Environmental Aspects and Recycling of Filter Dusts by Direct Injection or Use of Agglomerates in Shaft Furnaces

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In the last decades the recycling of filter dusts of the iron and steel industry has become more and more important due to environmental as well as economical reasons. Beside of so-called end of pipe technologies, processes are required which ensure an efficient waste management with regard to productivity and profitability of steelworks. In this context the development of integrated systems is necessary to recover and to recycle valuable components.

This paper describes possible techniques for an integrated treatment of filter dusts. On the one hand the injection of filter dusts in shaft furnaces is studied. For the trials a laboratory injection rig is used which simulates the injection of solids under conditions similar to the blast furnace. On the other hand the use of briquettes and pellets with embedded carbon in a shaft furnace is investigated by means of laboratory and industrial pilot trials.

The results will be described and discussed with regard to the reduction behaviour of different coal-dust mixtures.

KEY WORDS: dust recycling; injection process; blast furnace; cupola furnace; pellets; briquettes; reduction mechanism; iron and steel industry.

1. Introduction

The production of iron and steel is closely related to the recovery of high amounts of dusts and sludges. Approximately 1.016 Mio t dusts and sludges were collected in Germany.1) For these materials processes are required which ensure an efficient waste management with regard to productivity and profitability of steelworks. The development of integrated systems is necessary to recover and to recycle valuable components.

In the past the amount of dusts emitted could already be significantly reduced by better dust separation or better process technologies. However, this development is the result of an increasing public or legislative pressure and leads to an increasing amount of dust collected.

In Germany, the administrative regulations for the treatment of these materials are given by the Federal Immission Control Act (FICA) and its administrative regulations, the TA Luft (Technische Anleitung zur Reinhaltung der Luft). The legislation requires substantial and sustained environmental protection by means of saving raw material sources and avoidance of material going to landfill.2)

In accordance to the legislation steel producers have the opportunity to implement closed loop recycling processes. In this paper the attempt is made to meet legislative and operational requirements by two different ways of processing filter dusts in shaft furnaces: 1) Combined injection of coal and dust, 2) Use of carbonaceous agglomerates (briquettes, pellets).

2. Previous Investigations

2.1. Combined Injection of Coal and Dust into Shaft Furnaces

A combined injection of coal and dust into a shaft furnace may have the following advantages:

– avoidance of additional beneficiation or agglomeration steps,
– increase of the combustion degree of some coals by the “solid oxygen” supply from iron oxides and catalytic effects, respectively,
– use of steel plant residues which cause due to their very fine particle size difficulties during a pelletizing or briquetting process,
– recycling possibility for steel plants that do not operate a sinter plant,
– recycling possibility for materials that can cause emission problems or disturb the operation during the sinter process.

For a combined injection of coal and dust three types of shaft furnaces were considered: blast furnace, cupola fur-
nace and Imperial-Smelting furnace. With regard to an injection of dust the metallurgy and the product quality of each furnace must be considered.

For a stable operation of a blast furnace an increased input of alkalis, zinc and lead should be avoided. With regard to the product quality the limit for an input of copper, chromium and nickel is very low, especially for those plants that are specialised on flat products. Therefore the number of dusts that can be injected into a blast furnace is restricted to iron and carbon containing materials, e.g. blast furnace flue dust and mill scale.

In comparison to the blast furnace the cupola furnace offers some advantages. Those furnaces are usually operated discontinuously and the off-gas temperature is relatively high (ca. 300°C). Because of these characteristics a built up of inner circuits of alkalis, zinc and lead is hardly possible. The higher off-gas temperature leads to an increased output of volatile elements, which means that an enrichment of zinc and lead in the filter dust is favoured.

In this furnace an injection of BOF-(Basic Oxygen Furnace) dust or EAF-(Electric Arc Furnace) dust is possible without disturbing the process or the product quality.

The Imperial-Smelting furnace as zinc and lead producing unit is a shaft furnace, too, but its operation technique is completely different to the blast furnace or cupola furnace. One of the main differences is that at the furnace top secondary hot blast is injected that leads to a post combustion of carbon monoxide. This heat is necessary to keep zinc in gaseous state. After passing the furnace top zinc is cooled down and collected in a condenser. Instead of pig iron or cast iron, lead is tapped at the furnace bottom. In such furnace zinc rich dusts should be injected.

Although each of these furnaces has a typical operation practice, the conditions in the tuyere area are, taking into account certain restrictions, comparable. Therefore trials were performed at a laboratory injection rig, that simulates the conditions while injecting solids into the raceway of a blast furnace under blast furnace similar conditions (Fig. 1). The parts 1–4 of the experimental rig in Fig. 1 illustrate the simulated parts of the tuyere and the raceway as shown in the same figure. The aim of these investigations was to determine the injection behaviour of different coal-dust mixtures taking into consideration:

- the particle size,
- coal and dust type,
- the reduction behaviour of different iron oxides,
- the influence of dust additions on the combustion behaviour of coals,
- reduction and volatilisation behaviour of zinc-containing dusts.

At the beginning of the eighties, a laboratory rig was built at the Institute of Ferrous Metallurgy to investigate pulverised coal injection in detail. The rig simulates the behaviour of fines injected into the raceway of the blast furnace.

While simulating blast-furnace conditions the effect on the ignition and combustion behaviour of different coals such as anthracites or charcoal by varying parameters like coal porosity, particle size, content of volatile matter, carbon and ash or injection rate could be tested. Further investigations were performed to analyse the effect of catalysts on coal conversion, oxygen enrichment of the hot blast, preheating of the injected coals or different lance geometries.

Further experiments were performed to analyse the injection of plastic waste and automobile shredder residues into the blast furnace and cupola furnace. Another project did concern the measurement of the raceway depth. The raceway sensor consists of a short pulse laser and allows the measurement of distances inside the furnaces to an accuracy of a few centimetres by the time-of-flight technique. The influence of changing blast parameters like temperature, humidity and oxygen enrichment on the raceway depth was also investigated.

For the investigation of a combined injection of coal and fine iron ore a modified laboratory rig was built (Fig. 1) and pilot trials were performed at a charcoal blast furnace of the company Mannesmann S.A. (MSA), Brazil. The new apparatus was put into a vertical position without bends to avoid particles staying in the preheating or induction fur-
nace and to avoid molten particles to agglomerate on the inside of the tube. The sample is blown by a shock wave into preheated gas with 1 100°C, simulating the hot blast, mixed with it and passed through a high temperature zone of 1 700°C, simulating the raceway. The combustion gases are analysed to their contents of CO, CO₂, O₂, H₂ and CH₄ and the combustion degree is calculated. Further on an inlet of nitrogen was mounted near the filter to put the reaction products in an inert atmosphere for keeping them from further reactions on the filter right after each trial. The reaction products are analysed to their complete content of iron without concerning about valency (Fe₃⁺) and their contents of elementary iron (Fe⁺) and bivalent iron (Fe²⁺). From these values Fe₃⁺ is determined and the reduction degree is calculated. The existence of Fe²⁺ and Fe¹⁺ indicates an incomplete reduction and the presence of wustite and magnetite, respectively.

2.2. Reduction and Smelting of Agglomerates

In a shaft furnace process the kind of iron precipitation is of a great interest. In general three kinds of precipitations are known. Their existence is depending on temperature and partial pressure of the reducing gas (e.g. carbon monoxide). In Figure 2 the areas of their existences are shown. The precipitations can change the size and stability of agglomerates or lead to sticking and plating. By use of hydrogen instead of carbon monoxide for the reduction the catastrophic swelling and sticking as well as the decomposition can be reduced.

In the cohesive zone in the blast furnace “hollow icicles” have been found. Their origin can be explained as follows. The reduction by reducing gas can take place faster in the outer than in the inner part of the pellets. The temperatures necessary for reduction are reached faster outside the pellet and the reducing gas supply is higher. A steel shell with a melting temperature of more than 1 500°C is built up. The FeO-content, high carbon contents and low eutectic temperature in presence of SiO₂ in the inner part cause a melting above about 1 150°C. The contact areas between the pellets can not be reached by the reducing gas like the rest of the surface. At these places the reduction will be slowed down and FeO is still existing. The low melting point allows a smelting of the shell at these spots. The liquid phase from one pellet can flow down in a deeper one. A solid, connected steel shell is formed. Such a “hollow icicle” is shown in Fig. 3.

3. Results and Discussion

3.1. Experiments to the Combined Injection of Coal and Dust

Tables 1 and 2 show analyses of the dusts and the coals used for the experiments. By injecting iron containing materials it was found out throughout all tests that by using a coal with a low content of volatile matter (coal Niederberg) the highest reduction degree was reached. Thus results gained from earlier experiments could be confirmed.

The laboratory experiments have shown that a reduction of hematite iron oxide (e.g. in flue dust) to metallic iron is possible within the short residence time of 10–20 ms. The reduction degree is increasing continuously with increasing amount of coal in the mixture, see Fig. 4. During the injection of dusts that contained FeO or Fe⁺ (BOF- and EAF-dust, mill scale) a reoxidation of those components was observed. This behaviour is shown for BOF-dust in Fig. 5.

Further experiments were performed in order to determine the influence of dust additions on the combustion behaviour of an anthracite coal (Niederberg) with blast-furnace flue dust residues and rolling mill scale. Figs. 6 and 7 show the results when flue dust and oily mill scale were added.

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Chemical analysis has shown that hematite is reduced to metallic iron. Therefore it is very likely that the combustion of the coal is promoted by the “solid oxygen” supply from the iron oxide and by catalytic effects. Further on the reoxidation of FeO and Fe_{met} provides heat that promotes coal combustion.\(^{15}\)

In addition, trials were performed in which the volatilisation behaviour of zinc in the short residence time of 10–20 ms was investigated (Fig. 8). It was found out that the volatilisation degree is strongly dependent on the particle size. In case of a very fine particle size the volatilisation degree decreased. The particles form agglomerates which are difficult to reduce. In such cases the employment of a low volatile coal was necessary (coal Niederberg) whereas for zinc dusts with larger particle size the volatile matter of the coal was of minor significance. Due to these results it is very likely that an enrichment of zinc in the filter dust of e.g. a cupola furnace is possible.

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Fig. 4. Reduction degrees of a blast furnace flue dust/coal-mixture.\(^{31}\)

Fig. 5. Reduction degrees of a BOF dust/coal-mixture.\(^{31}\)

Fig. 6. Combustion behaviour of a blast furnace flue dust/coal-mixture.\(^{31}\)

Fig. 7. Combustion behaviour of oily mill scale/coal-mixture.\(^{31}\)
3.2. Experiments to the Reduction and Smelting of Agglomerates

For the theoretical understanding of the reduction of agglomerated dusts tests with hematite ores were performed in a Tamman furnace.\textsuperscript{29–31} The ores were mixed with different amounts of anthracite (6%, 12% and 18%) as a reductant and 3% bentonite as binder. Then they have been pelletized. The temperature range of the test series was 700 to 1500°C and the reduction time was 15 min. To exclude the influence of gases an inert atmosphere of argon has been built up in the furnace.

In the temperature range from 800°C to 1000°C a border between a lighter and a darker part inside the pellets has been observed with the pellets cut in half. A delay of 3 min was measured to reach the same temperature in the middle as at the outer part of the pellet. The amount of carbon in the middle of the pellets after the test was higher than at the outer part of the pellets because of the temperature difference at the beginning of the tests.

The chemical analysis showed furthermore a better reduction in the inner part of the pellet than in the outer part because of the argon atmosphere. The argon is able to dilute the produced CO gas in the outer parts of the pellets and the potential of the reducing gas is lowered.

A strong decrease of hematite could be seen up to 1100°C with 12% carbon as reductant. Until that temperature the amount of hematite in the inner part of the pellet was lower than at the outer part of the pellet. Higher amounts of carbon result in a faster reduction at temperatures up to 1100°C whereas less carbon shows a low degree of reduction of hematite.

Parallel to the decrease of hematite the amount of FeO increased up to temperatures of 1100°C. Above this temperature the content of FeO decreased again and first metallic iron occurred. The parallel decrease of FeO and increase of metallic iron is the result of the higher potential of produced reducing gas at these temperatures. Only with that high potential of the reducing gas hematite can be reduced to metallic iron. The test series showed the amount of embedded carbon is an important parameter for the degree of reduction. The produced reduction gas is able to reduce over 99% of the iron if the carbon content of the agglomerate is 18%. Lower amounts of carbon reduce only 57% of the iron with 12% carbon and 33% with 6% carbon (Fig. 9).

In the test series with 18% carbon it could be seen that Widmannstätten’sch Ferrit was formed. This can only happen if the oxygen is completely removed from the iron and a carburisation can take place.

For the industrial use the influence of stability and reduction behaviour of the briquettes is very interesting. Therefore agglomerates produced from different dusts, bound by different binders as well as mixed with or without carbon have been examined.

Lukat\textsuperscript{29} found out that cement bound briquettes have a high stability but an incomplete reduction. Due to the faster reduction of the iron oxides in the outer part of the dust briquettes a steel shell is formed, see Fig. 10. Further increase of temperature causes collapse of that shell. Finally a completely separated slag and metal phase are appearing. The chemical analysis of the metal is comparable to that of cast iron\textsuperscript{29,31}.

In tests briquettes with carbon mass contents of less than 18% showed a good reduction but no carburisation during heating and smelting. Based on the experience in laboratory tests a cupola furnace has been run with briquettes without binder and carbon contents of 18%. Exchange rates of 10, 20 and 30% during normal production have been reached.\textsuperscript{29,31,32}

4. Conclusions

The experiments carried out may lead to the following conclusions:

(1) The reduction behaviour of dust-coal mixtures is
dependent on the particle size and the composition of the dusts. A reduction of hematite iron oxides and a volatilisation of zinc, respectively is possible within a short residence time of 10–20 ms.

(2) The combustion degree of a low volatile coal can be increased by adding $\text{Fe}_2\text{O}_3$, FeO or Fe$_{\text{resid}}$. Taking into account that injected iron oxides will be reduced exclusive in the region of the direct reduction and that this fact will result in a higher coke consumption, the better combustion of the coal might lead to a minimisation of this negative effect.

(3) The injection of zinc containing dusts enables an enrichment of zinc in the filter dust. This way of converting residuals to value added charge materials offers the opportunity to reuse them within the plant or to sell them more profitably.

(4) Dust and slurries produced by various facilities of the iron- and steel industry have to be avoided. The recovery of dusts by charging pelletized or briquetted filter dusts into shaft furnaces offers a solution for this problem regarding to the circulation bill.

(5) Investigations at the Institute of Ferrous Metallurgy in Aachen extended the already known phenomena of collapsing smelting of pellets on iron ores and filter dusts with embedded carbon. Parallels during the reduction and partly smelting of conventional pellet specimen like the formation of an outer shell at higher temperatures but also differences were recognised due to the argon atmosphere used in the test series. The formation of a steel shell could be seen in tests with briquettes where carbon was added.

(6) These results and further basic research with iron ore pellets with embedded carbon trigger the development of new recycling processes for iron- and Steel Industry dusts, especially a new shaft furnace process. One test series to investigate the influence of different amounts of embedded carbon showed that at least 18% carbon are necessary to reach a complete reduction of the iron oxides. The temperature for the reduction has to be above 1 000°C to get metallic iron. Under this temperature only FeO is formed.

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References

1) G. Grund, K. Krone, J. Krüger, W. Hofmann and G. Rath: 2. Aachener Umwelttage, Aachen, Germany, (1992).
2) G. Klein: United Nations Economic Commission for Europe, Seminar on the Steel Industry and Recycling, (1995).
3) H. Denecke: PhD Thesis RWTH Aachen, (1999).
4) H. W. Gudenau, S. Wippermann and H. Denecke: Proc. Ironmaking Conf., ICSTI, Toronto, Canada, (1998), 517.
5) H. W. Gudenau and H. Denecke: Int. Symp. on Beneficiation, Agglomeration and Environment, ISiban, Bhubaneswar, India, (1999), 282.
6) B. Korthas: PhD Thesis RWTH Aachen, (1987).
7) T. Yang: PhD Thesis RWTH Aachen, (1985).
8) L. Birkhäuser: PhD Thesis RWTH Aachen, (1990).
9) H. W. Gudenau, T. Yang, T. Ariyama and B. Korthas: Fachber. Hüttenprax. Metallweiterverarbeit., 22 (1984), 930.
10) J. Cappel: PhD Thesis RWTH Aachen, (1990).
11) P. Assis: PhD Thesis RWTH Aachen, (1991).
12) R. Kiesler: PhD Thesis RWTH Aachen, (1992).
13) M. Joksch: PhD Thesis RWTH Aachen, (1993).
14) H. W. Gudenau M. Peters and M. Joksch: Stahl Eisen, 114 (1994), 81.
15) M. Rudack: PhD Thesis RWTH Aachen, (1993).
16) G. Schwaneckamp: PhD Thesis RWTH Aachen, (1997).
17) H. W. Gudenau and G. Schwaneckamp: VDI-Seminar 43-20-02 Thermische Behandlung von Abfällen, Düsseldorf, (1996).
18) F. Robert: PhD Thesis RWTH Aachen, (1997).
19) S. Wippermann: PhD Thesis RWTH Aachen, (1996).
20) H. W. Gudenau, L. Birkhäuser, M. Rudack and S. Wippermann: Proc. 11th Annual Int. Pittsburgh Coal Conf., vol. I, (1994).
21) H. W. Gudenau, F. Azevedo, H. Denecke and S. Wippermann: International Seminar Environmental Protection and New Technologies in the Iron and Steel Industry, Belo Horizonte, Brazil, (1995) 7.
22) H. W. Gudenau, F. R. S. Azevedo, L. Birkhäuser, H.-G. Rachner, H. Denecke, L. F. da Silva and S. Wippermann: Stahl Eisen, 117 (1997), 61.
23) H. W. Gudenau, M. Sasabe and K. Kreibich: Stahl Eisen, 97 (1977), 291.
24) H. W. Gudenau and K. Stoesser: Lecture at Kobe Steel Inc., (1997).
25) U. Gebel: PhD Thesis RWTH Aachen, (1989).
26) H. W. Gudenau, J. Fang, T. Hirata, U. Gebel: Steel Res., 60 (1989), 138.
27) R. Degel: PhD Thesis RWTH Aachen, (1996).
28) T. Sharma, R. C. Gupta and B. Prakash: ISIJ Int., 32 (1992), 812.
29) B. Lukat: PhD Thesis RWTH Aachen, (1999).
30) K. Stoesser: PhD Thesis RWTH Aachen, (2000).
31) L. Birkhäuser, H. W.- Gudenau, B. Lukat and K. Stoesser: Steel Res., 69 (1998), 391.
32) H. W. Gudenau and B. Lukat: TIMS/IEHK Metallurg. Symp., Cairo, (1997).