Sulphur loss from the slag during desulphurization of liquid steel

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ABSTRACT

Desulfurization of steel during ladle refining is governed by both thermodynamics and kinetics. For effective desulfurization, thermodynamically, a low partial pressure of oxygen at the steel-slag interface and highly basic slag which possess a large sulphide capacity are desired. Kinetically, the mass transfer coefficient of sulphur in the liquid steel and in the slag determines the rate of desulfurization. A fast desulfurization rate is achieved by maintaining sufficiently strong argon stirring of the melt.

In the present work, sulphur mass balance for steel and slag was performed after the desulfurization treatment for several industrial heats. The decrease in the sulphur quantity of the liquid steel was more than the increase in the sulphur quantity of the slag. The discrepancy in the sulphur mass balance suggests that the sulphur could be transferred to (a) the gas (via slag) phase or to (b) the refractory (crucible) phase. The preliminary investigation of the refractory samples taken at slag-refractory and steel-refractory interface showed no interaction of sulphur with the refractory. Therefore, the possibility of sulphur transfer to the gas phase was verified by carrying out melting experiments of sulphur containing slag in an argon/air atmosphere. Sulphur containing slag was initially melted in an MgO-C crucible under an argon atmosphere followed by creating the air atmosphere just above the melt. Careful sampling and analysis from the cold spots of the crucible, much above the melt surface, revealed formation of a fibrous structure. Scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDS) analysis of these fibrous deposits confirmed the presence of oxides and sulphides. Oxidation of sulphur containing slag under air atmosphere was also performed using a TGA setup. It showed a constant sulphur loss in the range of $1300 - 1500^{\circ}C$. Thermodynamic calculations carried out using FactSage 8.3 for these experimental conditions are in good agreement with the observed results.

INTRODUCTION

Delsulphurization is one of the main tasks performed at the ladle refining steel for many steel grades. The mechanism of desulphurization is well established. The Sulphur removal from steel is typically described using the following chemical reaction: $[S] + (O^{2-}) = [O] + (S^{2-})$, where $[\ ]$ and $(\ )$ represent species in the liquid steel and slag respectively. It is understood that low dissolved oxygen in steel and availability of free oxide ion in the slag favor the desulphurization process. These can be considered equivalent to higher aluminum level in steel and CaO level in slag. Hence, steel-slag desulphurization reaction is also written as: $[S] + (CaO) + 2/3[Al] = (CaS) + 1/3(Al_2O_3)$. It is important to mind lime saturation level in the slag. Bannenberg et al. (Bannenberg et al., 1992) showed that there exists an optimum level of lime addition that is beneficial for desulphurization. Any addition beyond that point can bring down desulphurization as mass transfer in the slag slows down in the presence of solids. Roy et al. (Roy et al., 2013) highlighted the role of parasitic reactions such as reduction of SiO_2, FeO and MnO leading to depletion of aluminium and its effect on retardation of desulphurization reaction. Kinetically, the desulphurization reaction is considered to be controlled by mass transfer in both steel and slag phase.

The interaction of the melt with the atmosphere is also of great importance. For example, the reoxidation of liquid steel at the slag eye can significantly impact the extent of steel-slag reaction and aluminium consumption during the ladle refining process. However, there are not many studies focused on the impact of slag-gas reaction on desulphurization reaction. Fincham and Richardson (Fincham & Richardson, 1954) reported that slag stores sulphur as sulphide ions for the partial pressure of oxygen below 10^{-5} atm and the storage capacity is presented as sulphide capacity of the slag. This range of partial pressure is relevant at the steel-slag interface. However, at slag-gas interface, p_{O2} may be higher and there could be formation of sulphate ions in the slag. The interaction of the molten slag with air is also important from the perspective of utilization of spent ladle slag which is often limited by its sulphur content. Pelton et al. (Pelton et al., 1974) performed kinetic studies on evolution of SO_2 during oxidation of slag at varied p_{O2}. They reported that the SO_2 evolution is rapid at low oxygen partial pressure (less than 0.1 atm) but becomes chemical kinetics limited at higher p_{O2} level probably due to surface poisoning. Allertz and Sichen (Allertz & Sichen, 2015) reported a similar study. However, in their work, the effect of the partial pressure of oxygen was not significant. The reaction rate, albeit slower, was found to be limited by the surface area at the slag-gas atmosphere. Wu et al. (Wu et al., 2021) reported the utilization of a mixture of $CaSO_4$

and CaSO$_3$ to remove sulphur present as CaS in the slag. The kinetics of sulphur removal using this method was much slower than that reported by previous studies. Zhao et al. (Zhao et al., 2016) reported oxidation of sulphur from the slag at high temperatures by flowing air. It was shown that up to 90% of the sulphur could be removed within one hour. The method can be potential useful for utilization of spent ladle refining slag.

In this work, the slag-air interaction is studied at different scales – industrial, laboratory scale induction furnace and using thermogravimetric techniques. Several steel and slag samples were collected during four industrial heats and sulphur balance was performed. It revealed the possibility of sulphur loss from slag potentially due to oxidation of sulphur in the slag by air. This was studied in a very carefully designed experiments using induction furnace. The slag was melted in an MgO-C crucible prepared from ladle bricks. Slag oxidation was carried out by passing air over molten slag. Similar experiments were carried out at a smaller scale using thermogravimetric technique. The rate of weight loss was recorded during the experiment.

PLANT OBSERVATION

Preliminary sulphur analysis of steel and slag analysis showed significant sulphur loss from the system during ladle refining of low carbon Al-killed steels. Four heats were closely tracked to understand the behaviour of sulphur. Steel and slag samples were periodically taken for sulphur analysis. Typical aluminium concentration in these heats were in the range of 0.03 – 0.05%. A basic slag was used; typical composition: 55% CaO, 32%Al$_2$O$_3$, 8% MgO, 3% SiO$_2$, 1% FeO, 1% S. the steel and slag weight towards end of the refining process were about 200 tonnes and 3.5 tonnes respectively. The slag mass was estimated by considering about 0.7 tonnes of the carryover slag from ConArc furnace and additions made at the ladle refining station. Initial and final concentration of sulphur in steel and slag, as measured using LECO, are shown in Table 1. The final sulphur concentration in the product was in the range of 50 – 70 ppm. It can be clearly seen that the increase in the sulphur concentration in the slag is much less than that expected from the sulphur loss from the steel. For example, for 220 ppm of sulphur loss from the steel (Heat-B), there should be 1.05% sulphur gain in the slag. Hence, significant amount of sulphur seems to be escaping the system.

Table 1. Sulphur analysis results for four heats

Heat	Sample	[S] ppm	(%S)
A	Initial	330	0.39
	Final (108 min)	70	0.82
B	Initial	280	0.49
	Final (55 min)	60	0.76
C	Initial	200	0.57
	Final (45 min)	60	0.80
D	Initial	180	0.66
	Final (48 min)	50	0.82

Sulphur analysis of steel and slag samples collected during these four heats were used to calculate the percentage of sulphur not accounted in the steel + slag system. The percentage was calculated with respect to combined initial sulphur amounts in steel and slag. Figure 1 shows the increase in sulphur loss percentage with time during the ladle refining process. The rate of sulphur loss is almost similar for Heats-A, B and D. Overall, the sulphur loss varies from ~20 – 40%.
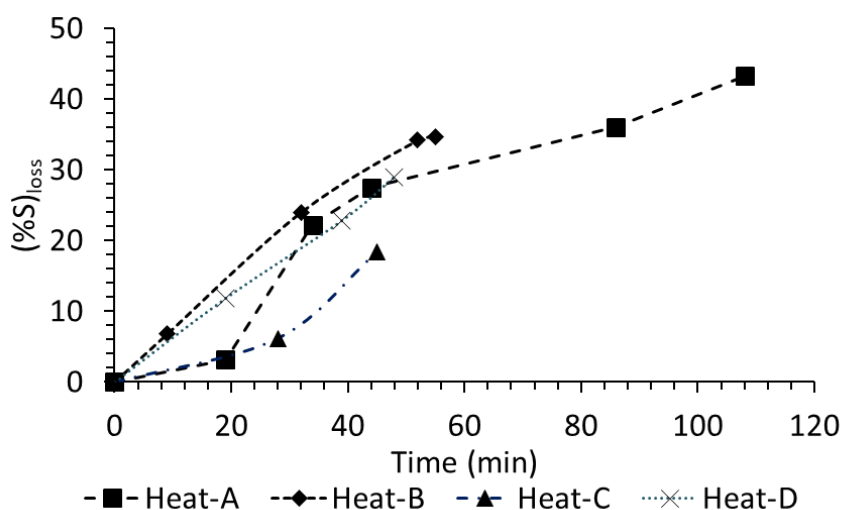
Figure 1. Sulphur loss with time for four heats

The refractory samples taken from the slag and steel region and analysed for sulphur using LECO. The sulphur amount at both locations were similar and relatively low (0.1 – 0.3%) at the end of the refractory life. Such small sulphur concentration is likely due to sulphide ions present in the slag and in the glaze layer. There was no clear evidence of sulphur removal through refractory based on this analysis. The likely reason for the sulphur loss is the oxidation of the slag in contact with air. The extent and rate of sulphur loss through this mechanism is expected to depend on 1) the partial pressure of SO_2 at the slag-air interface, 2) the rate of desulphurization of liquid steel and 3) the rate of mixing of slag due to argon stirring of the melt. The mass transport in the gas phase and oxidation reaction of sulphur are not expected to be rate limiting due to continuous supply of argon gas and high temperature of the process.

In order to test the feasibility of sulphur loss due to oxidation of slag, laboratory scale experiments were designed using induction furnace and TGA setup.

LABORATORY EXPERIMENTS

Induction furnace experiments

Oxidation of sulphur from the slag in the presence of air was studied by passing air over molten slag. Slag composition was selected based on expected slag composition during ladle refining process. Two slag compositions were prepared, see Table 2. Appropriate amounts of oxides were premelted in a graphite crucible at 1550°C. The premleted slag was crushed and decarburized before performing slag oxidation experiments. Slag oxidation experiments were performed at 1550°C in a MgO-C crucible of internal diameter 5.5 cm, wall thickness 1 cm and height 17 cm. The crucibles were prepared by machining MgO-C refractory bricks used for the steel refining ladle. Figure 2 shows a schematic of the induction furnace and related setup for conducting slag oxidation experiments. The induction furnace setup was placed in a stainless steel chamber. The chamber was first evacuated to 10^3 Pa using a rotary pump. Subsequently the chamber was filled with gettered argon. The argon was passed through a moisture trap followed by passing it over tubes containing copper and magnesium chips at 400°C to remove residual oxygen. The slag was re-melted under argon atmosphere at 1550°C. After 10 minutes of homogenisation, melting was confirmed by dipping a mild steel rod. The stainless steel chamber has a port directly above the melt to making additions. 10 g of FeS was added in the form of chunk by dropping it from the feeding tube inserted through the port. The port is normally closed with a silicon stopper. After melting of the slag, the port was opened and a 12.7 mm diameter mild steel tube was inserted to flow air at 500 sccm over the molten slag. Two experiments were conducted to ensure repeatability of the observation. Table 3 describes three experiments conducted using induction furnace. It should be noted that the experiment I-1 is essentially a slag premelting work for a similar slag composition. It serves as a blank experiment for the purpose of study of evaporation from molten slag under these experimental conditions. Three slag samples were collected during I-2 experiment by dipping a mild steel rod in the molten slag.

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The frozen slag layer over the mild steel rod was broken out, crushed and analysed for sulphur concentration using LECO. These three samples were taken as: after remelting (I2S1), after FeS addition (I2S2) and after completion of air blowing (I2S3).

Table 2. Composition of premelted slag

	%CaO	%MgO	%SiO₂	%Al₂O₃	%FeO	%MnO	Tm*
Slag-1	47	7	4.5	40	1.5	0	1350°C
Slag-2	46.6	6.8	4.5	40.1	1.5	0.71	1340°C

*T_m estimated from FactSage (Bale et al., 2016) corresponds to 95% liquid
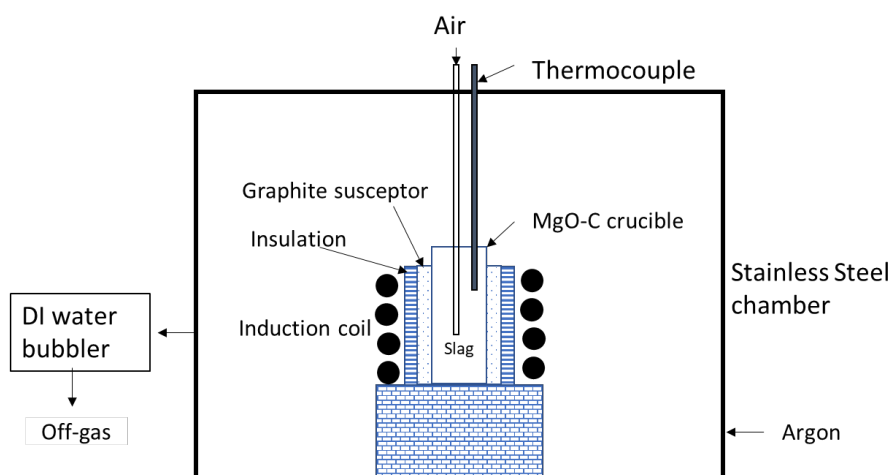

Figure 2. Schematic of induction furnace setup

Table 3. Description of induction furnace experiments

Exp.#	Slag composition And amount	Crucible	FeS added in molten slag	Air flow over molten slag
I-1	Slag-1, 600 g	Graphite	No	No
I-2	Slag-2, 200 g	MgO-C	Yes, 10 g	Yes, 500 sccm for 20 minutes
I-3	Slag-2, 120 g	MgO-C	Yes, 10 g	

TGA experiment

Thermogravitmetric analysis experiments were performed to accurately estimate the sulphur removal from the ladle refining slag. About 90 g of the premelted slag-1 (see Table 1) was pulverised in a vibrating cup mill for 4 minutes to ensure chemical homogeneity of the slag. The powdered slag was decarburized by placing it in a muffle furnace 950⁰C for 3 hrs. Two experiments (T1 and No.2) for the thermogravimetric analysis (TGA) of the slag were performed using Netzsch STA 449 F1 instrument. In these experiments, slag was placed in a platinum crucible and exposed to air (60 sccm) at a high temperature: 1300 – 1500°C. The samples were heated under argon atmosphere at the rate of 20°C/min. The heating rate was reduced to 5°C/min to allow the reaction between slag and air, if any.

Table 4. TGA experiment conditions

Exp.#	Slag amount	FeS amount	Air flow condition
T-1	7 mg	0	60 sccm, 1300 – 1500 °C, heating rate: 5°C/min
T-2	4.4 mg	0.6 mg	

In Experiment T-1, 7 mg of the powdered slag sample is taken in platinum crucible. The sample is heated to 1300^0C at 20^0C/min in the argon atmosphere and then to 1500^0C at 5^0C/min in the air atmosphere. Further, the sample is cooled to room temperature in argon atmosphere. In Experiment T-2, 5 mg of the sample is taken from a mixture of slag-1 and powdered FeS (8.8 g of slag with 1.2 g of FeS). Thermal profile as well as gas atmosphere were maintained in a manner similar to experiment T-1.

RESULTS AND DISCUSSION

The primary interest for conducting induction furnace experiment was to observe interaction between molten slag and gas phase. Based on the work of Kumar et al.(Kumar & Pistorius, 2017), further reaction in the gas phase followed by deposition of the solid products at colder regions were expected. Hence, crucible walls above the induction coil was carefully observed for all experiments. Figure 3 shows the SEM-EDS analysis of the fibrous deposits found on top of the graphite crucible wall. The deposit includes fibrous structure and micro-aggregates of MgO. High resolution image in Figure 3(a) shows that fibre thickness is about a micrometre or less. Many globular tips are observed in the fibrous structure, see bright regions of Figure 3 (b). The EDS analysis show presence of iron at those bright tips. Since FeO-MgO forms a liquid phase at this temperature, the likely growth mechanism is vapor-liquid-solid. The Mg and iron vapor forms due to reaction between slag and graphite crucible. FeO condenses at the top wall of the crucible (colder region). MgO dissolves in FeO and the supersaturation leads to the formation of MgO fibre. The presence of MgO micro-aggregates is likely through vapor-solid growth mechanism i.e. Mg and O in the gas phase reacts and deposits on MgO crucible wall. It is not clear whether graphite crucible acts as a substrate or pre-existing MgO fibre.
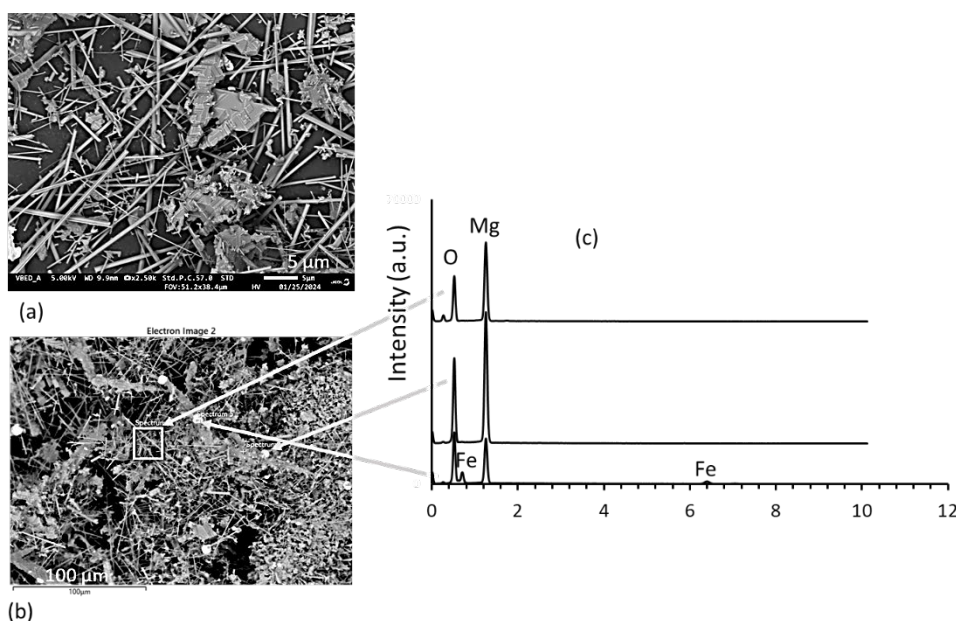

Figure 3. SEM analysis of fibrous deposit on top of the crucible wall for experiment I-1. (a) high resolution image of deposit, (b) showing spots for EDS analysis and (c) EDS spectra of various locations

Experiments I-2 and I-3 are very similar. Table 5 shows the Sulphur analysis of slag samples taken during experiment I-2. 5% FeS was added in the slag which corresponds to 1.8% of sulphur in the slag. Sulphur concentration in the slag after FeS addition was found to be 1.4%. The Sulphur addition looks reasonable. The sample taken after air purging show a remarkable decrease in sulphur concentration in the slag indicating oxidation of Sulphur from the slag during air blowing. Fibrous deposits were observed on top of the MgO-C crucible wall after both experiments I-2 and I-3. Figure 4 shows SEM-EDS analysis of the fibrous structure observed after experiment I-3. The EDS analysis of the fiber shows that these are primarily MgO. MgO formation is likely due to reduction of MgO from slag or MgO-C bricks by carbon. Sulphur is present in the structure in three forms as illustrated in the EDS spectra: a) Fe-S, b) Mn-S and c) small amount of Ca-S. It is not clear whether these are

sulphides or sulphates of iron, manganese and calcium. The removal of Sulphur from the slag during the oxidation experiment is clearly evident. The presence of almost iron free $MnS/MnSO_4$ further confirms that the source of Sulphur is not just reaction between FeS added and air.

Table 5. Sulphur analysis of slag samples taken during experiment I-2

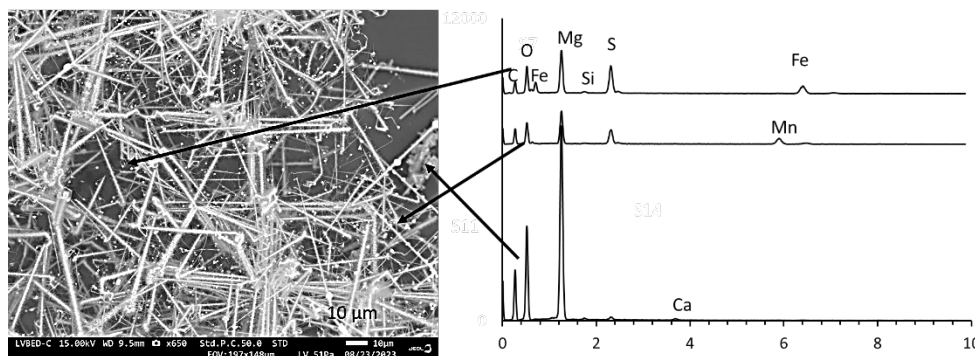| Sample#	Condition	S_{LECO}
I2S1	Molten slag-2	0.06%
I2S2	After FeS addition	1.4%
I2S3	After completion of air blowing	0.04%

Figure 4. SEM-EDS analysis of fibrous deposit on top of MgO-C crucible wall for experiment I-3

Induction furnace experiment shows that about 20 minutes of air purging at 200 sccm can reduce sulphur concentration to 0.04%. TGA experiments were conducted to demonstrate the same through weight loss measurements. TGA experiment can also be used to calculate the rate of sulphur removal as well. Figure 5 (a) and Figure 5 (b) show weight change during TGA experiments. It should be noted that the heating (up to 1300°C) and cooling was conducted under argon atmosphere. The gas atmosphere was switched to air at 1300°C and maintained so until 1500°C. Further the heating rate was only 5°C/minute. It should be noted that slag is expected to be 40% liquid at 1300°C, 93% liquid at 1330°C and 99% at 1450°C as calculated using FactSage 8.3(Bale et al., 2016). The overall weight loss for T-1 and T-2 was 1.28% and 4.72% respectively. It should be noted that 4.4% S equivalent FeS was added in the slag for experiment T-2. The additional weight loss was 3.44% in exp.# T-2 compared to T-1. Further the weight loss rate almost becomes zero at the onset of cooling i.e. as soon as the gas atmosphere is switched from air to argon. These results clearly demonstrate the sulphur loss from the slag due to oxidation by air. The rate of weight loss during the air oxidation appears to be constant at 0.18%/minute. It is interesting to note a constant sulphur removal rate with temperature and sulphur concentration in the molten slag. Allertz and Sichen (Allertz & Sichen, 2015) also reported that there was no significant effect of temperature on the rate of sulphur removal from the liquid slag. Hence, these results indicate that the sulphur removal is limited by gas phase mass transfer. Pelton et al. (Pelton et al., 1974) reported that the sulphur removal is limited by gas phase mass transfer control for $p_{O2}<0.1$ atm. In the current work, sulphur removal is found to be linear at a higher oxygen partial pressure (0.21). The likely reason is the presence of iron in the system. In their work, it was reported that the presence of transient metal ions can enhance the rate of reaction. The effect was found to be stronger for iron than manganese. Hence, it appears that in the presence of about 7.5% Fe in slag, the rate of sulphur removal remains controlled by gas phase mass transfer even for higher p_{O2} level. Coombs and Munir (Coombs & Munir, 1989) reported weight gain due to oxidation of FeS at low temperatures (425-525 °C) but the weight gain in the current experiments is much larger considering lower amount of FeS in the system. The reason for initial weight gain is not clear.
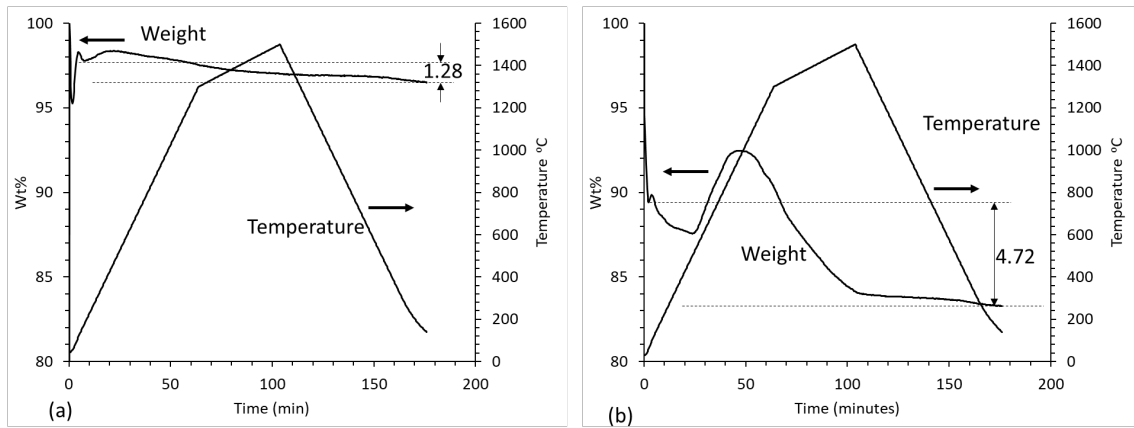
Figure 5. Weight change during TGA experiments; the gas atmosphere was switched from argon to air in the temperature between 1300 – 1500°C. (a)the slag without sulphur and (b) slag with sulphur

Figure 6 shows calculate partial pressure of SO_2 for the equilibrium between slag and inert/air atmosphere. The calculation was performed using FactSage 8.3. FToxid and FactPS databases were selected for these calculations. The equilibrium between slag and air was calculated by fixing p_{O_2} = 0.21. The partial pressure of SO_2 is significant in presence of air, the atmosphere becomes SO_2 saturated after 1480°C. The sulphur removal is also possible at a lower temperature as the chamber is continuously purged with fresh air. The partial pressure of SO_2 is negligible in inert atmosphere, it is unlikely to observe significant sulphur removal in the absence of air. As expected, FactSage (Bale et al., 2016) calculations show that sulphur is present in the slag as sulphate and sulphide in presence of air and inert atmosphere respectively. The activity of $CaSO_4$ and CaS in equilibrium with air is 1 and ~0 respectively at all calculated temperatures. These activities are ~0 and 0.6-0.85 in the inert atmosphere.
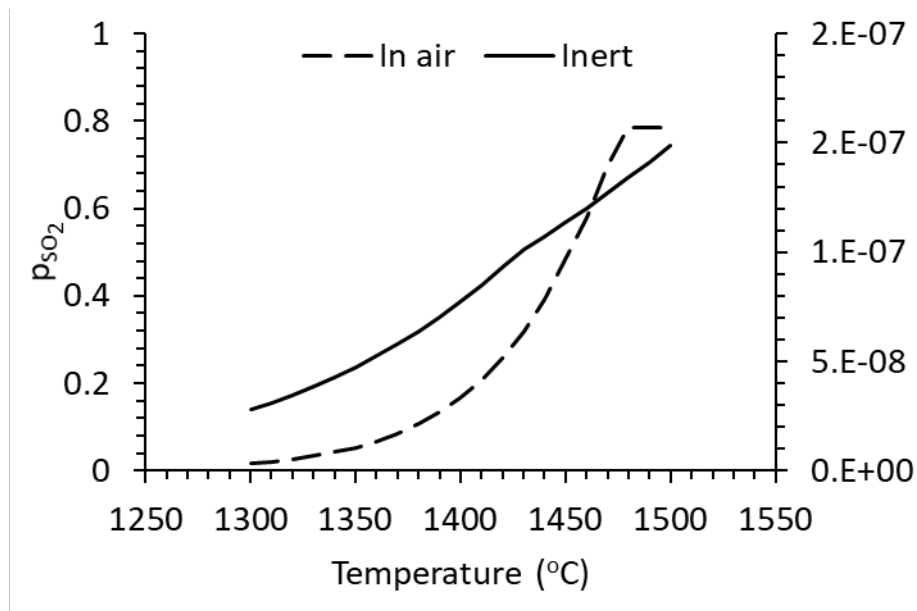

Figure 6 Partial pressure of SO_2 with and without air calculated using FactSage (Bale et al., 2016)

The current work highlights the role of ambient air on the potential Sulphur removal from steel refining slag. Certainly, more work is needed under laboratory conditions to clarify the effect of atmospheric condition on desulphurization of liquid steel. The steel-slag reaction needs to be studied in more detail using MgO-C crucible. Another potential implication of this study is to desulphurize steel refining slag using air at high temperature.

CONCLUSIONS

Following conclusions can be made based on the current work:

1. Plant observation show that sulphur may be oxidizing from the slag during ladle refining

2. There is a significant evaporation for molten slag in the presence of source of carbon (graphite crucible or C in MgO-C crucible). Magnesium consistently evaporate and form MgO. Fibrous deposits are consistently seen in the colder region.

3. Sulphur is also observed to be removed through gas phase during oxidation of slag experiment conducted using induction furnace. In this case, the fibrous structure showed presence of sulphur in association with Fe, Mn and Ca.

4. Oxidation of slag with and without sulphur was also studied using a TGA setup. A constant weight loss rate was observed for sulphur containing slag indicating the slag desulphurization to controlled by gas phase mass transport for such setup.

ACKNOWLEDGEMENTS

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