Evaluation of the impact of the CO/C reducer on the CO\(_2\) formation in the process of pyrometallurgical recovery of Fe from converter slag

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Abstract. The results of simulations of Fe recovery from steel slag containing iron oxides with C reducer dissolved in liquid slag and gaseous CO were presented in the paper. The simulations were performed with the use of a commercial program FactSage, and the calculations followed the procedure of dosing the reducer to slag in portions, each time reaching the state of thermodynamic equilibrium. The calculation procedure was realized sequentially, and the equilibrium composition of gaseous phase, nonmetallic phase and separated Fe was established at each calculation step. Gaseous products of CO and CO\(_2\) reduction were removed from the system with each successive calculation step. The simulation revealed that reaching comparable results of reduction requires using a considerable amount of CO. Moreover, the CO\(_2\) content in the gaseous phase and amount of separated Fe depend on the type of reducer. It was observed that the main mechanism was the reduction of iron with C. In this case the composition of gaseous products was mainly dominated by CO-CO\(_2\).

1. Introduction

The steel production technology generates industrial waste containing high quantities of metal-containing by-products, which can be recycled in iron-recovery processes [1-6]. The waste re-use operation lies in its reintroduction to the sinter mix as a furnace charge supplement, or the iron fraction is removed from the slag with a magnetic method. The main by-product of steel production is slag consisting mainly of: CaO, SiO\(_2\), Al\(_2\)O\(_3\), FeO, MgO and MnO [7, 8]. Slag from the furnace processes contains under 1.5 % FeO, therefore no Fe-oriented recycling is realized. A similar situation is observed for high phosphorus converter slags. Here the applicability is limited in the steel production processes as in the complete reduction conditions it returns to liquid metal. Neither slag after steel refining processes can be used for iron production and this is connected with the high aluminum oxide content. Attempts were made to manage this slag in a ladle furnace as part of calcium and fluorite substitute, though its applicability was limited because of the use of refractory materials and other problems with its processing [1]. The basic component of steel slag is FeO (7-30%), the content of which depends on the applied technology. The chemical composition also depends on the assortment of the produced steel; in the case of special steels, slag may contain MnO, Cr\(_2\)O\(_3\), V\(_2\)O\(_5\) and TiO\(_2\) [7, 8].

In the integrated steel plant, about 130-200 kg of slag is produced with the basic oxygen furnace (BOF) per ton of produced raw steel. The conventional way of managing slag as a blast furnace additive gives some side effects, i.e. higher coke consumption during slag processing, as well as higher CO and CO\(_2\) content. This does not comply with the present trend to reduce CO\(_2\) emissions.
The sustained development strategy is aimed at limiting waste production and unfavorable effects connected with their recycling. Accordingly, alternative methods are searched for to recover metals (Fe) and also to limit gas emissions. The basic technology of Fe recovery from slag is the pyrometallurgical reduction with carbonaceous materials [9].

2. Mineralogical composition and build of slag:

In the converter process, slag is produced with the main components FeO, CaO and SiO$_2$. Iron in slag may assume the form of Fe$_2$O$_3$ – hematite, which has a romboid shape, and Fe$_3$O$_4$ – magnetite having a crystalline structure of spinelle. There may be also present the maghemite (gamma) phase of Fe$_2$O$_3$ – an allotropic form having an isomorphic spinelle form (like magnetite) and ferromagnetic properties and chemical composition (like hematite). There is also present FeO phase –wustite with paramagnetic properties [10].

Each of the oxides has different chemical composition and build, which may consequently affect the course of processes in the presence of the reducer in liquid phase. When the SiO$_2$ content is increased in slag, pure wustite FeO in equilibrium with Fe contains about 10% Fe$_2$O$_3$, whereas after adding CaO to wustite, being in equilibrium with Fe, the Fe$_2$O$_3$ may reach 20%. Slag may also contain complex forms being a result of chemical processes taking place in the system. In the case of a system composed of FeO, CaO, SiO$_2$ presented on Figure 1 the possible presence of the following chemical compounds should be taken into account: Ca$_2$SiO$_4$, CaSiO$_3$, FeSiO$_3$, Fe$_2$SiO$_4$, Ca$_2$Si$_2$O$_6$ and Ca$_4$Si$_2$O$_8$ [10].

![Figure 1. Activity of FeO in liquid solution of FeO-CaO-SiO$_2$ at temp. 1550°C in equilibrium with liquid Fe.](image)

The chemical and mineral composition of slag in solid state was considerably well analyzed, but in the case of liquid systems we can infer on its build. In the analysis of the structure of liquid slag and its physicochemical structure, slag is treated as an ionic liquid, where one of the main components is silica appearing in a tetrahedral form built of big oxygen ions centrally surrounding the silicon ion (figure 2).
3. Iron recovery from iron with the participation of C and CO reducers

The pyrometallurgical reduction of iron oxides in liquid slag takes place as a result of reactions taking place on the interface [10]:

a) slag/coal (hard coal, coke, lignite or other)
\[
\text{FeO}_{(l)} + C_{(s)} = \text{Fe}_{(s/l)} + \text{CO} \quad (1)
\]
\[
\text{Fe}_{(s/l)} + C_{(s)} = \text{Fe-C}_{(l)} \quad (2)
\]

c) slag/gas
\[
\text{FeO}_{(l)} + \text{CO} = \text{Fe}_{(s/l)} + \text{CO}_2 \quad (3)
\]
d) coal/gas
\[
\text{CO}_2 + C = 2 \text{ CO} \quad (4)
\]

Reaction (1) takes place in the initial stage of high temperature reduction; the formation of gaseous CO product initiates reaction (3). Consequently, a mixture of gaseous products of reactions (1) and (3) is generated in the form of a CO-CO\(_2\) mixture on the surface of solid carbon reducer in the form of a gaseous bubble. The activity of FeO will affect the reaction parameters and equilibrium between phases.

\[
\frac{p_{\text{CO}_2}}{p_{\text{CO}}} = K \cdot \alpha_{\text{FeO}} \quad (5)
\]

Authors performed calculations relating to the formation of CO and CO\(_2\) phase during reduction of liquid converter slag with the use of C and CO\(_2\) with the use of FACTSage software.

4. Simulation Calculations

Simulations were performed at temperature 1700K for the reduction process with the use of CO and C. The reduction was realized for slags having chemical composition as in table 1. Simulated slags contained four basic components; CaO, SiO\(_2\), Al\(_2\)O\(_3\) and FeO. In all analyzed cases the FeO content was about 10%, and the basic differences were observed for SiO\(_2\) content (22.56 – 40.13%).

Table 1. Chemical composition of slags used in calculations (wt%).

| Slag | % CaO | % SiO\(_2\) | % Al\(_2\)O\(_3\) | % FeO |
|------|-------|-------------|-------------------|-------|
| S1   | 41.67 | 40.13       | 7.60              | 10.60 |
| S2   | 40.38 | 34.60       | 14.68             | 10.34 |
| S3   | 58.98 | 22.56       | 7.66              | 10.80 |

The first stage of calculations concentrated on the simulation of slags reduction with carbon portions (5 g) of solid reducer were introduced. In each calculation step, new phases were formed after the state of thermodynamic equilibrium was reached, i.e. liquid Fe and gaseous solution CO-CO\(_2\). The cycle was repeated till the moment minimum FeO content in slag was obtained. The same procedure
was applied for the reduction process making use of CO. In this case the reduction took place on the phase contact, i.e. on the liquid slag/gas interface, where gas appears in the form of CO bubbles, and the CO-CO$_2$ mixture is the product of the reaction. The calculations were performed at a temperature of 1700 K. It was observed that only FeO was reduced. The results of calculations of chemical composition of particular phases are presented in figures 3-6. The change of Fe content after the reaction of slags 1-3 with C and CO is presented in figure 3 and figure 4.

![Figure 3. Change of Fe content after reduction with C (T=1700 K).](image3)

![Figure 4. Change of Fe content after reduction with CO (T=1700 K).](image4)

The comparison of figures 3 and 4 reveals that the reduction with carbon is much more efficient than in the case of only gaseous CO. In this case the participation of gaseous reducer should be excessive. Moreover, at the final stages of reduction with the use of CO the reaction was observed to stop. At this stage the equilibrium concentration of CO$_2$ in gaseous phase was very low because of the
low FeO content, which results in considerable lowering of the reaction. The amount of produced Fe increased nearly linearly with the increase of added reducer. In the case of reduction realized with CO the amount of Fe obtained in each successive calculation step was lower.

Figures 5 a, b. Change of composition of gaseous phase for slags 1, 2, 3 for reduction with carbon.
The CO$_2$ concentration in the gaseous phase is considerably diversified and depends on the applied reducer. In the case of reduction with carbon, In the case of coal reduction, it does not exceed the value of $X = 0.035$ ($X = 0.0341$ for the slag 1) and decreases to the value of $X = 0.0084$ for the slag 3. In the case of reduction with CO, the amount of produced CO$_2$ is highest in the initial stages of reduction and considerably higher than in reduction with carbon.

Figures 6 a, b. Change of composition of gaseous phase for slags 1, 2, 3 for reduction with CO.
5. Conclusions
The presented simulation of reduction in the condition of thermodynamic equilibrium illustrates the course of elementary reactions of Fe phase formation and evolution of gaseous phase during these processes. The applied calculation procedure is considerably simplified as in each calculation step the produced solid Fe and gaseous phase are removed from the analyzed system. The comparison of the effect of use of two types of reducers suggests that the reduction with carbon is more efficient. The validity of the simulation has been verified experimentally and will constitute a separate study.

6. References
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