial-flow dust collector, the so-called spark separator. Subsequently, the furnace waste gases liberated from entrained sparks and coarse particles are supplied to the gas mixing chamber where they are mixed with the waste air of the hall. In the downstream fabric filter, the dust separation of the 80-100 °C hot mixed gas of some 1.2 million m³/h takes place. The filter dust accumulating in the fabric filter is discharged continuously, stored intermediately in a filter dust silo and recycled externally.

The adsorbent is directly fed into the mixed waste gas flow upstream of the fabric filter, which allows the gaseous pollutants to be reduced already in the dust-laden waste gas. The loaded HOK



Figure 3.
Overall view of the
activated lignite dosing system

is separated in the fabric filter together with the filter dust.

Process technology and safety concept

Both for process-related and safety reasons, the aim is to homogeneously distribute the activated lignite in the dust-laden waste gas. For intimate mixture and even distribution of the activated lignite over the waste gas pipe cross section, the activated lignite is fed into the gas flow at several injection points which are arranged symmetrically along the waste gas pipe's circumference (figure 3).

Due to its inactive behaviour, activated lignite can be safely used even at high waste gas temperatures. As with all carbon-containing sorbents, a precondition is compliance with safety requirements to avoid fire and explosion hazards.

In view of the process technology applied in electric furnace systems, fire and explosion protection is achieved through a combination of preventive measures such as HOK inertization by the filter dust, exclusion of active ignition sources through, e. g., the entry of sparks and spontaneous ignition

processes of the filter dust as well as limitation of the HOK portion in the filter dust. An essential point here is the assessment of the filter dust's ignition behaviour in a mixture with carbon-containing sorbents, so that it may be necessary in some cases to limit the carbon portion.

Depending on the type and composition of the process dust, a mixture of catalytically active process dusts and activated carbons/coke may have a higher propensity to ignite. To exclude such hazards, the amount dosed is limited in accordance with the safety requirements for the operation of the filter system. In collaboration with the Luxembourg steel mills, RWE Power clarified this fact for HOK use to the extent that such operational disturbances are reliably prevented through adjusted process parameters. Combined with the exclusion of any entry of active ignition sources, the reduced propensity to ignition of the HOK process dust mixture provides an additional and, hence, redundant fire protection measure.

Possible ignition sources that represent fire hazards are, for example, high-energy sparks which enter the fabric filter together with the waste gas. This is a problem frequently encountered by

many plants as the entering sparks burn holes into the filter cloth, which inevitably leads to higher dust emissions. To prevent dust emissions from reaching unacceptable levels and avoid fire hazards when applying entrained-phase adsorption it is frequently indispensable to employ spark separators. Spontaneous ignition reactions of the filter dust are reliably prevented through consistent avoidance of large-volume deposits in the plant section subjected to hot gas flows.

Under the above conditions, which can be attained by comparatively simple measures, entrained-phase adsorber operation is possible at all times. This is confirmed by the positive operational experience gained with this technique.

PCDD/F reduction

Comprehensive measurement programs performed in the waste gas flows of the electric arc furnaces at Ares and Profilarbed yielded dioxin and furan emission values of up to 1.44 ngTE/m³. The amount of PCDD/F emissions is influenced by the specific plant technology and feedstock applied (table 1).

The low PCDD/F emissions in the clean gas attainable with dosing rates below 30 mg/m³ illustrate the high adsorptive effect of HOK. Even with very low HOK dosing rates, remarkable separation efficiencies with clean gas values well below 0.1 ngTE/m³ can be reached.

A comparison of the PCDD/F concentrations measured at the Schifflingen melting plant using two HOK variants reflects the impact of the milling rate on the separation efficiency. Compared with the standard quality having a mean grain size diameter of 63 µm, the clean gas value could be cut by more than half with the dosing of reduced amounts of super-milled "HOK super". The dosing rate only amounts to 35 or 25 mg/m³. Several investigations revealed that a further reduction would only be possible with major losses in cleaning efficiency.

As far as compliance with the PCDD/F limit concentration is concerned, it remains to be said that not only the efficient adsorptive separation of the gaseous dioxins and furans by HOK but also reliable elimination

Plant	Gas flow 1,000 m ³ /h (stp)	Added HOK kg/h	Emission in clean gas ngTE/m ³
Ares,	750	without	0.178-1.44
Schifflingen	750	100 ¹⁾	0.085 - 0.226 (Ø 0.144)
	750	35 ²⁾	0.003 - 0.008 (Ø 0.006)
	750	25 ²⁾	0.023 - 0.092 (Ø 0.047)
Profilarbed,	850	without	0.072 - 0.722 (Ø 0.314)
Esch-Belval	850	40 ²⁾	0.007 - 0.032 (Ø 0.021)
Profilarbed,	770	without	0.040 - 0.714 (Ø 0.336)
Differdingen	770	50 ²⁾	0.005 - 0.075 (Ø 0.025)
Stahl Gerlafingen	690	without	< 2.0
	690	15 ²⁾	< 0.05
Ugine-ALZ, Genk	840	20 ²⁾	0.002 - 0.007

¹⁾ use of HOK standard (63 µm)
²⁾ use of HOK super (24 µm)

Table 1. PCDD/F reduction as a result of HOK addition (excerpt)

of the particle-bonded dioxins and furans are important prerequisites for PCDD/F reduction. Sound functioning of the dust separator and low dust emissions are fundamental conditions for the successful use of integrated entrained-phase adsorption, since already low dust discharge rates entail an increase in total PCDD/F emissions.

Filter dust use

The added HOK depositing in the fabric filter together with the filter dust usually only means an up to 3% weight increase in the carbon concentration in the dust to be processed. The external processing including recovery of the valuable materials, which is common at electric steel mills, is not affected by this, provided downstream filter dust processing is based on the application of carbon in the metallurgical process (such as the Waelz process).

Investigations show that the organic pollutants, such as PCDD/F, adsorbed on activated lignite are bonded irreversibly due to the high bonding forces and are reliably destroyed or catalytically decomposed during thermal treatment.

Operating performance

The first entrained-phase adsorption system installed at an electric melting furnace was commissioned in 1997 at the Schifflingen steel mill. When the first measured results revealed that the

standard product, pulverized activated lignite (HOK 63 µm), only allowed PCDD/F contents of just under 0.1 ngTE/m³ to be reached, a higher dosing rate of approx. 150 mg/m³ was adjusted. This, however, caused damage to the filter bags due to smouldering fire and dust deposits in the fabric filter. These events were found to be due to the reactivity of the process filter dusts which, in a mixture with the fed carbon, lead to a higher propensity to ignition of the filter dust mixture. Changing to the super-milled sorbent "HOK super", the larger surface area of which permits a low dosing rate, eliminated the disturbances and improved PCDD/F separation efficiencies. The following findings which should generally be considered in integrating entrained-phase adsorption into electric steel mills were derived from these initial disturbances.

At increased waste gas temperatures and in the presence of flying sparks, the filter dusts catalytically active in electric melting furnaces may lead to the ignition of the filter dust mixture and damage to the filter cloths. This is why the carbon portion in the filter dust mixture is limited.

To prevent smouldering particles from entering the fabric filter, a spark separator is to be installed upstream of the filter to ensure that the waste gas flow is technically free from sparks.

Filter dust discharge by the discharge cones is to be done continuously, i.e. large-volume dust accumulations in the filter area are to be avoided. For this reason, level probes were installed.

As the findings in terms of plant technology and operation made at the electric furnace system in the Schifflingen plant have been implemented in practice and no significant operational disturbances have occurred since then, it can be stated that the HOK technology has proved its worth as a reliable, low-maintenance technology for reducing PCDD/F emissions in electric steel mills. The operational experience gained in the five plants built so far has without exception been positive.

Conclusion

A total of five European electric steel mills successfully implement entrained-phase adsorption on HOK. The operational experience gained over several years has shown that the applied process and safety technology has proved its worth. Process-integrated entrained-phase adsorption on HOK has turned out to be a technically safe and at the same time low-cost process for reducing the PCDD/F emissions of electric steel mills. The 0.1 ngTE/m³ limit value specified for dioxins and furans is strictly adhered to.

For electric steel mill operation, the HOK technology provides the advantage of employing scrap preheating which otherwise is often not implemented because of the increased release of pollutants. Scrap preheating, however, allows higher efficiencies to be reached due to the better heat utilization during the melting process. Combined with RWE Power AG's several decades of experience in HOK, the low-cost mass sorbent activated lignite provides an integral solution for implementing innovative environmental protection in the steel industry. ■

References

- [1] Report by the working group of the Air/Technology sub-committee of the Immission Control state committee – Erarbeitung von Anforderungen zur Emissionsbegrenzung für Dioxine und Furane – April 1993
- [2] Puetz, R.: Dioxinproblematik bei metallurgischen Prozessen der Stahlindustrie, Doctoral thesis, Technical University of Aachen, 1996
- [3] Phillip, J.A.: Verringerung der Dioxinemission an Sinteranlagen; Final Report by the Federal Environmental Agency, 50441-5/217, Dec. 2002