Researches on the production of self-reducing briquettes from waste containing iron and carbon

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Abstract. The extension of the raw material basis for the steel making industry represents a priority nowadays, within the context of sustainable development. The issue is of utmost importance particularly now when the environment legislation sets strict dumping conditions on the one hand and, on the other hand, when huge quantities of waste, already deposited in dumps and ponds raise serious problems in terms of meeting such conditions. The paper introduces some researches on exploiting waste containing iron and carbon in steel making; this powdery and small-grain waste is to be processed into briquettes. The self-reducing briquettes can be used in steel elaboration in electric arc furnaces, replacing the scrap, which is scarce.

1. Introduction
The iron oxide reduction takes place by direct way with carbon and indirect with carbon monoxide and hydrogen. In practice, it frequently occurs the situation in which the reduction is combined both with carbon (solid reducing agent) and with reducing gas (carbon monoxide and hydrogen).

Typically, iron ores are used in obtaining pig iron in blast furnace, either directly or in the form of pellets, briquettes, and agglomerate or sponge iron. In the electric arc furnaces, iron ore can be used as the oxidizing material introduced during oxidation period. However, due to intensive exploitation of the deposits, the quantities of ore are greatly diminished.

Furthermore, in the context of sustainable development, increasingly they focus more on recycling wastes containing elements which are useful in steel plants, waste with a high content of iron and carbon, but low in the content of unwanted elements. Thus, wastes from iron and steel industry can be used, such as blast furnace dust, EAF dust, scale from mills, sludge from blast-agglomeration, sideritic wastes; also there may be used any waste from other industries, but with adequate chemical composition: red mud (resulting from the alumina production), thermo-energetic ash, etc [1–3].

2. Laboratory experiments
The experiments took place in the laboratories of the Faculty of Engineering Hunedoara, Polytechnic University of Timisoara, and aimed to obtain compacted self-reducing briquettes from small and pulverous waste with high content of iron and carbon [1,2].

To obtain the briquettes, there were used the following waste categories: dust from furnaces and steel plants, rolling mills scale, red mud, graphite powder and for chemical composition correction and for bonding, we used lime and bentonite. The briquettes chemical composition is presented in table.1.
In these experiments, we performed briquettes reducing at a temperature range of 500-1300°C, for a period of 22 minutes (average time). Experiments were made in a particular setting similar to the Hamborn furnace, and, in a certain degree, similar of FASMET process [4].

Table 1. Briquettes chemical composition, subjected to reduction processes

| No. recipe | Recipes chemical composition, [%] | FeO* | Fe₂O₃* | C   | SiO₂ | Al₂O₃ | CaO  | MgO  | MnO  | S     | P₂O₅ | other oxides |
|------------|-----------------------------------|------|--------|-----|------|-------|------|------|------|-------|------|-------------|
| 1          |                                   | 10.402 | 52.951 | 19.09 | 6.421 | 2.432 | 5.81 | 0.58 | 1.224 | 0.489 | 0.129 | 1.026       |

*Fe_total = 45.28%

For heating there have been used two resistance furnaces to reduce in a certain period of time several briquettes, on the one hand, and on the other, to provide charging the melting furnace with hot briquettes (newly reduced). In the first furnace (it may be heated up to 1200°C) has been heated to a temperature from 650°C to 1050°C and in the second furnace from 1050°C to 1300°C (it may be heated up to 1700°C). After a maintaining at temperature of 1050°C for a period of 15-16min., the briquettes were removed and placed in the second furnace where, after final heating, they were maintained for 6-7min. to a temperature of 1250-1300°C.

In the first furnace 24 briquettes can be heated at the same time, while in the second furnace can be heated only 4 briquettes. The total time of these operations was 115min (including times for transfer the briquettes in the other furnace). Randomly it was determined the metallization degree for 4 briquettes (equation (1)), the average of which is 93.48%, being considered for future technological calculations.

\[ g = \frac{\%Me_{\text{reduced}}}{\%Me_{\text{total}}} \times 100\% \]  

(1.)

Hot briquettes were introduced in Tamman furnace for melting. The Tamman crucible furnace has a capacity of 3kg cast iron, so, given the iron content of the briquettes and their specific weight, in the crucible was charged as melting 2.75kg briquettes. To obtain a slag basicity ratio \( I_B = \frac{\text{CaO}}{\text{SiO}_2} = 1.15-1.30 \) we made the addition of lime to 0.03 – 0.04kg.

Because the melting process has taken place in the graphite crucible, the carburization (with carbon from graphite) leads to advanced usage; so it has been made and addition of coke of 0.040kg/charge.

In the conducted experiments, we have produced a number of 3 charges, in Tables 2 and 3 being presented the chemical composition of cast iron and slag.

The melting time was 30 -35min.; when melting has been completed the molten metal (cast iron) and slag have been cast in the graphite ingot. After that it has been determined the weight of cast iron and slag, the metal removal (yield) have been presented in Table 2.

Table 2. Cast irons chemical composition

| Charge no. | C   | Mn  | Si  | P    | S    | Fe   | Yield, [%] |
|------------|-----|-----|-----|------|------|------|------------|
| 1          | 3.68| 0.78| 0.67| 0.14 | 0.06 | 93.77 | 49.13      |
| 2          | 3.95| 0.88| 0.79| 0.16 | 0.05 | 94.17 | 48.41      |
| 3          | 3.84| 0.92| 0.72| 0.16 | 0.05 | 94.31 | 48.09      |

Table 3. Slags chemical composition

| Charge no. | CaO  | SiO₂ | Al₂O₃ | MgO  | FeO  | MnO  | S   | CaO/SiO₂ |
|------------|------|------|-------|------|------|------|-----|----------|
| 1          | 43.21| 36.74| 8.42  | 5.82 | 0.97 | 0.81 | 1.81| 1.18     |
| 2          | 42.98| 35.84| 9.10  | 6.12 | 0.87 | 0.75 | 1.56| 1.20     |
| 3          | 44.34| 36.05| 9.56  | 8.05 | 0.91 | 0.96 | 1.83| 1.23     |
The second part of the experiments was performed in an induction furnace with a capacity of 10kg (cast iron /steel), with the metal bath volume of 1,45dm$^3$ (it was taken into account the molten metal that has a specific gravity equal to 6.9kg/dm$^3$ and 3kg/dm$^3$ for liquid slag). In the research it was considered that hot iron fills about 60% of the crucible volume and the rest returns to slag resulting from the reduction and smelting of the briquettes.

There have been developed 2 charges, in all cases the charges had 2 metal components (Table 4) as follows: 5kg solid cast iron + (3.0-3.5)kg briquette + 0.130kg lime (to provide a basicity ration CaO/SiO$_2$ = 1.15) + 0.100kg fluoride (to increase the fluidity of slag).

| Charge no. | Charge components, [kg] | Total, [kg] | Type briquettes |
|------------|-------------------------|-------------|-----------------|
| 1          | 5                       | 3.5         | 0.13            | 0.10         | 8.73         | Recipe 1 (table 1) reduced |
| 2          | 5                       | 3.0         | 0.15            | 0.12         | 8.27         | Recipe 1 (table 1) nonreduced |

As mentioned above, in each charge its loaded into a furnace a solid cast iron and then the furnace was connected, and, as melting progressed, it was gradually introduced all of the cast iron. Because the charge was clean, the amount of resulting slag was practically insignificant (after cast iron smelting we extract average of 215g slag). When that melting was completed, the temperature was measured and it was sampled to determine the metal melt chemical composition (Table 5). After heating for 5 min., it has been continued the charging of the briquettes, thus ensuring the continuity of addition. Along with the addition of briquettes there were also made additions of lime and fluorine to correct the slag chemical composition.

| Charge no. | Chemical composition, [%] |
|------------|---------------------------|
|            | C  | Mn | Si  | P  | S  | Fe  |
| 1          | 4.03 | 0.96 | 0.77 | 0.14 | 0.06 | 94.04 |
| 2          | 3.95 | 0.84 | 0.79 | 0.16 | 0.08 | 94.18 |

All the materials were weighed before charging into the furnace. After the completion of melting the entire furnace charging, it was maintained 5 minutes for thermal mixing and fluidization of slag, and then both the metal melt and the slag were poured in graphite ingots and were weighed after cooling with extracted slag, in order to perform mass balance.

Also for determining the recovery rate of iron from briquettes it was determined the chemical composition of cast iron and slag.

During the addition the following were determined:

- Charge No.1:
  - the addition of tubular briquettes, with a degree of metallization 93.48% it was in quantity of 2.46 kg briquettes, added as melting;
  - the shape and porosity of metal briquettes favored their melting in relatively short time 9 min.

- Charge No.2
  - the addition of tubular self - reducing briquettes but initially not reduced was in the amount of 3.00kg added as melting;
  - the tubular form of briquettes allow their rapid heating, which ensures intensive development of carbon reduction reactions, as demonstrated by the flames emitted from the surface of the metal bath, formed as a result of carbon monoxide combustion resulted from reduction reactions;
  - briquettes time melting was 13 min.

Below is the presented the charge balance and results of laboratory tests, final tests on iron and slag, and technical calculations.
### Table 6. Charge balance

| No. | Cast iron [kg] | Briquettes [kg] | Addition I [kg] | Addition II [kg] | Total [kg] | Cast iron I [kg] | Slag I [kg] | Cast iron II [kg] | Slag II [kg] | Total melt [kg] | Gases dust [kg] |
|-----|----------------|-----------------|-----------------|-----------------|-----------|-----------------|------------|-----------------|------------|-----------------|----------------|
| 1   | 5.0            | 2.46            | 0.230           | -               | 7.69      | 4.786           | 0.214     | 5.791           | 1.57      | 7.575           | 0.12           |
| 2   | 5.0            | 3.0             | 0.230           | -               | 8.23      | 4.797           | 0.203     | 5.707           | 1.31      | 7.22            | 0.41           |

1) lime + fluorine; 2) ferrosilicium and graphite powder; 3) cast iron + slag I + slag II.

### Table 7. Cast iron chemical composition

| Charge no. | Chemical composition, [%] |
|------------|---------------------------|
|            | C  | Mn  | Si  | P   | S   | Fe  |
| 1          | 3.27 | 0.71 | 0.66 | 0.12 | 0.05 | 95.29 |
| 2          | 2.65 | 0.42 | 0.54 | 0.13 | 0.08 | 96.18 |

### Table 8. Slag chemical composition

| Charge no. | Chemical composition, [%] | CaO/SiO₂ |
|------------|---------------------------|----------|
|            | CaO | SiO₂ | Al₂O₃ | MgO | FeO | MnO | S   | CaO/SiO₂ |
| 1          | 41.01 | 34.24 | 8.42  | 5.82 | 0.97 | 0.81 | 1.81 | 1.19    |
| 2          | 31.18 | 25.04 | 8.10  | 6.12 | 27.17 | 0.75 | 1.56 | 1.25    |

### Table 9. Iron balance

| Charge no. | Iron, [kg] | Ũ_{rec,Fe} [%] |
|------------|------------|----------------|
|            | Fe_{F.I}  | Fe_{F.II} | Fe_{F.I}−Fe_{F.II} | Fe_{briquettes} | Fe_{slag} | Ũ_{rec,Fe} |
| 1          | 4.5   | 5.518 | 1.018 | 1.104 | 0.086 | 92.21 |
| 2          | 4.518 | 5.489 | 0.971 | 1.346 | 0.375 | 72.13 |

1) The iron quantity from the cast iron before adding the briquettes
2) The iron quantity from the cast iron at 5 minutes after adding the briquettes

\[ \eta_{\text{rec,Fe}} = \frac{Fe_{F.II} - Fe_{F.I}}{Fe_{\text{briquettes}}} \cdot 100, [%] \] (2.)

where: \( \eta_{\text{rec,Fe}} \) - iron recovery degree from briquettes;
\( Fe_{F.I} \) - the quantity of iron in the cast iron before briquettes addition;
\( Fe_{F.II} \) - the quantity of iron in the cast iron at 5 min. after briquettes addition.

### 3. Conclusions

From the above data, it appears that, through the melting of reduced briquettes in furnaces where conditions for the dissolution of carbon are created, we can obtain pig iron.

Slag resulting from the melting of the sterile from briquettes and the addition of lime, corresponds in terms of basic chemical composition to blast furnace slag.

Therefore it can be considered that in processing briquettes in Hamborn furnaces, they will be subject to the same physicochemical processes.

Analysing from the technological point of view, the following results were found:
- by melting reduced briquettes in furnaces, where conditions for dissolution of carbon into the steel bath are created, pig iron can be obtained;
- slag resulting from melting of the sterile and the addition of lime from briquettes is fluid, it has a low content of FeO and from the point of view of the chemical composition corresponds to blast furnace slag;
- at melting of briquettes in induction furnace where an iron bath was previously formed, different values for the iron recovery efficiency are obtained;
the best values for the efficiency of iron recovery are obtained for the briquettes with a high degree of metallization, which can be explained by the fact that from their melting the slag that resulted had a lower oxidation capacity, on the one hand, and on the other slag has a lower fluidity;

- the lowest value for the iron recovery rate was obtained from melting of briquettes that are not initially reduced, condition caused by low slag flow resulting from the melting of the briquettes;

- the addition of the reducing mixture in furnace during the melting of briquettes lead to the increase of the iron recovery efficiency;

- given the variety of waste, both in terms of chemical composition and particle size, as well as small size waste beyond the smallest, but made in 250mm size, can be a viable technological solution for processing in Hamborn furnaces.

References

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