Scale Recycling Through Self-Reducing Briquettes to Use in EAF

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This work is part of a project which aimed to provide a theoretical and experimental basis for recycling of mill scale from mini-mill plants. The focus of the present study was to evaluate the kinetics and the mechanisms of reduction in self-reducing briquettes composed of scale, charcoal and binders, aiming its use in EAF. Such briquettes were submitted to the following tests: thermogravimetry in micro- and macro-thermobalances with analysis of the generated gas, evaluation of the temperature profile inside the briquette and the metallization degree obtained by tests carried out in muffle furnace at a high heating rate. Previous studies, concerning scale and charcoal taken together with the results of this work indicate that both, the kinetics of scale reduction and the heat transfer limit the overall reaction rate of the briquette. However, the relatively high metallization degree of 76% obtained in the high temperature tests indicates the interest in using such the briquettes for scale recycling in industrial plants. The risk of reoxidation is low due to the protective role of gas evolving from the briquette during self-reduction.

KEY WORDS: mill scale; charcoal; self-reduction; reoxidation; EAF.

1. Introduction

Economically viable recycling of wastes rich in iron, like mill scale from continuous casting and rolling mill processes, in form of self-reducing composites containing carbonaceous solid reductants, is a challenging problem for all steel works and especially for the mini-mills.

In fact, the mini-mills operate with the electric arc furnaces (EAF) conceived primarily for efficient steel scrap melting. Therefore, an addition to the EAF process, even in a limited form, a function of reduction of iron oxides needs to consider how the process parameters, optimized for quick scrap melting, fit with the conditions required for a heating and reduction of the iron oxides/carbon composites in form of briquettes, pellets or others agglomerates. It is clear that this process should occur in such a way that the iron oxides of scale could be reduced as far as possible before the charge melting thus avoiding an increase in the energy consumption and a decrease in the metallic yield of the process.

Many studies on the self-reduction process, reviewed yet in two previous papers,1,2 have indicated that the overall reaction rate in the iron oxides/carbon agglomerates is limited either by the chemical reactions or by heat transfer. The main reactions occurring when heating such the self-reducing mixtures are the gaseous reduction of iron oxides: Fe$_3$O$_4$ + y CO = x Fe + y CO$_2$; and the gasification of carbon by CO$_2$ (Boudouard reaction): C + CO$_2$ = 2 CO; the second regenerates a reducing potential of atmosphere enabling thus the first to go forward.

In the fundamental studies a mill scale was rarely used as an iron oxides bearing component of self-reducing mixture. Therefore, in the first paper,1 the chemical and morphological characteristics of the mill scale were investigated together with its reduction behaviors. The chemical and structural characterization of the mill scale showed that wustite is its major constituent, with the small amounts of hematite, magnetite and metallic iron. The gaseous reduction of scale by carbon monoxide has a topochemical character regardless of its initial morphology, but the reduced iron reveals the different morphologies, depending on temperature and gas composition. The unreacted shrinking core model with one interface fits quite well the kinetic data and the activation energy of reduction of the powdered scale by CO is about 80 kJ/mol.

In the second paper,2 the self-reduction experiments of mill scale with four potential carbonaceous reductants (charcoal, coal char, blast furnace coke and petroleum coke) were carried out by thermogravimetry. The highest rate of self-reduction was measured when charcoal was used as reductant whereas the lowest was found for petroleum coke. Based on the apparent activation energy value found at different conversion (reduction degree) it was concluded that under studied conditions the Boudouard reaction controls the rate of self-reduction with charcoal up to about 60% of conversion and even more for others reductants. These results demonstrate that the reactivity of reductant is of a capital importance for the self-reduction process. Firstly, it determines the temperature at which the reduction starts and secondly, when reaction progress under non-isothermal con-
ditions, it influences the temperature and reduction degree at which the rate controlling reaction shifts from carbon gasification to wustite reduction.

This reasoning applies well for the agglomerates small in weight and size (briquettes, pellets, powder poured into a crucible) used in the studies of self-reduction by thermogravimetry\textsuperscript{3–7} or chemical analysis of evolving gas\textsuperscript{8, 9} at laboratory scale. In these cases, it is implicitly admitted (and sometime experimentally proved) that there is not a significant temperature gradient inside the sample. Consequently, it is considered that the reactions occur homogeneously in its whole volume.

However, when a self-reduction of bigger in size and mass agglomerates is investigated (such as the industrial briquettes or the reaction systems, like fixed or moving bed), the temperature profile inside an agglomerate is greatly affected by endothermic effect of Boudouard reaction.\textsuperscript{10–15} Consequently, the heat transfer (external or/and internal) is found to play an important role in the process and it is claimed as the rate controlling step. In this case, the physical characteristics of the agglomerates (size, shape, porosity, heat conductivity of the constituents etc...) and the heating regime to which the briquette is submitted, influence on the overall reaction rate.

Hitherto, a self-reduction of iron oxides/carbon agglomerates was studied mainly having in mind their use in the blast furnace or various direct reduction process where the rate of heating is low and the time for reducing is relatively long. The present study is part of a project which aimed to provide a theoretical and experimental basis for recycling mill scale in form of self-reducing briquettes in a mini-mill plant\textsuperscript{8} via EAF where in contrast a heating rate will be high and time for reduction short. Taking this into account it deals with three specific aspects of the process. Firstly, the kinetics of self-reduction of briquettes is measured by a micro- and macro-thermobalance with a simultaneous analysis of evolving gas to better assess the self-reduction rate controlling phenomena. Secondly, the thermal profile inside the briquette of industrial size is measured during the heating and its impact on the final composition of reduced briquette is revealed. Finally, admitting that during a charging the atmosphere of EAF is at least partially oxidizing, the possibility of reoxidation of freshly reduced briquette is also examined.

2. Experimental
2.1. Raw Materials

The constituents of the mixture used in the manufacturing of self-reducing briquettes were: scale, charcoal and binders (molasses and lime). The chemical composition and the quantitative distribution of the iron phases of the scale, given in Table 1, were measured respectively by Inductively Coupled Plasma Spectroscopy and Mössbauer Spectrometry. The total reducible oxygen content deduced from chemical and phase analysis is 22.1%. The proximate analysis of charcoal given in Table 2 has been carried out according to the ISO standards. The moisture of the charcoal was 6.35 mass% on as received base.

The mill scale was introduced in the briquette as it was generated (particle size 85 mass% < 2.5 mm), while the charcoal fines were crushed to 85 mass% < 0.84 mm. The proportion between scale and charcoal aimed to reach a molar ratio C\textsubscript{fix}/O\textsubscript{red} near 1, for the fixed carbon (C\textsubscript{fix}) and reducible oxygen of scale (O\textsubscript{red}). The mixture composition of briquettes is shown in Table 3.

The briquettes were produced in an industrial plant with a rolling press machine. The mean weight of the briquettes was approximately 150 g and their external aspect and dimensions are presented in Fig. 1. Figure 2 shows the tex-
ture of fractured briquette with the bright particles of scale and the gray matrix consisted of charcoal and pores. Micrograph of the polished section of briquette in Fig. 3 shows the bright, elongated particle of scale and the charcoal particles with characteristic cellular microstructure. The big inter and intra particles pores (black) are also visible.

The pore size distribution of briquettes (as well as of the scale and charcoal), measured by mercury porosimetry, is shown in Fig. 4. The apparent density of briquettes (from mercury porosimetry) ranges from to 2.2 to 2.4 g/cm³ while the open porosity varies from 27 to 29%. From the pores size distribution curves, seen in Fig. 4, one can deduce that the porosity of briquette is mainly due to the charcoal, which has very high porosity (50–60%) and low density (1.2–1.4 g/cm³). On the other hand, the scale has low porosity (12%–27%) and high density (4.5–4.8 g/cm³). It is interesting to note, that taking into consideration only two main components of briquette (scale and charcoal), the volume fraction of briquette occupied by charcoal is 47 vol% (19 mass%), by scale 26 vol% (71 mass%) and by pores 27 vol%.

2.2. Thermogravimetric Study

To measure the kinetics of reduction and the final extent of reaction, two different set-ups and procedures were used:

- Netzsch STA 409 PC Luxx thermobalance, allowing the reduction of the small samples (100 mg) of powdered briquette in nitrogen with a limited heating rate (up to 50 K/min);
- Dasfos “macro-thermobalance” RF-33/TV set-up, presented schematically in Fig. 5, allows the reduction of a whole briquette (150 g) heated with a limited rate (40 K/min up to 800°C and 25 K/min above, up to 1 100°C) under controlled atmosphere (Nitrogen) and with analysis of evolved gas (CO, CO₂) by URAS3 infrared analyzer. The mass of the briquette is continuously monitored by electronic balance and the temperature measured by central thermocouple corresponds to the briquette surface.

The results of thermogravimetric measures of self-reduction are characterized by the evolution of sample relative Mass (%) and Conversion (X) defined as follow:

\[
\text{Mass}(\%) = 100 \times \frac{M(t)}{M_{\text{initial}}}, \quad X = \frac{M_{\text{initial}} - M(t)}{M_{\text{initial}} - M_{\text{final}}}
\]

where \(M(t)\) is an actual mass of sample at time \(t\), \(M_{\text{initial}}\) is an initial mass of sample and \(M_{\text{final}}\) is a final mass of completely reduced sample.

From the briquette composition given in Tables 1, 2 and 3 the theoretical mass losses and the conversion (X) corresponding to the main reactions and mass loss steps are calculated (Table 4). The first and second rows of this
table show respectively the mass losses due to the drying (2.41 mass%) and to the devolatilization of molasses and charcoal (8.18 mass%). These “theoretical” value of moisture and volatiles of briquettes are simply calculated as the sum of moisture and volatiles introduced by each briquette component.

The third row corresponds to the oxygen reduction (15.7 mass%) and the carbon gasification (11.78 mass%). Knowing that the reducible oxygen content in the scale is 22.1 mass% and that the briquette contains 71% of scale the mass loss corresponding to the complete reduction is thus 22.1*71/100 = 15.7%. The amount of carbon used for that depends on the composition of the gas produced (CO and CO₂) which can be expressed as CO₂/(CO+CO₂). When admitting that the produced gas contains only CO, the gasified carbon mass equals the oxygen mass loss multiplied by (12/16), i.e. 15.7*12/16 = 11.78%. Therefore, the calculated total maximum mass loss of sample is 38.07 mass%.

It should be noticed that in this calculation two hypotheses are necessary. The first concerns a possible partial reduction of the scale by volatiles. In fact, some contribution of volatiles in the self-reduction of iron oxides agglomerates with charcoal, coal and plastics was yet observed. It concerns especially the early stage of reduction, i.e. the reduction of the higher iron oxides (hematite and magnetite) to wustite. It is thus obvious that the contribution of the hydrocarbons in the reduction diminishes the solid (fixed) carbon consumption. The second hypothesis take into consideration the theoretical need of carbon depends also on the composition of gas produced by self-reduction. It could be just pure CO, but also a mixture of CO and CO₂ as it was shown in some studies. The higher is the oxidation ratio of evolving gas, the lower is obviously the theoretical carbon consumption and consequently a total calculated theoretical mass loss.

In the studied briquettes with scale as the main component, the total reducible oxygen stands for 15.7 mass% from which only 1.8 mass% corresponds to the reduction of the hematite and magnetite present in the scale to the wustite. The carbon gasified by the reduction (with hypothesis that the lone gaseous product of reduction is CO) thus stands for:

- 15.7*12/16 = 11.78 mass% - when all oxygen is reduced by carbon;
- (15.7–1.8)*12/16 = 10.43 mass% - when the reduction by volatiles is admitted.

With assumption that the evolving gas is partially oxidized, the consumption of carbon is lower and can be calculated as follows:

- 15.7*(12/16)/(1+(CO₂/(CO+CO₂))) = 9.81 mass% - without reduction by volatiles,
- (15.7–1.8)*(12/16)/(1+CO₂/(CO+CO₂)) = 8.67 mass% - when reduction by volatiles is considered.

In both cases CO₂/(CO+CO₂) was taken as 0.2.

Therefore, as it is shown in Table 5, the total theoretical mass losses due to the complete self-reduction of studied briquettes should be in the range of 38.07 to 34.96 mass%.

- Fractional reduction

Fractional reduction \( F \) is defined as the ratio of the reduced oxygen to the total reducible oxygen in the sample. Taking into consideration the initial mass losses due to moisture and volatiles elimination, the fractional reduction of the iron oxide \( F \) could be calculated as follows:

\[
F = 100 \times \frac{\text{Reduced oxygen}}{\text{Total reducible oxygen}}
\]

\[
F = 100 \times \frac{X(t) - 0.278}{1 - 0.278}
\]

for \( X \geq 0.278 \)

where 0.278 is the conversion relative to sample drying and devolatilization.

### 2.3. Temperature Measures in the Briquette during the Heating and Reduction

The temperature profile inside the briquettes was measured to evaluate the heat transfer during heating and reduction. A muffle furnace equipped with a sample holding device (mobile door coupled with a grid to suspend the briquette with the thermocouples), presented in Fig. 6(a), was used to carry out the measures. The grid from refractory steel was designed to place the briquette equidistant from the furnace’s walls. The thermocouples (type K – 1 mm in diameter) were placed in three different radial positions of the briquette: surface (T3), middle (T2) and center (T1) (Fig. 6(b)). Additionally, a thermocouple touching the wall (T4) was introduced to the central part of the furnace. For each test, after stabilization of furnace temperature at 950°C, the sample was quickly introduced to the furnace. During the heating the atmosphere in the furnace was slowly renewed by natural air draft. The measures last until stabilization of temperature measured by the thermocouples T1, T2 and T3.

### 2.4. Interrupted High Temperature Tests

To evaluate the self-reduction kinetic of the briquette in the conditions close to the EAF, these tests were carried out at the high heating rate (about 120°C/min) up to 1 400°C using a high-temperature muffle furnace with a vertically

| Table 5. Calculated mass losses according to the hypotheses concerning the reduction by volatiles and the evolving gas composition. |
|------------------|------------------|------------------|------------------|------------------|
| Hypothesis | Reduction by volatiles | CO₂/(CO+CO₂) | Partial mass losses due to: M+V+O+C* (mass%) | Total (mass%) |
| 1 (Max) | no | 0 | 2.41+8.18+15.7+11.78 | 38.07 |
| 2 | yes | 0 | 2.41+8.18+15.7+10.43 | 36.72 |
| 3 | no | 0.2 | 2.41+8.18+15.7+ 9.81 | 36.10 |
| 4 (Min) | yes | 0.2 | 2.41+8.18+15.7+ 8.67 | 34.96 |

* M – moisture, V – volatiles, O – reduced oxygen, C – gasified carbon
opening door. The furnace was first pre-heated to 1 050°C and then the briquette was introduced to the furnace and heated up in about 12 min to 1 400°C and maintained in this temperature for further 3 min. Next, it was quickly removed and cooled with liquid nitrogen (to avoid the oxidation/reduction reactions). A final reduction extent of the briquettes was calculated from mass loss and from the chemical analysis before and after testing.

2.5. Reoxidation Tests
Assuming that heating and reduction of briquettes in EAF occurs in an atmosphere which is slightly oxidizing, some reoxidation of freshly reduced briquette can also arise. To check this hypothesis, two series of measurements were done by thermobalance (Linzeis L81) in non-isothermal conditions with a relatively high rate of heating (150 K/min). In both series, a sample of powdered briquette, weighing approximately 1 g, was poured into an alumina crucible (I.D. – 10 mm). Then, placed on the sample holder, it was quickly introduced to furnace preheated to suitable temperature (ranging from 800 to 1 100°C).

To do that, the thermobalance, presented in Fig. 7, was used without a protective alumina tube. In the first series, the furnace stayed open at the top and the bottom thus allowing: firstly, its quick but controlled descent on the sample and secondly, the natural draft which procured an ascensionnel air flow around the sample. In the second series, the top opening of the furnace was obstructed by the ceramic plug to limit the natural draft and the access of oxygen to the sample.

3. Results
3.1. TG Tests
In the first series of experiences, the reduction of the small samples (100 mg) of powdered briquette was investigated to identify the different steps of self-reduction as well as the conditions of temperature and time to attain the complete reduction. Figure 8 shows the curves of mass evolution of two samples during the heating up to 1 050°C with two isotherm plateaus: first, at 150°C and the second, at 1 050°C. The dashed stepwise line represents the cumulated mass loss, calculated from the initial chemical composition of the briquette, as shown in Table 5. It is seen that at the first plateau, the moisture elimination was completed with about 2% of mass loss. Next, during the heating from 200 to about 700°C, the mass loss increased to 11% due to the devolatilization of the molasses and charcoal. During the last step, at the temperatures above 700°C, the iron oxides reduction and the carbon gasification by self-reduction mechanism increases the cumulated mass loss up to 37.1 mass% which enters into the calculated range of final mass loss (Table 5).

In Fig. 9, these three successive steps (i.e. drying, devolatilization and reduction/gasification) are well distinct on DTG curves. Moreover, it is worth to notice, at about 750°C, a relatively small peak which likely corresponds to the reduction of higher iron oxides (hematite and magnetite) to wustite.
3.2. Macro-thermobalance Tests

Figure 10 shows the weight loss curves of two entire briquettes reduced in two distinctive tests. As for the small powdered samples, the measured total mass loss (37.6 mass%) fits quite well the calculated mass loss range. It is also seen, that the mass loss curves are smoother, i.e. without clear boarders between the successive steps (drying, devolatilization, reduction). It is likely the effect of a higher heating rate and, even more, of the bigger sample size and weight.

Figure 11 shows the concentration of carbon oxide and dioxide in the evolving gas together with the curve of weight loss rate (DTG). The concentration of CO and CO₂ varies in the same way as the rate of mass loss. At low temperatures, during the drying and devolatilization, the maximum mass loss rate corresponds to the maximum concentration of CO₂. However, during this stage the gas composition is greatly impaired by the water and hydrocarbons which concentration was not measured. At temperatures above the devolatilization range, when CO and CO₂ became the main components of generated gas, the significant increase of CO concentration corresponds well to the raise of the gasification and reduction rates due to the temperature increase.

The concentration of CO and rate of reduction attain their maximum at almost the same time and later both decrease gradually even though the temperature remains the same (1 050°C), thus reflecting the slow-down of self-reduction rate with fractional reduction and gasification.

3.3. Temperature Profile in the Briquette during the Heating and Reduction

Figure 12 shows the evolution of temperature at different positions of the radial section in the briquette in the muffle furnace preheated to 950°C. The surface temperature of the briquette (T3) increases very quickly and faster than the temperature in the inner regions, reaching a maximum around 980°C. The higher temperature of the surface compared to furnace’s wall in the first minutes of the test (Fig. 12(b)) is likely related to the combustion of evolved volatiles in the oxidizing atmosphere of furnace. The temperatures of core (T1) and middle part of the briquette (T2) increase also quickly but only up to about 700°C and with some delay at the beginning (below 150°C) which clearly comes out at the thermocouple placed in the center (T1).
This relatively low heating rate measured at the middle and center of briquette in the first minutes (Fig. 12(a)), is due to the heat consumption for moisture evaporation.

Above 700°C the heating rate gradually decreases and a long temperature plateaus appear: at the middle of briquette (T2) at about 860°C and in the center (T1) at 800°C. The formation of these plateaus is due to the highly endothermic Boudouard reaction which acts as the heat sink maintaining the temperature almost steady as long as the couple of reactions (gasification and reduction) simultaneously occur. It is interesting to note that temperature T2 started to increase from plateau at 860°C to 950°C after about 30 min showing that the front of reaction attains a half of briquette thickness and goes forward to the center.

### 3.4. Interrupted High Temperature Tests

In this series of experiments the briquettes were heated up to 1400°C with a high heating rate and partially oxidant atmosphere. The briquettes submitted to these tests showed an average weight loss of about 33% which is less than the maximum of 38 mass% measured by macro-thermobalance (Fig. 10). This corresponds to the reduction degree of 82%. On the other hand the metallization degree \( \frac{\text{Fe}}{\text{Fe}_{\text{total}}} \) of the reduced briquette, obtained by wet chemical analysis, is 76%. Thus both measures indicate that there is still some residual wustite and carbon in the briquette.

The macroscopic observation of cross-section of the reduced briquette, presented at Fig. 13, reveals two different textures: gray, porous but well sintered shell and dark, grainy and still slightly brittle core. The wet chemical analysis and the carbon content measures (carried out by LECO CS – 225 analyzer) of these two parts shows their different composition: in the shell, the metallization is about 85% with only 0.2 mass% of carbon and in the core, the metallization is only 37% but there is still 3.8 mass% of carbon. It should be noted that the image of the cross-section of partially reduced briquette reveals that at macroscopic scale the self-reduction progress according to shrinking core model thus confirming the conclusions from the heat transfer measurements (Fig. 12). The observations of polished sections of briquettes (Fig. 14) show that at microscopic level the reduction of the single scale grains has also topochemi-

### 3.5. Test of Reoxidation

Figure 15 shows the mass evolution of a small powdered briquette sample heated with low heating rate (30 K/min) first to 1000°C in nitrogen which after the complete reduction is replaced by air. This replacement causes a quick mass increase which fits quite well the calculated mass increase due to the complete oxidation of freshly reduced iron (step 3) to Fe2O3 (step 4 of dashed line). It is thus highly probable, in the tests of self-reduction, that even in slightly oxidizing atmosphere, some oxidation can occur during the heating and self-reduction. In fact, this is demonstrated in Figs. 16 and 17 which show the self-reduction of powdered briquette samples heated quickly (150 K/min) respectively up to 1100°C and 810°C in a full open furnace conditions and in a limited air access atmosphere.

Figure 16 shows that at the high temperature (1100°C) and in the slightly oxidizing atmosphere the mass loss attains its theoretical maximum (about 38%) and only after that a slow mass increase due to the iron reoxidation appears. At the low temperature (810°C), the reduction is...
much slower and the mass loss stops already at about 33%, followed by a noteworthy mass increase due to the reoxidation which, apparently, becomes faster than the reduction.

In air, regardless a temperature, the self-reduction starts with a similar rate as in the limited air access conditions, but with its progression the mass loss rate decreases and gradually changes into the mass increase. In low temperature, this change happens yet at about 26% of mass loss (which correspond to about 50% of reduction) while in the high temperature, the mass loss slows down more sharply and stops at about 32 mass% (i.e. 80% of reduction). In both cases, after reaching a minimum, the mass of samples starts to increase with the rate which is bigger in higher temperature. Such the samples mass evolution indicates that it results from the competition between the reduction and the reoxidation. The balance of this competition depends on the furnace atmosphere composition, the heating rate as well as of the extent of self-reduction.

4. Discussion

In this work, firstly the questions related to the rate controlling factors were examined in the light of the results discussed in the earlier two works.\(^1,2\) In the first, the rate of gaseous reduction of the scale in pure carbon monoxide and in its mixture with carbon dioxide (90 vol% CO and 10 vol% CO\(_2\)) was measured in the isothermal conditions in the temperature range 800–1200°C\(^1\). In the second, the gasification rate of the charcoal by CO\(_2\) was measured in the same temperature range.\(^2\) Thus, in Fig. 18, through the results from these works, the rates of two main reactions of self-reduction measured separately are plotted for comparison. It shows that the rate of the charcoal gasification is slower than the scale reduction up to about 900°C. However, at higher temperature, the scale reduction becomes slower than charcoal gasification, suggesting that when occurring simultaneously in self-reducing mixture, depending on the temperature of process, one or another could limit the overall reaction rate.

At this point, it should be stress that a mill scale is rather less reducible than many other iron oxides bearing matters used in the self-reduction studies and, on the other hand, the charcoal is more reactive than the majority of reducing agents, such as coal, coke, anthracite, petcoke or graphite. Moreover, the activation energy of wustite reduction by CO is much lower than that of carbon gasification by CO\(_2\).
Therefore, the combination of a low reducibility of scale with a high reactivity of charcoal suggests that the reaction of reduction could influence on the overall kinetic at the relatively low temperature.

Some complementary information about controlling reactions comes also from the evolved gas composition which was measured in the tests of self-reduction at the macro-thermobalance. The change of this composition with temperature (corresponding to the results presented in Figs. 10 and 11) is shown in Fig. 19 together with the equilibrium diagrams of iron oxides reduction and carbon gasification. At the low temperatures (< 600°C), the reduction potential of evolving gas (CO/(CO + CO2)) is low (0.25) due to the oxygenated compounds introduced by drying and devolatilization products of molasses and charcoal. In the temperature range 600–800°C the reducing potential of gas increases (0.3–0.4) allowing the reduction of hematite and magnetite to wustite. Next, in the temperatures above 800°C, the gasification of charcoal effectively starts and increases a reduction potential of gas. In the temperature range 800–900°C, it is quite close to the Fe/FeO equilibrium (0.6). This means that the overall rate of self-reduction is controlled by carbon gasification rate. When the temperature increases further (900–1 050°C) the composition of the evolving gas moves away from the Fe/FeO equilibrium, but it still stays far from the Boudouard reaction equilibrium.

At first glance, such the evolution could be interpreted as the take of the overall rate control by the reduction of wustite and this conclusion would be correct for the tests with a small sample which temperature could be considered as uniform and under control by a heating program. However, in the case of the bigger samples (like the entire briquettes used in this study) their temperature is not uniform as show the measures examined in the chapter 3.3. The temperature gradient inside the briquette implies that at the different positions the self-reduction proceeds with different rate and produces the gas of different composition: in the core (where the temperature and reduction degree are lower) the gas stays more oxidized than in the shell (where the temperature and reduction degree are higher). However, the reason of this is not a low intrinsic rate of Boudouard reaction but a limited heat transfer. In fact, when the rate of gasification rises with the temperature and when simultaneously the reduction front progress deeper into the briquette, the heat transfer cannot satisfy the increasing needs of highly endothermic gasification in the reaction zone.

Thus the results of this work confirm and explain the conclusions of some earlier studies where the role of heat transfer as a controlling step was demonstrated experimentally or postulated on the base of mathematical modeling. Moreover, the results of this work suggest that it is not enough to increase the reactivity of reductant to accelerate self-reduction rate if there are not some simultaneous measures in order to increase the heat transfer in the agglomerate (for example by increasing density and heat conductivity of self-reducing mixture, by optimizing agglomerate size and shape, by intensifying heat transfer condition in a furnace, etc.)

Concerning the risk of reoxidation of partially reduced briquette in a moderately oxidizing atmosphere of EAF (during the charging), this study shows that the self-reduction up to 70–80% could proceeds without significant reoxidation. In fact, during the heating the gas generated by self-reduction creates around the briquette a kind of protective cloud (film). At the beginning, it is composed by the devolatilization products (H2O, CO, CO2, hydrocarbons and hydrogen) and later, when self-reduction intensively occurs, it is just a mixture of CO and CO2. This cloud acts effectively (in the first phase of self-reduction) as a barrier, in which oxygen diffusing from bulk atmosphere of the furnace is consumed reacting first with hydrocarbons and later with CO. When, at higher conversion (in the second phase of self-reduction), the flux of gaseous products (CO and CO2) across the porous shell decreases, the oxygen can attain the surface of briquette. The schematic representation of such mechanism is drawn in Fig. 20.

At this sketch one can distinguish three zones inside the briquette and the adjacent gas film:

- **unreacted core**, wherein after drying and devolatilization the gas has the composition close to the iron/ wustite equilibrium \((p_{\text{CO}} \approx p_{\text{Fe}/\text{FeO}}^{eq})\) and where the rate of Boudouard reaction is very slow due to the temperature relatively low and controlled by the heat consumption in the reaction zone;

- **reaction zone (R.Z.)**, wherein simultaneously the reduction and gasification occur at the temperatures higher than in the core of the briquette. However, this temperature increases more slowly than the temperature of shell due to the heat consumption by Boudouard reaction, which rate depends more on the heat balance than on the intrinsic gasification kinetics;

- **shell** of the reduced iron containing small amounts of the residual wustite and carbon and wherein the partial pressure of CO is higher than at wustite/iron equilibrium \((p_{\text{CO}} > p_{\text{Fe}/\text{FeO}}^{eq})\). Depending on the external temperature and the bulk gas composition this shell could undergoes some physicochemical changes like sintering, melting and even reoxidation.

- **adjacent gas film**, which is formed by gas generated in R.Z. which flows outside due to the slight pressure gradient resulting from non-equimolar character of Boudouard reaction. The extent and composition of this gas film vary with time. At the beginning of self-reduction (first phase), oxygen diffusing towards the briquette surface is consumed.

![Fig. 19. Evolution of the reduction potential of gas generated during self-reduction of briquette at macro-thermobalance.](image-url)
by combustion of CO to CO₂. As long as the partial pressure of CO₂ stays below equilibrium value for iron to wustite oxidation (p_{\text{CO}_2} < p_{\text{CO}_2}^{eq, \text{Fe/FeO}}) the reaction of reoxidation is not possible. However, later (second phase) when the decreasing flux of evolving gas cannot balance the oxygen flux, the partial pressure of CO₂ becomes higher than equilibrium value (p_{\text{CO}_2} > p_{\text{CO}_2}^{eq, \text{Fe/FeO}}). Consequently, the reduced iron is reoxidized by CO₂ or even directly by O₂, first at the surface and later deeper in the briquette.

It is clear that the bigger is a briquette size, the bigger is the flux of evolving gas and consequently the thickness of adjacent gas film which reduces the risk of reoxidation. In contrast, the increasing of the briquette size increases the risk of early heat transfer control.

5. Conclusion

The performance of self-reducing briquettes composed of scale and charcoal was evaluated in light of its use in EAF. Details concerning the particular characteristics of mill scale reduction and charcoal gasification obtained in recent works were a fundamental step to elucidate the phenomena arising when heating entire briquettes of “industrial” size in the condition close to EAF.

Taking together into account the evolution of briquette mass losses, the generated gas composition, the temperature profile inside the briquette during a heating and the chemical composition profile of partially reduced briquette it appears that the heat transfer to the reaction zone for covering heat of self-reduction is a main rate controlling step.

The time for complete reduction at a relatively slow heating rate up to 1 050°C under nitrogen is about 70 min. Such a long time for self-reduction is not available in EAF process. However, in the tests with a rapid heating up to 1 400°C in 15 minutes 76% of metallization was obtained.

The reoxidation of freshly reduced iron before melting seems to be limited due to the protective role of the “gas cloud” formed around the briquette by devolatilization and self-reduction gaseous products which stops the diffusion of oxygen inside the briquette.

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