

Optimisation of hot metal desulphurisation slag in the CaO/Mg co-injection process to improve slag skimming performance

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Abstract: Co-injection of lime and magnesium is one of the most commonly used hot metal desulphurisation processes in BOF steelmaking plants. The post-desulphurisation slag is comprised of blast furnace slag carryover, the residual from previous heat(s) in the hot metal ladle and the reaction products of the injected CaO and Mg. The formation of MgO and the injected CaO can increase the melting temperature and viscosity of the post-desulphurisation slag. Therefore, the skimming of the post-desulphurisation slag can be more difficult due to the increased slag bulk, altered slag consistency and deteriorated slag conditions. Total iron (TFe) content in the skimmed slag was found to be up to 75 wt% in the form of iron droplets dispersed in the slag, which is one of the big yield losses in the steelmaking process. Efficient slag skimming may not be possible without slag modification for the heats with low hot metal temperature (<1300 °C) and high CaO/Mg injection for producing ultra-low sulphur steel grades.

In this study, the effect of the post-desulphurisation slag chemistry on the separation of metal from slag was investigated for the varying hot metal desulphurisation conditions (e.g. BF slag carryover, the amount of CaO/Mg injected, hot metal temperature) via theoretical calculation and laboratory experiments, that is, flow temperature measurement by hemisphere method and metal settling experiments. It was found that slag basicity (%CaO/%SiO₂) and MgO content are the two key factors to control. A model for optimising the slag chemistry was proposed and applied successfully in the plant production.

Keywords: slag, hot metal desulphurisation, metal yield

1. Introduction

Sulphur is one of the elements that greatly affects the processing and properties of steel. High sulphur content in steel is detrimental to bendability, ductility, toughness, formability, weldability and corrosion resistance of the steel. On the other hand, there is an increasing demand on improved quality and service performance of steel products, such as thickness reduction and increased deformation, with the development of modern industry and the application of the steel products under more severe conditions.

Co-injection of lime and magnesium is one of the most commonly used hot metal desulphurisation processes in BOF steelmaking plants with increases in the tonnage of steel produced and the amount of low sulphur steel grades required. The post-desulphurisation slag is comprised of blast furnace slag carryover, the residual from previous heat(s) in the hot metal ladle and the reaction products of the injected CaO and Mg. The formation of MgO and the injected CaO can increase the melting temperature and viscosity of the post-desulphurisation slag. Therefore, slag skimming after hot metal desulphurisation can be more difficult due to the increased slag bulk, altered slag consistency and deteriorated slag conditions (e.g. powdery slag). Total iron (TFe) content in the skimmed slag was found to be up to 75 wt% in the form of iron droplets dispersed in the slag, which is one of the big yield losses in the steelmaking process. Furthermore,

efficient slag skimming may not be possible without slag modification for the heats with low hot metal temperature (<1300 °C) and high CaO/Mg injection for producing ultra low sulphur steel grades.

In this study, the effect of the hot metal desulphurisation slag chemistry on the separation of metal from slag was investigated for the varying hot metal desulphurisation conditions (e.g. BF slag carryover, the amount of CaO/Mg injected, hot metal temperature, etc.) via theoretical calculation and laboratory experiments. The flow temperature of the slag was measured as a function of slag composition using a high temperature microscope (hemisphere method). Settling experiments of iron droplets from slag were carried out for various slag compositions and temperatures. It was found that slag basicity (%CaO/%SiO₂) and MgO content are the two key factors to control. A model for optimising the slag chemistry was proposed and applied successfully in the plant production.

2. Slag design (Thermodynamic Calculation)

The post-desulphurisation slag is mainly from the following sources:

- (1) The blast furnace slag carryover with major components of CaO, SiO₂, Al₂O₃ and MgO. A normalised blast furnace slag composition (wt%) is 42.29%CaO, 36.78%SiO₂, 12.46%Al₂O₃ and 7.63%MgO.
- (2) The injected CaO/Mg and their reaction products. The amount of CaO/Mg injected is decided by the initial sulphur content in the hot metal and the sulphur specification of the steel grades to be made.
- (3) The residual from previous heat(s) in the hot metal ladle which can be effectively reduced by clean ladle practice.

The formation of MgO and the injected CaO increase the slag basicity (%CaO/%SiO₂) and MgO content, and consequently increase the melting temperature and viscosity of the post-desulphurisation slag. Therefore, without modification the post-desulphurisation slag in the hot metal ladle can be considered as a quaternary CaO-SiO₂-Al₂O₃-MgO slag with higher basicity and MgO content compared to the blast furnace slag, which results in the increase in the melting temperature and viscosity.

In order to generate a more fluid slag and to reduce the amount of hot metal entrapped within the slag, slag modifying agent is often added with the desulphurising agent or directly into the hot metal ladle before or after hot metal pouring to decrease the viscosity and melting temperature of the post-desulphurisation slag. Various materials can be used as slag modifying agents, e.g. fluorspar, dolomitic lime, silica, sodium carbonate, sodium chloride, potassium chloride, potash, cryolite, potassium cryolite, colemanite, calcium chloride, calcium aluminate, sodium fluoride, anhydrous borax, nepheline syenite and soda ash. [1] The slag modifying agents are basically at least one of the components SiO₂, Al₂O₃, Na₂O+K₂O and CaF₂. Any F-containing slag modifying agents should be restricted due to possible environment related issues.

The initial attempt of this study is not focused on any particular modifying agents but in general optimisation of the post-desulphurisation slag composition. Therefore, this study aims to adjust the slag composition with SiO₂, Al₂O₃ and Na₂O+K₂O to achieve:

- (i) increased fluidity of the slag in the hot metal ladle by decreasing its melting temperature, especially for the heats with low hot metal temperature and a high amount of CaO/Mg injection for producing ultra-low sulphur steel grades; and

(ii) improved skimming operation, i.e. reduced iron loss and shortened skimming time.

As the initial step, the effect of slag composition on its liquidus temperature was calculated by using the thermochemical software and database Factsage [2]. The results are shown in Fig. 1.

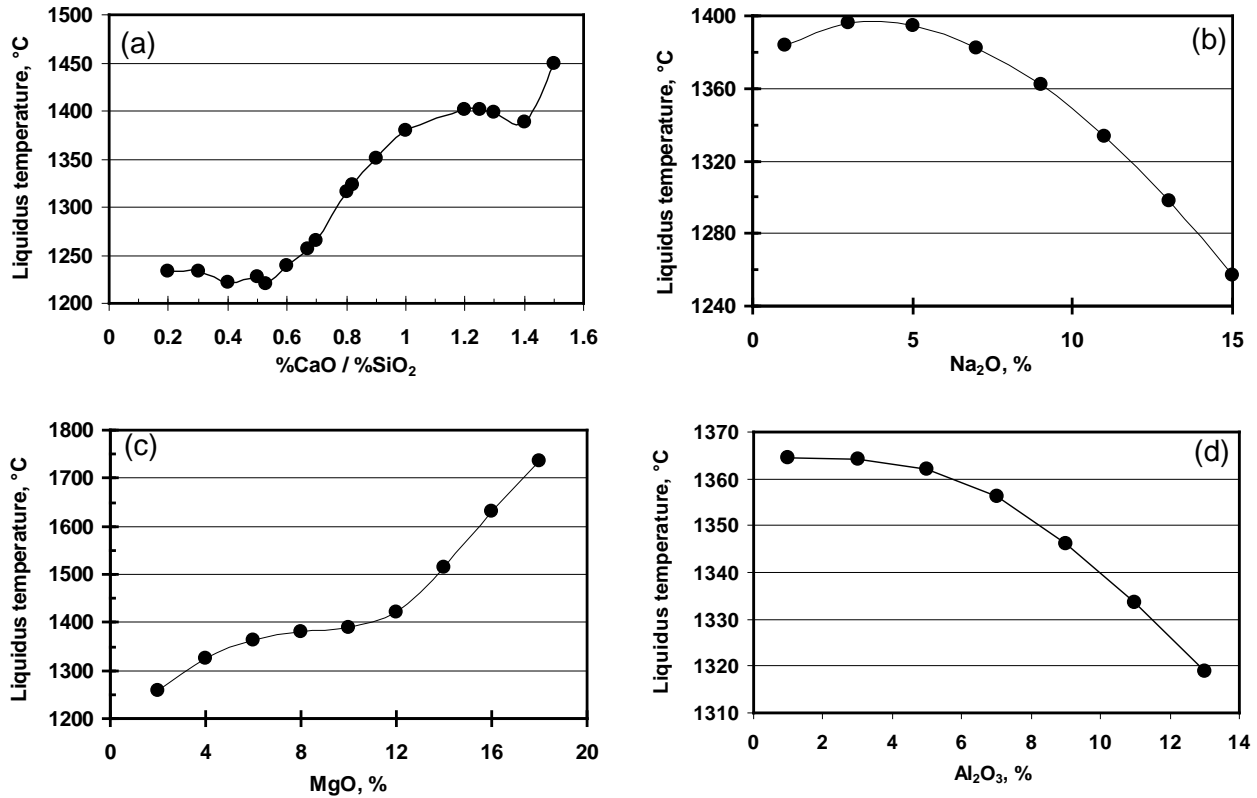


Fig. 1 Effect of slag composition on its liquidus temperature calculated by using FactSage [2]. The basic slag is CaO-SiO₂-2%MnO-5%Al₂O₃-6%MgO-9%Na₂O with %CaO/%SiO₂=1.0.

As shown in Figure 1(a), the calculated slag liquidus temperature in general decreases with decreasing the slag basicity from 1.5 to 0.53 although not much change is observed in the range of slag basicity from 1.1 to 1.4. If the post-desulphurising slag is expected to be liquid at hot metal temperature which is considered to be beneficial for metal separation, a slag with the basicity of 0.9 is suitable for hot metal with a temperature ~1350°C while for hot metal with a temperature ~1250 °C a slag with the basicity of as low as 0.6 is required.

Figure 1(b) shows the effect of Na₂O content on the calculated liquidus temperature of the slag investigated. In the range of 3 to 7% Na₂O, increasing slag %Na₂O content slightly decreases its liquidus temperature from 1395 °C to 1380 °C. If the slag liquidus temperature is required to be below 1360 °C, the calculation shows that the Na₂O content should be above 9%, which can not be achieved by adding Na₂O-containing modifying agent. It should be noted that Na₂O comes from either Na₂O-containing modifying agent or soda ash. However, a previous hot metal desulphurisation practice with soda ash has been proved to have various environmental issues. Therefore, a high amount of Na₂O additions is not considered as a reasonable option and the Na₂O content is fixed to be 6%.

The effect of MgO content on the liquidus temperature of the slag is shown in Figure 1(c). The calculated liquidus

temperature of slag increases with increasing MgO content in the slag. The MgO content in the post-desulphurisation slag is likely to be higher than that in the blast furnace slag, that is, above 7% in this study. Under extreme conditions it may go up to 18% for producing ultra-low sulphur steel grades. The calculated liquidus temperature of the slag with >6% MgO is above 1360 °C, which is above the average hot metal temperature after desulphurisation operation in the BOS plants concerned.

The liquidus temperature of slag increases with decreasing the Al₂O₃ content in the slag as shown in Figure 1(d). The effect of Al₂O₃ content on liquidus temperature is relatively small compared to those of slag basicity and MgO content.

The above analysis shows that the calculated liquidus temperature of the post-desulphurisation slag is greatly affected by its composition, mainly basicity %CaO/%SiO₂ and MgO content. The liquidus temperature is likely to be above the average hot metal temperature after desulphurisation operation in the BOS plants concerned. On the other hand, completely liquid slag may not be beneficial to the slag skimming operation. Therefore, the liquidus temperature of the slag is not considered as a major index for optimising slag composition in this study. Instead, as described in the next chapter, the flow temperature of the slag is measured and used for optimising slag composition.

3. Flow temperature

The flow temperature of the slags is measured by using a high temperature microscope (hemisphere method, up to 1600 °C) under air atmosphere. Slag ingredients from chemical agents were mixed according to the required slag chemistry. The powder mixture was melted and ground three times to homogenise the slag. Cylindrical experimental samples in the size of φ2×3 mm were made using water as the binder. The flow temperature was measured by heating the sample on an alumina plate at preset temperature programmes. In this study, the flow temperature is defined as the temperature at which the sample height is ¼ of its original height. Figure 2 shows the change in the sample shape as a function of temperature determined by the high temperature microscope.

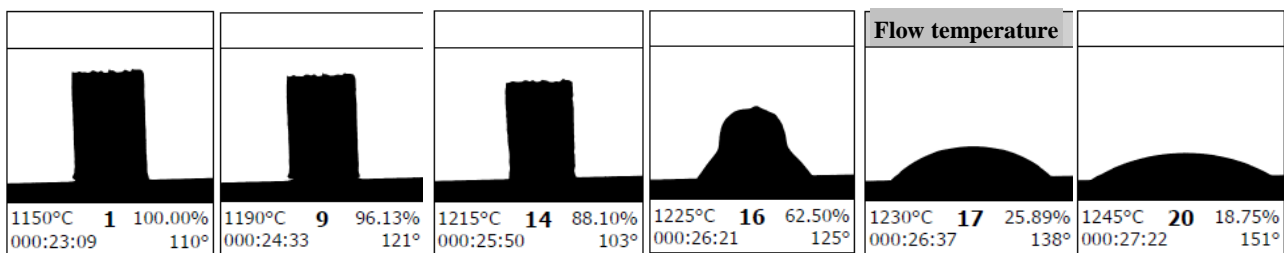


Fig. 2 The change in the sample shape as a function of temperature determined by the high temperature microscope.

The flow temperature of the synthesised post-desulphurisation slags is shown in Figure 3 as a function of %CaO/%SiO₂ (Figure 3(a)) and MgO content (Figure 3(b)). The basic slag is CaO-SiO₂-2%MnO-5%Al₂O₃-6%MgO-9%Na₂O. As shown in Figure 3(a) the flow temperature of a slag with a basicity of 1.3 is similar to the average hot metal temperature after desulphurisation operation (i.e. 1350 °C) while a slag with a slag basicity of 1.0 is fine for hot metal with as low a temperature as 1250 °C after the desulphurisation operation. However, as shown in Figure 3(b), the injected Mg markedly increases MgO content in the slag, and subsequently increases its flow temperature. On average the flow temperature increases by 7.3 °C per 1% MgO. Therefore, the results shown in Figure 3(a) should be further adjusted by the actual MgO content in the slag, i.e. if the MgO content in the slag is 10% (from 6% in Figure 3(a)), the slag basicity should be reduced to ~1.2 for achieving a

slag flow temperature of 1350 °C. An optimisation model can be built based on these results in terms of slag flow temperature.

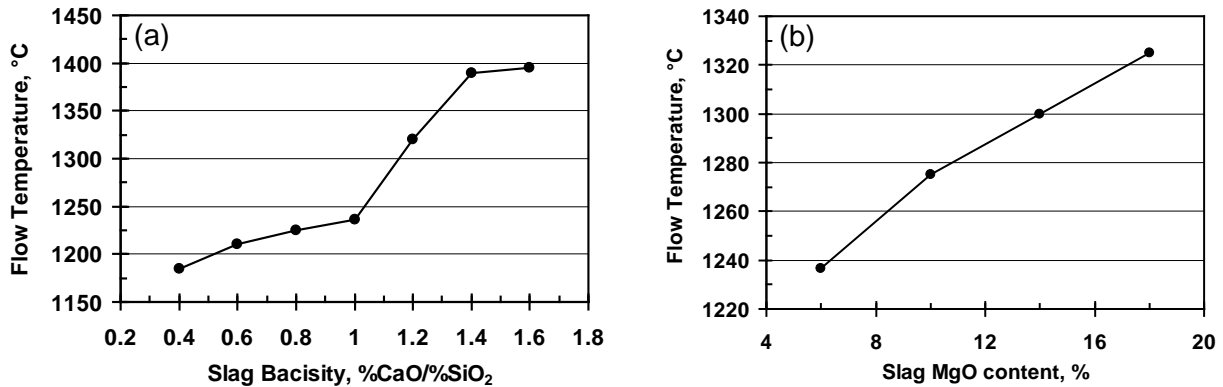


Fig. 3 Flow temperature of the synthesised slags as a function of (a) %CaO/%SiO₂ and (b) MgO content.

4. Metal settling experiment

Metal settling experiments were carried out to validate the optimised slag composition for improving metal yield. The experiments were carried out using a graphite crucible in a muffle furnace. The raw materials for the experiment were divided into two parts: 100 g premelted slag (ground to powder) and a mixture of 50 g premelted slag (ground to powder) and 75 g pig iron granules with a size of less than 2.5 mm. Firstly the 100 g premelted slag was molten in a graphite crucible, held at the required temperature for 30 minutes, and then taken out of the muffle furnace. Then the mixture of the 50 g premelted slag and 75 g pig iron granules was added onto the top of the molten slag. The graphite crucible was placed back to the furnace and held at the required temperature for another 30 minutes. Finally the graphite crucible was taken out of the furnace and cooled naturally. The experimental sample was then physically separated. The metal settled at the bottom of crucible was measured and expressed as a percentage of the total amount of metal added. The result is shown in Figure 4 as a function of slag basicity, MgO content and temperature.

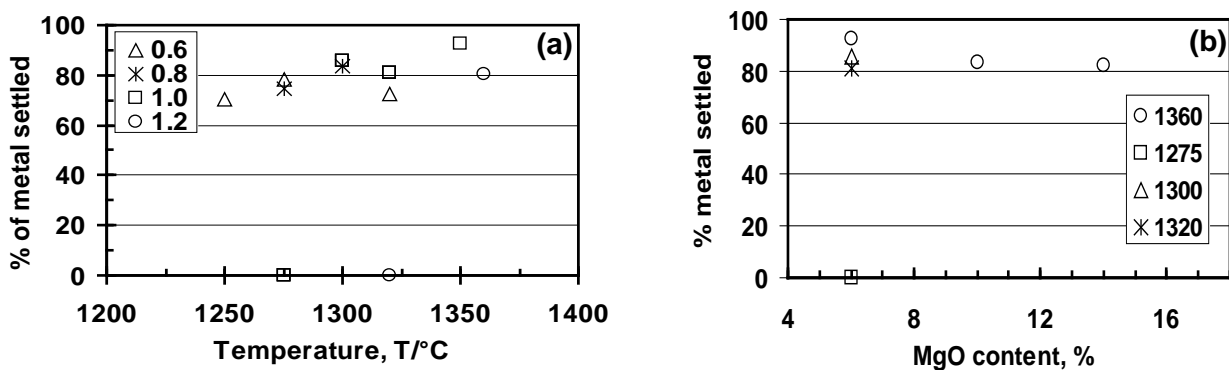


Fig. 4 The percentage of metal settled at the bottom of the crucible as a function of slag basicity, MgO content and temperature.

Figure 4(a) shows the percentage of metal settled at the bottom of crucible as a function of temperature and slag basicity. Generally as the hot metal temperature is increased a slag with a higher slag basicity can be used, which

indicates less modifying agent is needed for the post-desulphurisation slag. For hot metal with low temperature (<1300 °C) a slag basicity of less than 1.0 is required, while a slag with a basicity of 1.2 can be used for hot metal with a temperature of >1350 °C after desulphurisation. This result gives a regime of slag basicity according to the hot metal temperature in terms of metal separation from slag. Figure 4(b) shows the percentage of the metal settled at the bottom of the crucible as a function of MgO content and hot metal temperature. At 1360 °C the percentage of metal settled at the bottom of the crucible decreased slightly with increasing MgO content from 6 to 14 wt%, however, the overall percentage is still above 80%. For the same slag composition, the percentage of metal settled at the bottom of the crucible increases with increasing the heating temperature. A slag regime can be obtained according to the hot metal temperature after desulphurisation operation in terms of metal separation from slag.

5. Industrial Trial

Based on the results of flow temperature measurement and metal settling experiments, a model was proposed to optimise the composition of the post-desulphurisation slag aiming to improve slag skimming performance in terms of metal yield improvement. This model provides the optimised slag basicity and MgO content according to the hot metal desulphurisation conditions, i.e. the estimated hot metal temperature after desulphurisation, the estimated blast furnace slag carryover, the initial hot metal sulphur level and the sulphur specification for the steel grade to be made which decides the amount of CaO and Mg to be injected. This model provides the amount and types of slag modifying agents to be added.

This model was applied in a hot metal desulphurisation station with the CaO/Mg co-injection process. The charge amount of hot metal is ~270 t. The slag modifying agent(s) were added to the ladle before hot metal pouring by initially lifting bags and now using a silo system. It was found that the metal content in the skimmed slag was reduced from up to 75% to less than 30% on average. The time from slag skimming was also reduced from >10 minutes to less than 8 minutes on average. Figure 5 shows a microstructure of the skimmed hot metal desulphurisation slag. As shown in Figure 5, although entrapped metal droplets can still be found in the slag sample (Figure 5(d)), the majority of the slag was almost metal free.

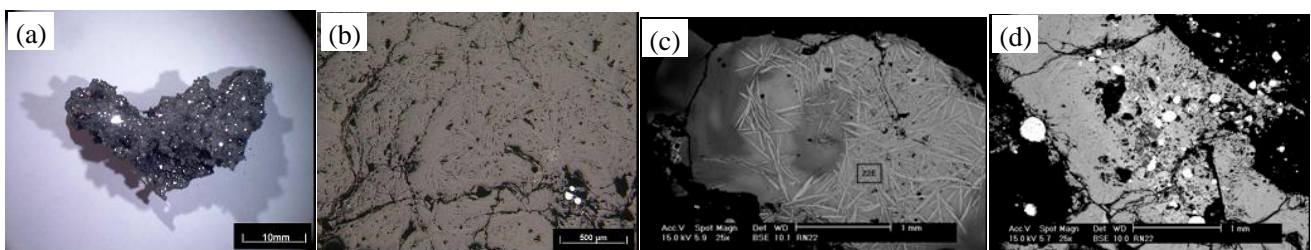


Fig. 5 Photos showing the skimmed slag for the heat with optimised slag composition. (a) & (b): under optical microscope; (c) & (d): SEM images. (d): local area with entrapped iron droplets.

6. Conclusion

In order to improve the slag skimming performance in the CaO/Mg co-injection process, especially reducing the metal yield loss and shortening the skimming time, the hot metal desulphurisation slag is optimised via flow temperature measurement and metal settling experiments. The effect of the post-desulphurisation slag chemistry on the

separation of metal from slag was investigated for varying hot metal desulphurisation conditions (i.e. BF slag carryover, the amount of CaO/Mg injected, hot metal temperature) via theoretical calculation and laboratory experiments, that is, flow temperature measurement by hemisphere method and metal settling experiments. It was found that slag basicity (%CaO/%SiO₂) and MgO content are the two key factors to control. A model for optimising the slag chemistry was proposed and applied successfully in the plant production. The metal loss in the skimmed slag was reduced from up to 75% to less than 30% on average. The time from slag skimming was also reduced from >10 minutes to less than 8 minutes on average.

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