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Recycling of Waste Oxides in Steelmaking

Final Report for Project 9760 – 04/01/1998 – 11/30/2000

R. J. Fruehan

November 2000

Work Performed Under Contract No. DE-FC07-97ID13554

**For
U.S. Department of Energy
Assistant Secretary for
Energy Efficiency and Renewable Energy
Washington, DC**

**By
American Iron and Steel Institute
Pittsburgh, PA**

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Final Report

RECYCLING OF WASTE OXIDES IN STEELMAKING

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RECYCLING OF WASTE OXIDES IN STEELMAKING

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Abstract:

The U.S. steel industry produces over 3 million tons of waste oxides, as dusts and mill scale, per year. This research primarily examined the use of these materials in basic oxygen furnace (BOF) as waste oxide briquettes (WOBs), and in particular, the reasons for and methods to reduce slopping in BOFs when WOBs are used. Also, the recycling of EAF and stainless steelmaking dusts were examined. Slopping occurs, when WOBs are used in the BOF, because the slag contains more FeO early in the blow causing high gas generation rates in a highly foamable slag. It is found that at a critical FeO content in the slag, metal drops emulsify increasing the reaction area and rate drastically, promoting slopping. Recommendations were made to delay the build-up of FeO in the slag to this critical value, thus reducing slopping.

Although recycling of EAF dusts in the EAF increases energy use and decreases productivity, it provides Fe units, reduces dust disposal by 25-40%, and increases the Zn content of the dust to acceptable levels for use by Zn-producers.

Stainless steelmaking dusts can also be recycled as WOBs adding Cr to the melt and generating CO gas resulting in good slag foaming.

TABLE OF CONTENTS

<u>Contents</u>	<u>Page</u>
TABLE OF CONTENTS	iii
LIST OF FIGURES	iv
EXECUTIVE SUMMARY	1
1.0 INTRODUCTION	2
2.0 EXPERIMENTAL RESULTS AND DISCUSSIONS	4
3.0 CONCLUSIONS	6
4.0 APPENDICES:	
Appendix A	13
Appendix B	48
Appendix C	58
Appendix D	74
Appendix E	83

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 1: Dependence of rate on FeO content of the slag at 1440° C	8
Figure 2: Schematic diagram representing the reaction of a 1 gram Fe-C-S droplet with a slag containing 20 wt% FeO at 1440° C	9
Figure 3: The expected foam height of BOF slag during the first half of the Blowing as a function of the decarburization rate	10
Figure 4: Effect of EAF dust recycling on energy consumption and productivity	
Figure 5: The dust generation rate on Zn content with continuous recycle at 1%	12

EXECUTIVE SUMMARY

The U. S. steel industry produces over 3 million tons of dusts and millscale per year. These materials can be recycled in steelmaking. This research primarily examined the use of these materials in the Basic Oxygen Furnace (BOF) and in particular, the reasons for and methods to reduce slopping. The research also examined the recycling of Electric Arc Furnace (EAF) and stainless steelmaking dusts. The major findings include:

- When waste oxide briquettes (WOBs) are used in a BOF, slopping occurs because the slag has more FeO early in the blow causing high gas generation rates in a highly foamable slag.
2. At a critical FeO content in the slag, metal drops emulsify increasing the reaction area and rate drastically. To avoid slopping, this critical FeO content should not occur too early during the oxygen blow.
 3. Recommendations were developed to reduce slopping when using WOBs.
 4. It seems not feasible to separate zinc oxides from zinc ferrites in EAF dusts by size.
 5. Recycling of EAF dusts in the EAF was evaluated. Whereas this process increases energy consumption and decreases productivity, it provides Fe units, reduces dust disposal by 25-40% and increases the Zn content of the dust to acceptable levels.
 6. Stainless steel dusts can be recycled as WOBs adding Cr to the metal and generating CO gas resulting in good slag foaming.

1.0 INTRODUCTION

The US steel industry produces over three million tonnes of waste oxide dusts per year. The major sources are blast furnace (BF), basic oxygen furnace (BOF), and electric arc furnace (EAF) dusts and mill scale. These materials should not be considered wastes but rather as valuable by-products since they contain valuable iron (Fe) units and alloying compounds. In most countries, BF and BOF dusts are recycled in sinter plants and used in the BF. However, in the US, most sinter plants have been closed and considerable amounts of dust are simply being landfilled. Also, sinter plants have significant environmental problems. EAF dusts are classified as hazardous wastes and must be disposed of in special landfills at a high cost or treated. EAF dust treatment processes have had limited success. To be economical, the Zn and Pb must be removed and sold as a raw material for Zn product, and a suitable reduced iron product produced for recycling into the EAF. In addition, dusts generated in the production of stainless steel in the EAF and argon oxygen decarburization (AOD) vessels contain valuable alloying elements; in particular, chromium and nickel should be used effectively.

An obvious but somewhat difficult use of these by-products is to recycle them directly into the steelmaking furnaces, i.e. in the BOF or the EAF. Several steel companies produce waste oxide briquettes (WOBs) from BF and BOF dusts and mill scale. These are often used in the blast furnace. However, their use in the blast furnace is somewhat limited because they soften at lower temperatures than sinter or pellets causing an increased pressure drop in the furnace and thus reducing productivity. They also cause excessive Zn build-up in the furnace, which can cause scaffolding. WOBs can also be used in the BOF but reduce scrap melting, increase the Zn content of the dust, and cause excessive slopping.

At a meeting in Pittsburgh at the beginning of the research project, slopping when using WOBs, was identified as the critical issue. Plant trials were conducted in which the FeO and basicity of the slag were measured during the BOF process with and without WOB additions. Slopping occurs when there is an increase in gas evolution into a highly foamable slag. Excessive gas generation occurs when over-oxidized slag with high FeO contents reacts with carbon in iron drops producing CO. High foamable slags are those with high viscosity. These slags have a low basicity and temperature and are present in the first 50% of the blow when slopping occurs.

EAF dusts can and are recycled into the EAF. The difficulties include increased power consumption, decreased productivity, and Zn build up in the dust. Zn build up in the dust can actually be a benefit if the Zn content can be high enough so that the dust can be used as a fertilizer or as a raw material for Zn metal production. Stainless steelmaking dusts can be recycled adding chromium to the steel but they also increase power requirements and decrease productivity.

The objectives of this work were to:

- Task I. Measure the rate of reaction of FeO in slag and C in metal relevant to slopping.
- Task II. Measure the foamability of slags relevant to slopping.
- Task III. Make recommendations to reduce slopping when using WOBs.
- Task IV. Examine the vaporization of Zn from scrap.
- Task V. Evaluate the effect of recycling EAF dusts on energy consumption, productivity and Zn content of dust.
- Task VI. Determine the recovery of Cr from stainless steelmaking dusts during recycle and their effect on foaming.

2.0 EXPERIMENTAL RESULTS AND DISCUSSION

The experimental techniques, results and implications of these results with respect to steelmaking operations are discussed in detail in Appendices A, B, C, D and E. The highlights are summarized below.

Task I. Extensive research was conducted on the rate of reaction of FeO in slag by C in Fe for steelmaking conditions and resulted in two publications (Appendices A and B). The experimental technique was the constant volume pressure increase (CPVI) technique, the details of which are given in Appendix A. Briefly, a piece of Fe-C alloy (2g) is heated to about 1200°C and then dropped into the slag. The moles of CO generated as a function of time are measured by the increase in pressure. The CO is from the reaction:

Typical results are shown in Figure 1. As indicated in Figure 1, at about 5% FeO, the rate increases drastically and is much faster than the calculated value based on our current understanding. There must be a change in the basic mechanism.

To understand what is happening, x-ray fluoroscopy was used to view the reaction as it was happening. Below about 5% FeO in the slag, the metal droplet remained as a single drop; at higher FeO contents, the drop emulsified greatly increasing the surface area. When the reaction stopped, it reformed into a single drop. This is shown schematically in Figure 2. This is an important new finding. In fact if this did not occur, the fast decarburization reaction for the BOF would not occur.

The rate was measured as functions of temperature, FeO in the slag, Fe₂O₃ in the slag, carbon in the metal and sulfur in the metal. The results are detailed in Appendices A and B. From these, the critical condition for the fast reaction, which is necessary for slopping, were defined.

Task II. Slag Foaming: Slopping requires a high reaction rate and a foamable slag. Therefore, the foamability of slags relevant to slopping conditions was measured. The detailed experimental technique and results are given in Appendix C. The experimental technique consisted of measuring the foam volume as a function of gas flow rate through the foam. The foam index (Σ), defined by equation (2), is the accepted measure of foamability.

$$\Sigma = \frac{V_f}{Q} \quad (2)$$

V_f = foam volume

Q = gas flow rate

In general, the foamability of a slag increases with viscosity. Therefore, a slag with low basicity, low FeO content, and at low temperatures has high foamability; these are the conditions at about 25-50% into the blow when slopping occurs. In Figure 3, the foam height in a BOF is plotted versus decarburization rate for different parts of the blow. As seen in this figure, if the fast decarburization rate occurs too early in the blow, the foam height will become excessive and slopping will occur. (See Appendix C for details).

Task III Recommendations for Reducing Slopping: Based on the results of Tasks I and II, recommendations for reducing foaming when using WOBs were developed. The details are given in Appendix B. Briefly,

- 1) Add the WOBs after about 30% of the blow, to reduce the chances of an over-oxidized slag when the slag basicity and temperature are higher.
- 2) Add the WOBs continuously to avoid excessive build up of FeO.
- 3) Reduce the time the lance is in the high position early in the blow to reduce the amount of FeO in the slag.
- 4) If all else fails, reduce the oxygen blowing rate at between 25% and 40% of the blow to decrease CO generation.

Task IV. Examination of Zn Vaporization: In general, zinc oxide (ZnO) and zinc ferrite (ZnFeO₂) form in EAF and BOF dust. For commercial purposes, ZnO is preferred. Its particle size in the dust is slightly larger than ZnFeO₂. Experiments were conducted to examine the formation of these particles. Zn was vaporized from Zn coated scrap or liquid Zn, and iron from liquid iron at a higher temperature. The condensed particles were examined using a scanning electron microscope (SEM) for their size and composition. These experiments proved to be very difficult and critical. ZnO and zinc ferrite did form in the gas phase, but there was no correlation with regards to particle size or how they vaporized. The results did not indicate whether it was possible to control the size or composition of the Zn oxides or ferrites.

Task V. Recycling EAF dusts: The effect of recycling EAF dusts on energy consumption, productivity and Zn content of the dust was evaluated using an energy and material balance for the EAF with dust as part of the charge and a dust composition model to compute the dust generated. The detailed results are given in Appendix D. Dust recycling, at a typical recycling rate of 1.1% of the charge, about 11 kg per tonne or 22 lbs. per ton of steel, increases energy consumption by about 15 kwh/tonne and decreases productivity by about 3% as shown in Figure 4. For a typical dust load of 12.5 kg per tonne of steel (25 lbs. per ton) for a normal heat, when recycling 1% dust, the dust load reaches a steady state level of 18 kg per tonne and the Zn content increases to about 50% (Figure 5). This Zn-enriched dust can be used by a Zn producer. Moreover, the amount of dust to be disposed of is reduced to 8 kg per tonne of steel.

Task VI. Recycling of Stainless Steelmaking Dusts: In the final year of the project, industry experts defined two critical issues for the recycling of stainless steelmaking dust. These are the recovery of valuable chromium and the potential of the WOBs to provide

foaming. Exploratory research was conducted on the thermodynamics and kinetics of Cr recovery into the metal. The preliminary results are given in Appendix D. These results indicate that most of the Cr can be recovered. This work is continuing with funds from other sources.

Another critical issue is the use of WOBs not only to provide Cr and Ni but also to aid in foaming. When making stainless steel in the EAF, slag foaming is not as good as for carbon steels. This may be because of poor slag foamability or the inability to generate gas by the injection of carbon into the slag. The paper in Appendix E describes measurements of the foamability of stainless steelmaking slags and the relative rates of reactions (3) and (4):

The results in Appendix E show that liquid stainless steelmaking slags have similar foamability as those for carbon steelmaking. However, due to the low solubility of Cr_2O_3 excessive solid phases form making the slag partially solid or “chunky”, and then, the slag cannot foam. The work also shows that the reaction (3) is much faster than the reaction (4). This means that gas generation, when producing carbon steels, is better because the reaction (3) produces sufficient gas, whereas for stainless steels, the reaction (4) does not produce sufficient gas for foaming.

WOBs for stainless steel contain Cr_2O_3 , FeO, CaO and C plus other minor compounds. When these are added to the slag, the C and FeO react according to the reaction (3) and good foaming results. This was demonstrated in the work discussed in Appendix C.

3.0 CONCLUSIONS

This work examined several critical issues when using recycled waste oxides in steelmaking. The major results were:

- When using WOBs in a BOF, slopping occurs, because the slag has more FeO early in the blow, causing high gas generation rates in a highly foamable slag.
2. There is a critical FeO content in the slag when metal drops emulsify increasing the reaction area and rate drastically. To avoid slopping, this should not occur too early during the blow.
3. Recommendations were developed to reduce slopping when using WOBs.
4. It does not appear feasible to separate zinc oxide from zinc ferrite in EAF dusts by size.
5. Recycling of EAF dusts in the EAF was evaluated. Whereas this process increases energy consumption and decreases productivity, it provided Fe units, reduces dust disposal by 25-40% and increases the Zn content of the dust to acceptable levels.

Figure 1. Dependence of rate on FeO content of the slag at 1440°C (weight of metal = 1 gram)

Figure 2. Schematic diagram representing the reaction of a 1 gram Fe-C-S droplet (2.91 wtC, 0.011 wt%S) with a slag containing 20wt%FeO at 1440°C)

Figure 3. The expected foam height of BOF slag during the first half of the blowing as a function of the decarburization rate.

Figure 4. Effect of EAF dust recycling on energy consumption and productivity.

Figure 1. The generation of Zn content in the dusts recycled.

Appendix A

The Reaction Behavior of Fe-C-S Droplets in CaO-SiO₂-MgO-FeO Slags

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ABSTRACT

The rate of reduction of FeO in the slag by carbon in iron droplets (2.9wt%C, 0.01wt%S) was studied for CaO-SiO₂-MgO slags containing between 3 and 35wt%FeO for temperatures ranging from 1643-1763K. The effects of Fe₂O₃ additions to the slag and sulfur variations in the metal on the reaction rate were also examined. It was found that the behavior of the metal droplets in the slag, as observed by x-ray fluoroscopy, changed significantly with FeO content in the slag. Below 10wt%FeO, the droplet remained intact while reacting with the slag, however, at higher FeO concentrations, the droplet became emulsified within the slag. The large increase in surface area of the metal droplet due to emulsification caused the rate of reaction to be one to two orders of magnitude faster than for droplets that did not become emulsified. It was suggested that when the droplet is emulsified, the surface area and reaction kinetics are greatly increased, and the rate becomes controlled by mass transfer of FeO as Fe²⁺ and O²⁻ ions in the slag to the emulsified droplet. At low FeO contents for which the droplet does not emulsify, the rate is controlled by dissociation of CO₂ on the metal. It was also found that a critical temperature exists for a given FeO content at which point the rate of CO evolution increases dramatically. Additions of Fe₂O₃ to the slag and sulfur to the metal caused significant changes to the rate of reaction possibly by affecting the emulsification behavior of the droplet.

INTRODUCTION

One of the fundamental steelmaking reactions is the reduction of FeO in the slag by carbon in the metal as follows:

The mechanisms influencing the rate of this reaction have been studied in great detail.¹⁻⁷ Mulholland et al.¹ were the first to observe the presence of a gas halo surrounding Fe-C-S droplets (0.8-4.5wt%C, 0.04 and 1.0wt%S) while they reacted with a 47wt%CaO-38wt%SiO₂-15wt%Al₂O₃-10-30wt%Fe₂O₃ slag between 1723 and 1873K. The presence of the gas halo gave rise to theories in which gas-slag and gas-metal interfacial reactions influence the rate of Reaction (1). In a more recent study, Min and Fruehan⁴ developed a model to describe the mechanisms controlling the rate of Reaction (1) for CaO-SiO₂-4.6wt%Al₂O₃ slags with a basicity (%CaO/%SiO₂) of 1 containing 2-10wt%FeO. The Fe-C-S droplets contained 2.3-4.2wt%C and 0.001-0.08wt%S, and the temperature ranged from 1673-1723K. In their study, they considered five possible mechanisms to be rate-limiting:

3) mass transfer of FeO as Fe²⁺ and O²⁻ ions through the slag

4) mass transfer of C through the metal

5) mass transfer of CO-CO₂ through the gas halo

These mechanisms are shown schematically in Figure 1. According to Min and Fruehan, it was found that step (1) was rate-limiting if the sulfur content of the metal was

$\geq 0.01\text{wt}\%$. Step (3) was also found to contribute to the overall rate. Steps (2), (4), and (5) were fast and therefore not considered to be influencing the rate of reaction (1).

Figure 1: Schematic diagram representing the reaction of an Fe-C droplet with FeO in the slag as presented by Min and Fruehan⁴

Despite the extensive work that has been conducted on Reaction (1), limited work has been done on the behavior of Fe-C-S droplets in CaO-SiO₂-MgO slags with FeO contents $\geq 20\text{wt}\%$ at temperatures ranging from 1643-1798K such as is experienced during the early stages of the oxygen steelmaking process. Understanding the behavior of Reaction (1) during this process may be critical to understanding slopping behavior, an unfavorable result of excessive slag foaming in steelmaking. Therefore, this study focuses on measuring the rate of Reaction (1) for Fe-C-S droplets containing approximately 2.9wt%C and 0.01wt%S and for slag FeO contents ranging from 3 to 35wt%FeO. In addition, the behavior of the metal droplets within the molten slag was

studied using x-ray fluoroscopy. Finally, the effects of temperature, additions of Fe_2O_3 to the slag, and the sulfur content of the metal on the rate of Reaction (1) were investigated.

EXPERIMENTAL WORK

Measurement Of The Rate Of Reduction Of FeO By $\underline{\text{C}}$: The rate of Reaction (1) was determined by using a constant volume pressure increase technique (CVPI) in which one mole of CO gas produced is equivalent to one mole of FeO reduced. Thermodynamically, a small amount of CO_2 can also form. The equilibrium amount of CO_2 is proportional to the FeO content, and the maximum equilibrium amount that can form is less than 9% for the highest FeO contents studied. In several tests, the amount of CO_2 was measured and found to be negligible. A pressure transducer with a sensitivity of approximately $2 \times 10^{-4} \text{ atm}$ was used to measure the pressure increase with time for each experiment. The compositions of the metal and aim compositions of the slag used are represented in Table I.

Table 1: Experimental Variables Used for the Measurement of the Rate of Reduction of FeO in the Slag by $\underline{\text{C}}$

Aim wt%FeO ^{**}	0	3	5	10	15	20	30	35
Aim wt%Fe ₂ O ₃ ^{**}	5	0	0,5	0,5	0	0,5	0	0
wt%C	2.91	2.91	2.91	2.91	2.88	2.11- 3.86	2.91	2.91
wt%S	0.011	0.011	0.011	0.011	0.014	0.003- 0.42	0.011	0.011
Temp (K)	1713	1713	1713	1663- 1763	1663- 1763	1643- 1763	1643- 1763	1713

* Basicity ($\% \text{CaO} / \% \text{SiO}_2$) = 1.2, MgO ~ 12wt% for all experiments

**The FeO content measured following each experiment was 1-2wt% less than the aim composition. The Fe_2O_3 was measured prior to each experiment and was within 0.5wt% of the expected composition.

The Fe-C-S alloys were prepared by melting the appropriate amount of analytical grade iron chips (99.5%Fe), graphite rod (99.5%C), and FeS in an induction furnace under an argon atmosphere. Samples were pipetted out of the molten bath using a quartz tube (i.d. = 5.0mm). The samples were quenched and sectioned into approximately 1 gram pieces. The FeO was prepared by heating reagent grade Fe_3O_4 powder placed into a steel crucible to 1273K under an argon atmosphere. Once at temperature, a 1:1 CO/CO_2 gas mixture was blown through an alumina tube onto the surface of the Fe_3O_4 powder at a flowrate of approximately $600\text{cm}^3/\text{min}$ for approximately 12 hours. The system was then cooled to 1073K, removed and quenched in a room temperature water bath while maintaining a high flowrate of argon on the surface of the sample. The composition of the final FeO product was verified qualitatively by x-ray diffraction.

Approximately 60 grams of a synthetic slag ($\%\text{CaO}/\%\text{SiO}_2=1.2$, $\text{MgO}=12.0\text{wt}\%$) containing the appropriate amount of FeO were charged into a high purity MgO crucible (i.d. = 3.8 cm, o.d = 4.3 cm, h = 9.0 cm). To limit sulfur transfer from the metal to the slag, a specified amount of CaS was added.⁸ The crucible was placed into the reaction chamber of a molybdenum disilicide resistance furnace and was heated to the experimental temperature in a purified argon atmosphere. Once the slag reached temperature, the furnace was sealed, and an approximately one gram Fe-C-S alloy pellet of the appropriate composition was released from a rotary compartment into a tapered mullite tube centered over the slag bath. A schematic of the experimental set-up is in Figure 2. Once the pellet melted, it was released as a metal droplet from the tapered end of the tube, falling into the slag bath where it began to react. The pressure increase due to the evolution of CO gas was measured by the pressure transducer in terms of mV and was

converted to total moles of FeO reacted with time. After the reaction appeared to cease (indicated by a constant pressure transducer reading), another pellet was released and measurements were taken. As many as three metal pellets were released into the slag during an experiment. After reaction of the last pellet ceased, the furnace was cooled down to room temperature in an argon atmosphere, and the MgO crucible containing the metal-slag mixture was removed. The metal and slag were then analyzed for C and FeO, respectively.

Figure 2: Experimental set-up for the measurement of the rate of Reaction (1)

Observation Of The Reaction Using X-ray Fluoroscopy: X-ray fluoroscopy was used to observe the behavior of the metal droplet while it reacted with slags containing 10 and

20wt%FeO and for a slag containing 5wt%Fe₂O₃ at 1713K. X-ray video recording began as soon as the Fe-C-S pellet (2.91wt%C, 0.011wt%S) was released into the tapered mullite tube centered over the slag bath. Recording continued until reaction of the droplet with the slag appeared to cease. At that time, another pellet was released and recording began once again. As many as three pellets were observed during the course of an experiment.

RESULTS

Results for the Measurement of the Rate of Reduction of FeO by C: Typical results for the measurement of the rate of reduction of FeO in the slag by carbon in the metal for 10, 20, and 30wt%FeO and for temperatures ranging from 1643-1763K are presented in Figures 3 to 5. In each figure, the variation of the total moles of CO evolved (equal to the moles of FeO reduced) was plotted with respect to time. Several observations were made from these experiments. Two distinctive rates, defined by the slope of the linear portion of the data ($\Delta n_{CO}/dt$ where n_{CO} represents the total moles of CO evolved and t represents time) were observed for each condition studied. For 10wt%FeO, the initial rate varied greatly with temperature. At 1713K,

Figure 3: Variation of the Total Moles of CO evolved with time (s) for 10wt%FeO from 1713-1763K (weight of metal = 1.1g)

the initial rate was calculated using linear regression to be 3.0×10^{-5} moles/s and increased by an order of magnitude to approximately 2.0×10^{-4} and 3.0×10^{-4} moles/s 1738 and 1763K, respectively. Note that the rates are in moles/s with no surface area included. This is because, as will be discussed further, after the metal droplet emulsified, the surface area increased significantly and was unknown. In all cases, the rate was for metal droplets weighing 1.1 grams. For 20wt%FeO, this same temperature dependence of the initial rate was observed as the temperature increased from 1643-1663K. In this case, the rate increased from 5.0×10^{-5} to 1.0×10^{-4} moles/s for metal droplets weighing 1 gram. Further increases in temperature resulted in only a small increase in the initial rate. For the slag containing 30wt%FeO, the initial rate showed some dependence on temperature from 1643-1763K where the rate ranged from 7.8×10^{-5} to 3.1×10^{-4} moles/s for droplets weighing gram. The secondary rate for all the conditions studied at 10, 20 and

30wt%FeO ranged from 7.5×10^{-7} to $.9 \times 10^{-6}$ moles/s. In Table II, the rates of FeO reduction for all FeO contents studied are listed.

Figure 4: Variation of the Total Moles of CO Evolved with time (s) for 20wt%FeO from 1643-1763K (weight of the metal = 1 gram)

In Figure 6, the total moles of CO evolved as a function of time was plotted for 3-30wt%FeO at 1713K in order to demonstrate the large dependence of the rate on FeO content. As evidenced from this plot, below 10wt%FeO, only one distinctive rate was observed and was estimated to be 3.0×10^{-6} moles/s, two orders of magnitude slower than the initial rate measured at 20 and 30wt%FeO.

Figure 5: Variation of the Total Moles of CO evolved with time (s) for 30wt%FeO from 1643-1763K (weight of metal = 1gram)

For experiments performed as a function of Fe_2O_3 content in the slag and sulfur content in the metal, the shape of the total moles vs. time plots appeared similar to those observed for slags containing $\geq 10\text{wt}\%\text{FeO}$. Table III lists the rates for each of these conditions studied. The results from all the experiments are discussed below.

Table II Rates of evolution of CO (moles/s) for aim FeO contents ranging from 3-35wt% for temperatures of 1643-1763K and metal droplets weighing ~1gram

Aim wt%FeO	Temperature (K)	Initial Rate (moles/s)	Secondary Rate (moles/s)
3	1713	3.3×10^{-6}	-
5	1713	3.0×10^{-6}	-
10	1663	2.5×10^{-5}	1.1×10^{-6}
10	1713	3.0×10^{-5}	1.0×10^{-6}
10	1738	2.0×10^{-4}	8.5×10^{-7}
10	1763	3.0×10^{-4}	8.5×10^{-7}
15	1663	5.0×10^{-5}	1.1×10^{-6}
15	1713	1.8×10^{-4}	1.0×10^{-6}
15	1763	2.6×10^{-4}	1.2×10^{-6}
20	1643	5.0×10^{-5}	1.8×10^{-6}
20	1663	1.3×10^{-4}	1.9×10^{-6}
20	1713	2.0×10^{-4}	1.1×10^{-6}
20	1763	2.4×10^{-4}	1.4×10^{-6}
30	1643	7.8×10^{-5}	8.5×10^{-7}
30	1663	1.9×10^{-4}	8.8×10^{-7}
30	1713	2.1×10^{-4}	7.5×10^{-7}
30	1763	3.1×10^{-4}	1.2×10^{-6}
35	1713	2.0×10^{-4}	1.2×10^{-6}

Table III Rates of Evolution of CO (moles/s) for Experiments Performed as a Function of Fe_2O_3 in the Slag and Sulfur Content in the Metal

Aim wt%FeO	Aim wt% Fe_2O_3	wt%C	wt%S	Temp (K)	Initial Rate (moles/s)	Secondary Rate (moles/s)
0	5	2.91	0.011	1713	1.7×10^{-5}	1.1×10^{-6}
5	5	2.91	0.011	1713	2.7×10^{-5}	2.0×10^{-6}
10	5	2.91	0.011	1713	2.2×10^{-4}	2.3×10^{-6}
20	5	2.91	0.011	1713	2.9×10^{-4}	1.3×10^{-6}
20	0	2.11	0.42	1713	5.1×10^{-5}	1.6×10^{-6}
20	0	3.45	0.094	1713	1.2×10^{-4}	1.0×10^{-6}
20	0	3.84	0.003	1713	7.8×10^{-5}	1.0×10^{-6}

Figure 6: Variation of the Total Moles of CO evolved with time (s) for 3-30wt%FeO at 1713K (weight of metal = 1.0-1.1g)

Results for the X-ray Fluorescopy Experiments: X-ray fluorescence experiments were completed for slags containing 10 and 20wt%FeO as well as 5wt%Fe₂O₃ at 1713K. Although it was originally uncertain as to how visible the drop would appear within the slag due to the slag's high density, many observations were made during the course of an experiment. The behavior of the droplet in the slag for the slag containing 20wt%FeO is summarized in a series of schematic diagrams in Figure 7. First, the pellet melted in approximately 40 seconds and fell as one droplet into the molten slag. Next, within 1 second after the droplet fell into the slag, the initial reaction period began. During this period, the droplet emerged out of the thick slag while a foamed slag layer was

Figure 7 Schematic diagram representing the reaction of 20wt%FeO slag with 2.91wt%C, 0.011wt%S droplet at 7 K

simultaneously being formed. The droplet quickly became emulsified, increasing to over two times its original diameter or over 10 times in volume. X-ray images of the emulsified droplet are represented in Figure 8. As this fast reaction period continued, the emulsified droplet remained suspended in the foamed slag which was heavily agitated by gas evolution. The diameter of the bubbles being released from the surface of the emulsified droplet were difficult to distinguish due to low contrast of the x-ray video, however, each was estimated to be between 1 and 2mm. After approximately 6 seconds, the emulsion collapsed, and the droplet quickly recoalesced and entered the thick slag layer. This marked the end of the fast reaction period. The droplet then rapidly fell to the bottom of the crucible. During this time, an occasional gas bubble of relatively small diameter in comparison to the diameter of the droplet was released from the droplet and rose to the surface of the thick slag layer. The foamed slag began to collapse at the end of the fast reaction period and virtually disappeared after approximately 30 seconds. At that point, another metal pellet was released, and the same behavior was observed. Release of a third pellet again resulted in a similar behavior. The overall behavior of the droplet in the slag containing 10wt%FeO was similar to that described above, however, it took approximately 9 seconds for the emulsified droplet to grow to a maximum size of over double its original diameter. Consequently, formation of the slag foam was not as fast as was observed for the slag containing 20wt%FeO.

The behavior of the droplet while it reacted with a slag containing 5wt%Fe₂O₃ at 1713K was much different than the behavior observed at 10 and 20wt%FeO. As the droplet fell into the slag, reaction began within 2 to 3 seconds. Unlike the results of the experiments described above, the droplet did not become emulsified as it reacted with the

slag, but remained virtually intact. Also, at times the droplet appeared to be surrounded by a thin layer of slag less dense than the bulk slag. The reaction of the droplet with the slag continued for approximately 50 seconds. The formation of stable foam was not observed during the reaction. Once reaction ceased, the droplet slowly sank to the bottom of the crucible. This behavior was similar to that observed by Min and Fruehan⁴ for slags with low FeO contents (<5wt%). The results from the x-ray experiments are discussed in the following section.

Figure 8: X-ray image of a 1gram Fe-C-S droplet (2.91wt%C, 0.011wt%S) reacting with a slag containing 20wt%FeO at 1713K; a) at $t = 3$ s, b) at $t = 6$ s, and c) at $t = 8$ s

DISCUSSION

Figure 9 represents the variation of the rate of evolution of CO (moles/s) with wt%FeO in the slag at 1440°C. Based on the current results for experiments conducted using 3 and 5wt%FeO in the slag, Min and Fruehan's model holds, and the rate is defined by the gas-metal reaction expressed as follows:

$$Rate\left(\frac{\text{moles}}{s}\right) = k_{g/m} A (P_{CO_2} - P_{CO_2}^{eq}) \quad (4)$$

where:

$k_{g/m}$ = rate constant for Reaction (2) (moles/cm²satm)

A = surface area of the droplet (cm²)

P_{CO_2} = equilibrium partial pressure of CO₂ defined by Reaction (3) (atm)

$P_{CO_2}^{eq}$ = partial pressure of CO₂ for Reaction (2) (approximately zero)

or in terms of wt%FeO:

$$Rate\left(\frac{\text{moles}}{s}\right) = k_{g/m} AKC(\text{wt}\%FeO) \quad (5)$$

where:

K = equilibrium constant for Reaction (3)

C = constant relating the activity of FeO to wt%FeO

The rate constant, $k_{g/m}$, takes into account the effect of the sulfur content in the metal on the rate. The value of $k_{g/m}$ was taken from the results of Sain and Belton⁹ who measured the rate of Reaction 2 with Fe-C-S melts. The calculated rate for the gas-metal reaction is represented as a dashed line in Figure 9. At FeO contents of $\geq 10\text{wt}\%FeO$, the observed

rate was much faster than that predicted by Min and Fruehan's model. Typically, a dramatic increase in rate signifies a change in mechanism associated with a large increase in reaction surface area. Based on the x-ray video for slags with these higher FeO contents, it was found that there was a significant increase in surface area of the droplet due to emulsification. Because Min and Fruehan's model relies on the droplet remaining intact (they observed with x-ray fluoroscopy no emulsification of the droplet at FeO contents less than 5 wt%) , it can not be applied when the droplet becomes emulsified. Therefore, new mechanisms such as mass transfer of FeO into the emulsified droplet were considered and are discussed below.

Effect of FeO Content in the Slag on the Rate of CO Evolution: According to the results of this study, the FeO content of the slag has a significant effect on the behavior of the metal droplet while it reacts with the slag. The dependence of the rate on FeO content in the slag at 1713K is represented in Figure 9. As previously mentioned, below 10wt%FeO, the droplet remains intact while it reacts with the slag, and the rate of CO evolution is defined by Reaction (2). However, when the FeO content of the slag is increased to 10wt% and higher, the droplet's surface area increases drastically as it becomes emulsified, and the rate of reaction is very rapid. The emulsification behavior is believed by the present researchers to be due to the increased oxygen potential of the slag present with high concentrations of FeO. This phenomenon was first observed by Mulholland et al.¹, but their study was qualitative in nature and dealt primarily with observation of the gas halo around Fe-C-S droplets. Emulsification of the droplet was only briefly mentioned. In a later study, Gaye and Riboud² indirectly observed emulsification of Fe-C-S droplets while the droplets reacted with iron oxide containing

slags. During their study, they used a total Fe content of 17wt% (Fe^{2+} and Fe^{3+}) and measured fast initial reaction rates similar to those of the present study. They found by quenching the slag-metal samples following the fast reaction period that the metal was fragmented. This was attributed to vigorous gas evolution during decarburization, and it was proposed that sulfur in the metal further enhanced fragmentation of the droplet by lowering the slag-metal interfacial tension. In their study, Gaye and Riboud used the terms “fragmentation” and “emulsification” interchangeably.

In the present study, the droplet was observed to recombine following emulsification. It is believed that the metal filaments in the emulsion are interconnected. Therefore, no fragmentation of the droplet occurred.

A phenomenon similar to that observed during the present study was observed by researchers during the decarburization of carbon-saturated iron droplets by gases with high oxygen potentials at 1873K.¹⁰⁻¹⁴ For these studies, the droplets were observed to become heavily agitated with gas within a few seconds after exposure to the oxidizing gas. This phenomenon was referred to as “boiling” and emphasis was placed on the nucleation behavior of CO according to the following overall reaction:

It was postulated by Robertson and Jenkins¹⁰ that nucleation of CO was neither heterogeneous nor homogeneous but was referred to as “vortex nucleation”. They suggested that the access of oxygen to the droplet surface was restricted by the counter-diffusing carbon monoxide which was not being quickly burnt to carbon dioxide within the boundary layer during the initial decarburization period. Finally, they postulated that

Figure 9: Dependence of the rate of CO evolution (moles/s) on FeO content in the slag for a) <10wt%FeO and b) 3-30wt%FeO at 1713K and for a metal droplet weighing 1 gram where the dashed line represents the calculated rate based on Reaction (2)

turbulence at the surface of the droplet may have been due to rapid mass transfer significantly enhanced by oxygen since oxygen decreases the surface tension of liquid iron. In a more recent study, Gao et al.¹⁵ postulated that sulfur may enhance oxygen absorption into the bulk metal causing the build-up of internal CO pressure to be accelerated leading to the boiling phenomenon. They also found that the time to initiate boiling of the droplet decreased as the oxygen content of the gas increased, however, the exact cause of emulsification was not identified.

The current understanding is that at high oxygen potentials, oxygen is not consumed rapidly enough by carbon at the surface of the metal droplet. Therefore, the oxygen diffuses into the droplet and reacts with carbon internally producing CO. The internal nucleation and growth of the CO bubbles cause the droplet to boil or become emulsified within the slag.

It is possible that once emulsification begins, the rate is controlled by mass transfer of FeO as Fe²⁺ and O²⁻ ions to the external surface of the emulsified droplet. Any oxygen reaching this external boundary is then quickly consumed by Reaction (2). The flux of FeO ('FeO' is used rather than Fe²⁺ and O²⁻ for mathematical puposes) to the surface of the emulsified droplet can be expressed as follows:

$$J_{FeO}(\frac{moles}{scm^2}) = m_s(C_{FeO}^b - C_{FeO}^s) \quad (7)$$

$$J_{FeO}(\frac{moles}{s}) = \frac{m_s \rho_s A (\%FeO - \%FeO^s)}{100mw_{FeO}} \quad (8)$$

where:

m_s = mass transfer coefficient in the slag (cm/s)

C_{FeO}^b = concentration of FeO in the bulk slag (moles/cm³)

C_{FeO}^s = concentration of FeO at the surface (moles/cm³)

ρ_s = density of the slag (2.87g/cm³)

A = external surface area of the emulsified droplet (cm²)

mw_{FeO} = molecular weight of FeO (g/mole)

%FeO = FeO content of the bulk slag

%FeO^s = FeO content at the surface of the droplet (approximately 0 for this mechanism)

From the measured rates of the present study for 10 and 20wt%FeO at 1713K, the mass transfer coefficient was computed using Equation (8) assuming liquid phase mass transfer was controlling the rate. In order to make this calculation, the surface area, A , of the emulsified droplet was required. This was determined by observation of the x-ray videos obtained for 10 and 20wt%FeO. Figure 10 represents typical plots of the estimated external surface area of the emulsified droplet as a function of reaction time. From these plots, it was observed that the outer surface area of the emulsified droplet became stable after 2 seconds of reaction for the slag containing 20wt%FeO, but took over 9 seconds to become stable for the slag containing 10wt%FeO. Using the stabilized external surface area, the calculated value for the mass transfer coefficient in the slag, m_s , for 10 and 20wt%FeO was approximately 1.3×10^{-3} and 3.8×10^{-3} cm/s, respectively.

Ibl and Venczel¹⁶ developed a penetration model to determine the mass transfer coefficient in the slag. In this model, the effect of the rate of gas evolution within the slag on the mass transfer coefficient was taken into account according to the following overall equation:

$$m_s = \sqrt{\frac{12Dv(1-B)}{\pi d_b}} \quad (9)$$

where:

D = diffusivity (cm²/s)

v = gas evolution rate per unit area (cm³/cm²s)

B = degree of surface coverage (0<B<1)

d_b = average diameter of bubble (cm)

The diffusivity, D, was determined by Argawal and Gaskell¹⁷ for Fe in CaFeSiO₄ slags. They found reasonable agreement between the self-diffusion of Fe and the interdiffusivities of iron and oxygen in iron oxide melts. At 1713K, D is approximately 7.7x10⁻⁶(cm²/s). From the x-ray experiments, it appeared that there was a good degree of surface coverage of the emulsified droplet by gas bubbles resulting in B being close to unity. The value of B was chosen to be 0.9 based on a study by Sarma et al.¹⁸ who also used Equation (9) to determine the mass transfer coefficient of FeO in CaO-SiO₂-Al₂O₃ slags (for FeO contents less than 10wt%). The diameter of the bubble was estimated from the x-ray video to be 1mm. Using Equation (9), the value for the mass transfer coefficient in the slag, m_s, was calculated for 10 and 20wt%FeO. Equation (8) and the calculated experimental values for the mass transfer coefficient yielded values in the range of 1.3x10⁻³ to 1.3x10⁻²cm/s, and m_s increased with increasing FeO content. It should be noted that typically the mass transfer coefficient should not increase with FeO content but does so because of the increase in the gas evolution rate. Sarma et al. also saw this effect in their study. For the assumed conditions, the value of m_s from the experimental data was about one third the value computed from Ibl and Venczel's model.

Figure 10: Variation of the external surface area of the emulsified droplet (cm²) with time (s) for 10 and 20wt%FeO at 1713K

Considering the uncertainty in B , d_b , and D this is not unreasonable agreement. For example, if $B=0.95$ and $d_b=2\text{mm}$, m_s would decrease by a factor of two. Therefore, it is possible that for the present study mass transfer of FeO in the slag contributes to the rate of decarburization for slags containing $\geq 10\text{wt\%FeO}$. A better understanding of the emulsification phenomenon of the droplet in the slag is needed in order to better define the possible rate-limiting mechanisms.

Effect of Temperature: Based on the results of this study, the behavior of the droplet while reacting with FeO in the slag was not only dependent on the FeO content in the slag, but also on the experimental temperature. The natural logarithm of the rate of CO evolution (moles/s) for approximately 1 gram droplets is plotted as a function of inverse temperature for 10-30wt%FeO in Figure 11. From this plot, it appears that there is a critical temperature at which point the rate increases significantly for each FeO concentration. This effect was most pronounced for the slag containing 10wt%FeO where the rate increased by nearly an order of magnitude from 3.0×10^{-5} moles/s to 2.0×10^{-4} moles/s when the temperature increased from 1713K to 1738K. For 20 and 30wt%FeO, the rate increased significantly as the temperature increased from 1643K to 1663K. From the x-ray experiments performed for 10wt%FeO at 1713K, the droplet became emulsified as it reacted with the slag similar to the emulsification observed for the slag containing 20wt%FeO at the same temperature. However, the expansion of the emulsified droplet to over double its original diameter for the lower FeO containing slag took nearly ten times longer. It is postulated that the expansion rate of the emulsified droplet at 1738K for the 10wt%FeO slag was significantly faster than at 1713K, thus leading to the pronounced increase in reaction rate. This behavior may have been influenced by the viscosity of the

slag or metal, the interfacial energy between the slag and metal, and/or the diffusivity of Fe^{2+} and O^{2-} ions in the slag, all parameters dependent on temperature. However, the degree of influence each of these parameters has on the reaction rate is unclear. More work is necessary in order to determine the effect these parameters have on the emulsification behavior of the droplet while reacting with high FeO contents in the slag.

Figure 11: Variation of the Rate of CO Evolution (moles/s) with $1/T \times 10^4 (\text{K}^{-1})$ from 1643-1763K (weight of metal~1gram)

Effect of Fe_2O_3 : The results of the experiments conducted as a function of Fe_2O_3 content in the slag are presented in Figure 12 in which the rate is plotted as a function of wt%FeO where:

$$\text{wt\%Fe}_i\text{O} = \text{wt\%FeO} + 0.9\text{wt\%Fe}_2\text{O}_3 \quad (10)$$

Figure 12: Variation of the Rate of CO Evolution (moles/s) with wt%Fe₁O at 1713K for ~1 gram droplets

According to these results, the rates were typically faster for the slags containing Fe₂O₃. At 4.5wt%Fe₁O (5wt%Fe₂O₃), the droplet was observed by x-ray fluoroscopy to remain intact during reaction, and a gas halo was observed around the droplet indicating that Reaction (2) from Min and Fruehan's model may still be rate-limiting. Because the value of P_{CO_2} for this mechanism (Equation (4)) depends on the oxygen potential of the slag, it is not surprising that the rate was faster for the slag containing Fe₂O₃. Other researchers also observed faster rates for slags containing Fe₂O₃.¹⁻³ It is hypothesized that the rates were faster for the higher FeO slags containing Fe₂O₃ because the Fe₂O₃ increased the oxygen potential of the slag further promoting emulsification.

Effect of Sulfur: Previous Studies have indicated that the sulfur content of the metal may influence the rate of decarburization of metal droplets by FeO in slag in two ways:^{1-5,9,19,20}

- 1) as a surface active element, sulfur blocks reaction sites at the droplet's surface and the rate becomes controlled by Reaction (2)
- 2) sulfur decreases the surface tension of the metal thereby enhancing emulsification of the droplet. The large increase in surface area leads to faster decarburization rates.

In order to determine the effect sulfur may have on the decarburization rate for the present study, experiments were performed using 1 gram metal droplets with carbon and sulfur contents ranging from 2.11-3.45wt% and 0.003-0.42wt%, respectively. The slag for these experiments contained approximately 20wt%FeO, and the experimental temperature was 1713K. The results for these experiments are presented in Figure 13 where the initial rate is plotted as a function of the calculated activity of sulfur, h_s , using data compiled by Sigworth and Elliott²¹. According to these results, the initial rate was observed to increase significantly as the sulfur content in the metal increased from 0.003 to 0.011wt%. This may have been due to a decrease in the surface tension of the metal. In a study by Cramb and Jimbo²², the surface tension of an Fe-4wt%C alloy was found to decrease significantly at 1723K as the sulfur content increased from approximately 0 to 0.025wt%. Therefore, it is possible that the decrease in surface tension was significant enough to contribute to emulsification of the metal droplet leading to a faster rate. At higher sulfur contents, Cramb and Jimbo found that the decrease in surface tension was less prominent. This may explain why the rate did not increase further when sulfur contents greater than 0.011wt% were used in the present study. Instead, the initial rate of decarburization was observed to decrease gradually as the sulfur content increased from

0.011wt% to 0.42wt%. This decrease in the rate may have been due to sulfur blocking reaction sites for decarburization. However, because the droplet was observed to become emulsified at the FeO content used to study the effect of sulfur, it is difficult to define the complete surface area that the sulfur would affect.

Figure 13: Variation of the Initial Rate of CO Evolution (moles/s) with activity of sulfur, h_s , for 20wt%FeO at 1713K (weight of metal~1 gram)

Mass Balance and Transition to Secondary Rate: At the completion of each experiment, a mass balance was performed by chemically analyzing the FeO content of the slag and the carbon content of the metal. The FeO content of the slag was typically 1 to 2wt% lower than the original content charged into the crucible (dilution of the slag with MgO from the crucible contributed to this decrease). For 3 and 5wt%FeO, the final carbon concentration of the metal measured by chemical analysis was approximately the same as that determined by the pressure transducer measurements. However, for slags

with $\geq 10\text{wt}\%\text{FeO}$, the final carbon content of the metal determined by chemical analysis was lower than the content calculated from the moles of CO produced.

One possible explanation is that carbon from the metal droplet dissolves into the slag during the course of reaction. According to past research, it was found that a slag with a basicity ($\%\text{CaO}/\%\text{SiO}_2$) of 1.1 may contain up to $0.05\text{wt}\%\text{C}$ for unit carbon activity at 1883K .²³ In the present study, $0.05\text{wt}\%\text{C}$ corresponds to 2.4×10^{-3} moles of carbon for the slag weight (60 grams) used in each experiment. Experiments lowering the slag weight showed less carbon loss supporting this explanation. Also, below $5\% \text{FeO}$, when no emulsification occurred, carbon was not lost to the slag presumably because the rate of dissolution for the much smaller surface area is slow. Experiments to determine if carbon deposition, as to determine if carbon deposition, as indicated by equation 11 at

lower temperatures was reducing the volume of gas measured. CO gas was injected into the reactor and no decrease in gas volume was observed. Whereas we are unsure why the carbon balance was not exactly closed it appears that carbon is dissolving in the slag.

This research focussed on determining the mechanisms influencing the observed initial rates of reaction, however, it was also necessary to identify the cause for the rapid decrease in the rate. The transition from an initial to secondary rate was observed for slags containing $\geq 10\text{wt}\%\text{FeO}$ and for all slags containing Fe_2O_3 as represented in Figures 3 to 6 and Tables II and III. As discussed above, it is hypothesized that carbon dissolves rapidly into the slag when the droplet becomes emulsified within the slag. Therefore, the rapid decrease in the rate may occur because the droplet begins to solidify. At 1713K , the droplet would begin to solidify upon reaching approximately $1.3\text{wt}\%\text{C}$ according to

the equilibrium Fe-C phase diagram.²⁴ Another possibility is that the rate becomes controlled by mass transfer of carbon through the metal droplet. In order to better define the mechanisms influencing the rapid decrease in rate, more work on the observed emulsification phenomenon is required.

CONCLUSIONS

The behavior of Fe-C-S droplets in CaO-SiO₂-MgO slags with FeO contents ranging from 3-35wt% was studied at temperatures ranging from 1643-1763K. The rate of the FeO-C reaction was measured using the CVPI method, and the reaction of droplets in the slag was observed using x-ray fluoroscopy. The effects of Fe₂O₃ additions to the slag and sulfur variations in the metal were also studied. From this study, the following was found:

- 1) The FeO and Fe₂O₃ content of the slag have a significant influence on the behavior of the Fe-C-S droplets as they react with FeO in the slag. At 1713K, the droplet remained intact while reacting with slags containing <10wt%FeO, and the rate was defined by Reaction (2). At higher FeO contents, the droplet was observed to become emulsified within the slag. The large increase in surface area due to emulsification is believed to have caused the increase in rate by one to two orders of magnitude when increasing the FeO content from 5 to 20wt%.
- 2) The present study is the first to demonstrate the change in phenomenon from a droplet that remains intact to one that is emulsified as it reacts with FeO in the slag. This study is also the first to speculate reaction rates for emulsified droplets in slag. Without the use of x-ray fluoroscopy the emulsification of the droplet during the reaction would not have been discovered.
- 3) The effect of temperature on the rate of Reaction (1) was studied for slags containing 10-30wt%FeO from 1643 to 1763K, and it was found that there was a critical temperature for each FeO concentration at which point the rate increased dramatically. The cause for this increase was not determined. However, it is believed that the surface tension and viscosity of the slag or metal and the diffusivity of the Fe²⁺ and O²⁻ ions in the slag may have contributed to the emulsification behavior of the Fe-C-S droplet leading to a large increase in reaction rate with relatively small increases in temperature.

4) The effect of Fe_2O_3 in slags with and without FeO on the rate of reaction was studied. Similar to past studies, it was found that the rate was faster for slags that contained Fe_2O_3 than for those without. It is postulated that this increase was due to an increase in oxygen potential of the slag which influenced emulsification of the droplet.

5) The dependence of the reaction rate on sulfur content in the metal was studied for slags containing 20wt% FeO at 1713K. It was found that as the sulfur content increased from 0.003 to 0.011wt%, the rate increased significantly believed to be due to a decrease in surface tension of the metal droplet which further promoted emulsification. As the sulfur content increased from 0.011-0.42wt%, the rate decreased gradually which may have been a result of sulfur blocking reaction sites on the metal surface.

6) It is possible that without the droplet emulsification the decarburization reaction in oxygen steelmaking would be significantly slower, resulting in more iron oxidation and yield loss thus making this process uneconomical.

Whereas this research has significantly enhanced the knowledge of the decarburization reaction in steelmaking, more work is required to fully understand the behavior observed. For example, what is the exact cause for the emulsification of the droplet and what is the direct influence of FeO content in the slag? What affect does metal droplet size have on the droplet behavior? Finally, what causes the rate to slow down at low carbon contents?

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REFERENCES

1. E. W. Mulholland, G. S. F. Hazeldean, and M. W. Davies, "Visualization of Slag-Metal Reactions by X-Ray Fluoroscopy: Decarburization in Basic Oxygen Steelmaking", Journal of the Iron and Steel Institute, September 1973, p.632.
2. H. Gaye and P. V. Riboud, "Oxidation Kinetics of Iron Alloy Drops in Oxidizing Slags", Metallurgical Transactions B, Vol.8B, September 1977, p.409.
3. T. Gare and G. S. F. Hazeldean, "Basic oxygen steelmaking: decarburization of binary Fe-C droplets and ternary Fe-C-X droplets in ferruginous slags", Ironmaking and Steelmaking, No.4, 1981, p.169.

4. D. J. Min and R. J. Fruehan, "Rate of Reduction of FeO in Slag by Fe-C Drops", Metallurgical Transactions B, Vol.23B, February 1992, p.29.
5. G. G. Krishna Murthy, Y. Sawada, and J. F. Elliott, "Reduction of FeO dissolved in CaO-SiO₂-Al₂O₃ slags by Fe-C droplets", Ironmaking and Steelmaking, Vol.20, No.3, 1993, p. 179.
6. G. G. Krishna Murthy, A. Hasham, and U. B. Pal, "Removal of FeO during Foaming of CaO-Al₂O₃-SiO₂-FeO Slags by Low Carbon-Iron Melts", ISIJ International, Vol.34, No.5, 1994, p.408.
7. G. G. Krishna Murthy, A. Hasham, and U. B. Pal, "Reduction rates of FeO in CaO-SiO₂-Al₂O₃-X slags by Fe-C droplets", Ironmaking and Steelmaking, Vol.20, No.3, 1993, p.191.
8. R.J. Fruehan, editor, The Making, Shaping and Treating of Steel, 11th Edition, Steelmaking and Refining Volume, The AISE Steel Foundation, Pittsburgh, PA, 1998, p.134.
9. D. R. Sain and G. R. Belton, "The Influence of Sulfur on Interfacial Reaction Kinetics in the Decarburization of Liquid Iron by Carbon Dioxide", Metallurgical Transactions B, Vol.9B, September 1978, p.403.
10. D. G. C. Robertson and A. E. Jenkins, "The Reaction of Liquid Iron and Its Alloys in Pure Oxygen", Heterogeneous Kinetics at Elevated Temperatures, Plenum Press, New York, 1970, p.393.
11. J. H. Swisher and E. T. Turkdogan, "Decarburization of Iron-Carbon Melts in CO₂-CO Atmospheres; Kinetics of Gas-Metal Surface Reactions", Trans. AIME, Vol.239, May 1967, p.602.
12. L. A. Baker, N. A. Warner, and A. E. Jenkins, "Decarburization of a Levitated Iron Droplet in Oxygen", Trans. AIME, Vol.239, June 1967, p.857.
13. L. A. Baker and R. G. Ward, "Reaction of an Iron-Carbon Droplet During Free Fall Through Oxygen", JISI, July 1967, p.714.
14. P. A. Distin, G.D. Hallett, and F. D. Richardson, "Some Reactions Between Drops of Iron and Flowing Gases", JISI, August 1968, p.821.
15. K. Gao, V. Sahajwalla, and R. Dry, "Carbon Boil Phenomenon and Oxygen Absorption by Metal Drops in Direct Iron Smelting", 1998 ICSTI/Ironmaking Conference Proceedings, April 1998, p.1489.

16. N. Ibl and J. Venczel, *MetallOberfläche*, Vol.24, 1970, p.365.
17. D.P. Agarwal and D.R. Gaskell, *Metallurgical Transactions B*, Vol.6B, 1975, p.263.
18. B. Sarma, Reduction of FeO from Smelting Slags by Solid Carbon, Ph.D Thesis, Carnegie Mellon University, Pittsburgh, PA, January 20, 1992, p.30-31, 149.
19. D. R. Sain and G. R. Belton, "Interfacial Reaction Kinetics for the Decarburization of Liquid Iron by Carbon Dioxide", *Metallurgical Transactions B*, Vol.7B, June 1967, p.235.
20. F. J. Mannion and R. J. Fruehan, "Decarburization Kinetics of Liquid Fe-C_{sat} Alloys by CO₂", *Metallurgical Transactions B*, Vol.20B, December 1989, p.853.
21. G.K. Sigworth and J.F. Elliott, "The Thermodynamics of Liquid Dilute Iron Alloys", *Metal Science*, Vol.8, 1974, p.298.
22. A.W. Cramb and I. Jimbo, "Surface Tension Values For Use In Casting", 1994 Turkdogan Symposium Proceedings, p.195.
23. R.A. Berryman and I.D. Sommerville, "Carbon Solubility as Carbide in Calcium Silicate Melts", *Metallurgical Transactions B*, Vol.23B, April 1992, p.223.
24. T.B. Massalski, Binary Alloy Phase Diagrams, Second Edition, Vol.1, ASM International, U.S., December 1990, p.843.

Appendix B

Waste Oxide Recycling During Oxygen Steelmaking

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The U.S. steel industry generates more than 3 million tons of waste oxides that contain significant amounts of metallic iron and iron oxide. Stringent restrictions imposed on all by-products, as well as limited landfill space, make disposal of these materials expensive.

Currently, companies such as Ispat Inland Inc., East Chicago, IN, and National Steel Corp., Mishawaka, IN, recover the iron units from these waste oxides by recycling them in the form of briquettes into the blast furnace and the basic oxygen furnace (BOF). However, when using the waste oxide briquettes (WOBs) in the BOF, high degrees of slopping have occurred. Slopping is also a general problem even when WOBs are not used.

The goal of this research was to determine the mechanisms influencing slopping behavior of the slag during oxygen steelmaking with and without WOB additions. In particular, the rate of reduction of FeO in the slag by carbon from iron droplets was studied using the slag and metal compositions representative of the

New strategies have been developed for the addition of recycled waste oxide briquettes to reduce slopping in the BOF.

first 50 percent of the blow. Slopping was reported as early as 30 percent into the blow. The effect of temperature on the rate of reduction of FeO by carbon in the metal was also studied.

The results of this study, as well as those from a study characterizing the foaming properties of BOF slags, were applied to the oxygen steelmaking process and slopping behavior during the early stages of the blow. From this, new strategies that reduce the possibility of slopping were developed. These included altering the timing of the WOB additions and/or altering the blowing practice.

INTRODUCTION

In the oxygen steelmaking process, gaseous oxygen is jetted onto the surface of the metal bath, promoting decarburization of the metal by the following overall reaction:

The underline in the equation indicates elements dissolved in molten iron.

However, most of the oxygen initially oxidizes iron to FeO, which then dissolves into the slag. The oxygen jet and reaction (1), which produces two moles of CO per mole of oxygen, force metal droplets up into the slag layer. These metal droplets are subjected to an oxidizing environment because of the presence of FeO in the slag. They are decarburized by the following overall reaction:

Where:

FeO = FeO dissolved in the slag

Steelmaking slags also contain Fe_2O_3 , which increases the oxygen potential of the slag and further promotes decarburization. Based on data reported by Ispat Inland, early additions of WOBs to the furnace may increase the total FeO content of the slag. The additions may have also resulted in slopping as early as 30 percent of the blow time.¹

The hypothesis of this study is that slopping occurs by the sudden release of excessive CO gas into a foamable slag. The FeO acts as "stored oxygen" — much of which may not be reduced until the rate of reaction (2) is sufficiently rapid. The gas produced according to reaction (2), as well as that produced by normal decarburization, reaction (1), may become excessive. This results

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in slopping of the slag out of the vessel. Another possibility is that the stored oxygen reacts by reaction (2) early in the blow when the foamability of the slag is increased because its temperature and basicity are low.

Although reaction (2) has been studied in great detail in terms of the possible rate-limiting mechanisms, none of the previous work has reflected the conditions existing during the earlier stages of the blow.²⁻⁸ Therefore, the goals of this study were to determine how the composition of the slag and metal, as well as temperature of the slag consistent with the first 50 percent of the blow, affects the rate of reaction (2).

EXPERIMENTAL WORK

Measurement of the Rate of Reduction of FeO by C

The rate of reaction (2) was determined by using the constant volume pressure increase technique (CVPI) in which one mole of CO gas produced is equivalent to one mole of FeO reduced.

Thermodynamically, a small amount of CO₂ can also form (< 9.6 percent). A pressure transducer with a sensitivity of approximately 2×10^{-4} atm was used to measure the pressure increase with time for each experiment. The compositions of the metal and aim compositions of the slag used are represented in Table I. These compositions represent not only the first 50 percent of the blow (> 10 weight percent FeO) as estimated by data provided by Ispat Inland,

but also other conditions that were found necessary to investigate.

Approximately 60 g of a synthetic slag (percent CaO/percent SiO₂ = 1.2, MgO = 12 weight percent) containing the appropriate amount of FeO were charged into a high purity MgO crucible (inside diameter = 3.8 cm, outside diameter = 4.3 cm, height = 9 cm). To limit sulfur transfer from the metal to the slag, a specified amount of CaS was added.⁹ The crucible was placed in the reaction chamber of a molybdenum disilicide resistance furnace and heated to the experimental temperature in a purified argon atmosphere. Once the slag reached temperature, the furnace was sealed. An approximately 1 g Fe-C-S alloy pellet of the appropriate composition was released from a rotary compartment into a tapered mullite tube centered above the slag bath. Figure 1 represents the experimental setup.

Once the pellet melted, it was released as a metal droplet from the tapered end of the tube, falling into the slag bath and starting to react. The pressure increase resulting from the evolution of CO gas was measured by the pressure transducer in terms of mV and was converted to total moles of FeO reacted with time. After the reaction appeared to cease (indicated by a constant mV reading), another pellet was released and measurements were taken. As many as three pellets were released into the slag during the experiment.

After reaction of the last pellet ceased, the furnace was cooled down to room

temperature in an argon atmosphere, and the MgO crucible containing the metal/slag mixture was removed. The metal and slag were then analyzed for C and FeO, respectively.

Observation of the Reaction Using X-Ray Fluoroscopy

X-ray fluoroscopy was used to observe the behavior of the metal droplet while it reacted with slags containing 10 and 20 weight percent FeO, as well as 5 weight percent Fe₂O₃ at 1,440°C. X-ray video recording began as soon as the Fe-C-S pellet (2.91 weight percent C, 0.011 weight percent S) was released into the tapered mullite tube centered above the slag bath.

Recording continued until the reaction of the droplet with the slag appeared to cease. At that time, another pellet was released, and recording started again. As many as three pellets were observed during the course of an experiment. The results from these experiments and from the measurement of the rate of reaction (2) are presented and discussed in the following sections.

RESULTS

Typical results for the measurement of the rate of reduction of FeO in the slag

Table I Experimental Variables Used for the Measurement of the Rate of Reaction (2)

Aim wt. % FeO**	0	3	5	10	15	20	30	35
Aim wt. % Fe ₂ O ₃ **	5	0	0.5	0.5	0	0.5	0	0
Wt. % C	2.91	2.91	2.91	2.91	2.88	2.91	2.91	2.91
Wt. % S	.011	.011	.011	.011	.014	.011	.011	.011
Temperature (°C)	1,440	1,440	1,440	1,390-1,490	1,390-1,490	1,370-1,490	1,370-1,490	1,440

Basicity (%CaO/%SiO₂) = 1.2, MgO ~ 12 weight percent for all experiments

** The FeO content measured following each experiment was 1 to 2 weight percent less than the aim composition. The Fe₂O₃ was measured prior to each experiment and was within 0.5 weight percent of the expected composition.

Figure 1 An experimental apparatus for reduction reaction experiments is shown.

by carbon in the metal for 10 and 20 weight percent FeO, and for temperatures ranging from 1,370 to 1,490°C, are presented in Figures 2 and 3. In each figure, the variation of the total moles of CO evolved (equal to the moles of FeO reduced) was plotted with respect to time in seconds in accordance with the appropriate pressure transducer measurements made with time. Many observations were made from these experiments.

Two distinctive rates defined by the slope of the linear portion of the data ($\Delta n_{\infty}/dt$, where n_{∞} represents the total moles of CO evolved and t represents time) were observed for each condition studied. For 10 weight percent FeO, the initial rate varied significantly with

temperature. At 1,440°C, the initial rate was calculated, using linear regression, to be 3×10^{-4} moles/second and increased by an order of magnitude to approximately 2×10^{-4} and 3×10^{-4} moles/second at 1,465 and 1,490°C, respectively. In all cases, the rate was for metal droplets weighing 1.1 g.

For 20 weight percent FeO, this same temperature dependence of the initial rate was observed as the temperature increased from 1,370 to 1,390°C. In this case, the rate increased from 5×10^{-5} to 1×10^{-4} moles/second for metal droplets weighing 1 g. Further increases in temperature resulted in only a small increase in the initial rate. The secondary rate for all the conditions studied at 10 and 20 weight percent FeO ranged from 8.5×10^{-7} to 1.9×10^{-6} moles/second. The rates of FeO reduction for all FeO contents studied are listed in Table II.

In Figure 4, the total moles of CO that evolved as a function of time were plotted for 3 to 30 weight percent FeO at 1,440°C. This demonstrates the large dependence of the rate on FeO content. As evidenced from this plot – below 10 weight percent FeO – only one distinct rate was observed. Estimated to

be 3×10^{-6} moles/second, this rate was two orders of magnitude slower than the initial rate measured at 20 and 30 weight percent FeO.

For experiments performed as a function of Fe_2O_3 content in the slag, the shape of the total moles vs. time plots appeared similar to those observed for slags containing ≥ 10 weight percent FeO. Table III lists the rates for each of these conditions studied. The results from all the experiments are discussed in the following sections.

X-Ray Fluoroscopy Experiments

X-ray fluoroscopy experiments were completed for slags containing 10 and 20 weight percent FeO, as well as 5 weight percent Fe_2O_3 , at 1,440°C. Although uncertainty originally existed as to how visible the drop would appear within the slag because of the slag's high density, many observations were made during the course of an experiment (Figure 5).

The behavior of the droplet in the slag containing 20 weight percent FeO is summarized in a series of diagrams (Figure 6). First, the pellet melted in about 40 seconds and fell as one droplet into the molten slag. Second, within one second

Figure 2 The variation of the total moles of CO evolved with time (seconds) for 10 weight percent FeO from 1,440 to 1,490°C (weight of metal = 1.1 g).

Figure 3 The variation of the total moles of CO evolved with time (seconds) for 20 weight percent FeO from 1,370 to 1,490°C (weight of metal = 1 g).

Table II Rates of Evolution of CO (moles/second) for Aim FeO Contents Ranging From 3 to 35 Weight Percent for Temperatures of 1,370 to 1,490°C and Metal Droplets Weighing Approximately 1 g

Aim Wt. % FeO	Temperature (°C)	Initial Rate (moles/second)	Secondary Rate (moles/second)
3	1,440	3.3×10^{-6}	—
5	1,440	3.0×10^{-6}	—
10	1,390	2.5×10^{-5}	1.1×10^{-6}
10	1,440	3.0×10^{-5}	1.1×10^{-6}
10	1,465	2.0×10^{-4}	8.5×10^{-7}
10	1,490	3.0×10^{-4}	8.5×10^{-7}
15	1,390	5.0×10^{-5}	1.1×10^{-6}
15	1,440	1.8×10^{-4}	1.0×10^{-6}
15	1,490	2.6×10^{-4}	1.2×10^{-6}
20	1,370	5.0×10^{-5}	1.8×10^{-6}
20	1,390	1.3×10^{-4}	1.9×10^{-6}
20	1,440	2.0×10^{-4}	1.1×10^{-6}
20	1,490	2.4×10^{-4}	1.4×10^{-6}
30	1,370	7.8×10^{-5}	8.5×10^{-7}
30	1,390	1.9×10^{-4}	8.8×10^{-7}
30	1,440	2.1×10^{-4}	7.5×10^{-7}
30	1,490	3.1×10^{-4}	1.2×10^{-6}
35	1,440	2.0×10^{-4}	1.2×10^{-6}

after the droplet fell into the slag, the initial reaction period began. During this period, the droplet emerged out of the thick slag while a foamed slag layer was simultaneously being formed. The droplet quickly emulsified, increasing to more than two times its original diameter. An x-ray image of the emulsified droplet for the slag containing 20 weight percent FeO is shown in Figure 5.

As this fast reaction period continued, the emulsified droplet remained in the foamed slag, which was heavily agitated by gas evolution. The diameter of

bubbles being released from the surface of the emulsified droplet were difficult to distinguish because of the low contrast of the x-ray video. However, each was estimated to be between 1 and 2 mm.

After about six seconds, the emulsion collapsed and the droplet quickly re-coalesced and entered the thick slag layer. This marked the end of the fast reaction period. The droplet then rapidly fell to the bottom of the crucible. During this time, an occasional gas bubble of relatively small diameter, in comparison to the diameter of the droplet, was released from the droplet and rose to the surface of the thick slag layer. The foamed slag began to collapse at the end of the fast reaction period and virtually disappeared after about 30 seconds. At that point, another pellet was released and the same behavior was observed. The release of a third pellet resulted in a similar behavior.

The overall behavior of the droplet in the slag containing 10 weight percent FeO was similar to that described previously. However, the emulsified droplet took nine seconds to grow to a maximum size of more than double its original diameter.

Consequently, formation of the slag foam was not as fast as was observed for the slag containing 20 weight percent FeO.

The behavior of the droplet when it reacted with a slag containing 5 weight percent Fe_2O_3 at $1,440^\circ\text{C}$ was much different than the behavior observed at 10 and 20 weight percent FeO. As the droplet fell into the slag, reaction began within two to three seconds. Unlike the experiments described previously, the droplet did not become emulsified as it reacted with the slag, but remained virtually intact. Also, at times the droplet appeared to be surrounded by a thin layer of slag less dense than the bulk slag. The reaction of the droplet with the slag continued for about 50 seconds. The formation of a stable foam was not observed during the reaction. Once reaction ceased, the droplet slowly sank to the bottom of the crucible. The results from the x-ray experiments are discussed in the following section.

DISCUSSION

Reaction (2) was studied in great detail in terms of the possible rate-limiting mechanisms.²⁻⁸ Five possible steps were determined that may limit the rate of decarburization:

Figure 4 The dependence of rate on FeO content of the slag at $1,440^\circ\text{C}$ (weight of metal = 1 g) is shown.

Table III Rates of Evolution of CO (moles/second) for Experiments Performed as a Function of Fe_2O_3 in the Slag at $1,440^\circ\text{C}$

Aim Wt. % FeO	Aim Wt. % Fe_2O_3	Wt. % C	Wt. % S	Initial Rate (moles/second)	Secondary Rate (moles/second)
0	5	2.91	.011	1.7×10^{-5}	1.1×10^{-6}
5	5	2.91	.011	2.7×10^{-5}	2.0×10^{-6}
10	5	2.91	.011	2.2×10^{-4}	2.3×10^{-6}
20	5	2.91	.011	2.9×10^{-4}	1.3×10^{-6}

Figure 5 An x-ray image of a 1 g Fe-C-S droplet (2.91 weight percent C, 0.011 weight percent S) reacting with a slag containing 20 weight percent FeO at $1,440^\circ\text{C}$ at: (a) 3 seconds; (b) 6 seconds; and (c) 8 seconds is shown.

Figure 6 A diagram representing the reaction of a 1 g Fe-C-S droplet (2.91 weight percent C, 0.011 weight percent S) with a slag containing 20 weight percent FeO at $1,440^\circ\text{C}$ is shown.

- (1) Gas-metal reaction:
 $\text{CO}_2 + \text{C} = 2\text{CO} \quad \dots\dots(3)$
- (2) Gas-slag reaction: $\text{CO} + (\text{FeO})$
 $= \text{CO}_2 + \text{Fe} \quad \dots\dots(4)$
- (3) Mass transfer of FeO as Fe^{2+} and O^{2-} ions through the slag
- (4) Mass transfer of C through the metal
- (5) Mass transfer of CO-CO_2 through the gas halo

According to Min and Fruehan,⁵ who conducted a study similar to this work, step (1) was rate-limiting if the sulfur content of the metal was ≥ 0.01 weight percent. Step (3) was also found to be rate-limiting under some conditions. Steps (2), (4) and (5) were fast and therefore, not considered to be rate-limiting.

Figure 7 represents the variation of the rate of evolution of CO (moles/second) with weight percent FeO in the slag at 1,440°C.

Based on the current results for experiments conducted using 3 and 5 weight percent FeO in the slag, Min and Fruehan's model holds, and the rate is defined by the gas-metal reaction expressed as follows:

$$\text{Rate} \left(\frac{\text{moles}}{\text{s}} \right) = k_{g/m} \frac{A(P_{\text{CO}_2} - P_{\text{CO}_2}^{\text{eq}})}{\dots\dots(5)}$$

Where:

$k_{g/m}$ = Rate constant for reaction (3)
 (moles/cm² satm)

A = Surface area of the droplet
 (cm²)

P_{CO_2} = Equilibrium partial pressure of CO_2 defined by reaction (4)
 (atm)

$P_{\text{CO}_2}^{\text{eq}}$ = Partial pressure of CO_2 for reaction (3) (approximately zero)

Or in terms of weight percent FeO:

$$\text{Rate} \left(\frac{\text{moles}}{\text{s}} \right) = k_{g/m} \text{AKC}(\text{wt. \% FeO}) \quad \dots\dots(6)$$

Where:

K = Equilibrium constant for reaction (4)

C = Constant relating the activity of FeO to weight percent FeO

The rate constant, $k_{g/m}$, takes into account the effect of the sulfur content in the metal. The calculated rate for the gas-metal reaction is represented as a dashed line in Figure 7. At FeO contents of ≥ 10 weight percent FeO, the observed rate was much faster than that predicted by Min and Fruehan's model.

Typically, a dramatic increase in rate signifies a change in mechanism

associated with a large increase in reaction surface area. Based on the x-ray video for slags with these higher FeO contents, the surface area of the droplet was found to have increased significantly because of emulsification. Because Min and Fruehan's model relies on the droplet remaining intact, that application can no longer be made when the droplet becomes emulsified. Therefore, new mechanisms, such as mass transfer of FeO into the emulsified droplet, were considered and are discussed elsewhere in detail.

Effect of Temperature on the Rate of CO Evolution

Based on the results of this study, the behavior of the droplet when reacting with FeO in the slag was not only dependent on the FeO content in the slag, but also on the experimental temperature. The natural logarithm of the rate of CO evolution (moles/second) for approximately 1 g droplets is plotted as a function of inverse temperature for 10 to 30 weight percent FeO in Figure 8.

From this plot, when a critical temperature appears to have been reached, the rate increases significantly for each FeO concentration. This effect was most pronounced for the slag containing 10 weight percent FeO, in which the rate increased by nearly an order of magnitude from 3×10^{-5} to 2×10^{-4} moles/second

when the temperature increased from 1,440 to 1,465°C. For 20 and 30 weight percent FeO, the rate increased significantly as the temperature increased from 1,370 to 1,390°C. From the x-ray experiments performed for 10 weight percent FeO at 1,440°C, the droplet emulsified as it reacted with the slag. This was similar to the emulsification observed for the slag containing 20 weight percent FeO at the same temperature. However, the expansion of the emulsified droplet to more than double its original diameter for the lower FeO containing slag took nearly 10 times longer.

Claims have been made that the expansion rate of the emulsified droplet at 1,465°C for the 10 weight percent FeO slag was significantly faster than at 1,440°C, thus leading to the pronounced increase in reaction rate. This behavior may have been influenced by the viscosity and surface tension of the slag or metal and the diffusivity of Fe^{2+} or O^{2-} ions in the slag – all parameters dependent on temperature. However, because of limited data available on the systems studied, the degree of influence each of these parameters has on the reaction rate is unclear. More work is necessary to determine the effect these parameters have on the emulsification behavior of the droplet while reacting with high FeO contents in the slag.

In Figure 9, the critical temperature at which point the rate increases by five to 10 times is plotted as a function of FeO content in the slag. The critical temperature appears to be linearly dependent on the FeO content of the slag, decreasing as the FeO content increases, as demonstrated in the following equation:

$$T_c(^{\circ}\text{C}) = -5(\text{wt. \% FeO}) + 1,508 \quad \text{.....(7)}$$

Note that this relationship might only be relevant to the present conditions, and that no theoretical basis for a linear dependency exists. The existence of this

critical temperature could be significant to oxygen steelmaking and slopping behavior. For example, if the FeO content is as high as 30 weight percent and the temperature is 1,370°C, the rate of CO evolution will be much faster than for a slag containing less than 20 weight percent FeO. This rapid generation of CO gas early in the blow, when the slag is highly foamable because its temperature and basicity are low, could result in slopping. These results are further discussed in this article, in which they are applied to the various stages of the oxygen steelmaking process.

Effect of Fe_2O_3 on the Rate of CO Evolution

During oxygen steelmaking, the slag contains both FeO and Fe_2O_3 . According to measurements made by Ispat Inland, the Fe_2O_3 may be as high as 2 weight percent from 20 to 50 percent into the blow and is not affected by WOB additions, despite high concentrations of Fe_2O_3 . Although not well-defined, Fe_2O_3 increases the oxygen potential of the slag and therefore might affect the emulsification behavior of the droplet as discussed previously. In order to study the effect of Fe_2O_3 on the decarburization rate, the rate was measured for slags containing approximately 5 weight percent Fe_2O_3 and zero to 20 weight percent FeO at 1,440°C. These results are presented in Figure 10, in which the rate is plotted as a function of weight percent FeO.

Where:

$$\text{Wt. \% Fe}_2\text{O}_3 = \text{wt. \% FeO} + 0.9 \text{ wt. \% Fe}_2\text{O}_3 \quad \text{.....(8)}$$

According to these results, the rates were typically faster for the slags containing Fe_2O_3 . At 4.5 weight percent FeO (5 weight percent Fe_2O_3), the droplet was observed by x-ray fluoroscopy to remain intact during reaction, and a gas halo was observed around the droplet. This indicated that reaction (3) from Min and Fruehan's model might still be rate-limiting. Because the value of P_{CO_2} for this mechanism in Equation (5) depends on the oxygen potential of the slag, the fact that rate was faster for the slag containing Fe_2O_3 was not surprising.

The hypothesis has been made that the rates were faster for the higher FeO slags containing Fe_2O_3 , because the Fe_2O_3 increased the oxygen potential of the slag, further promoting emulsification. Other researchers also observed faster rates for slags containing Fe_2O_3 .²⁴ The results of the present experiments indicate that if the concentration of Fe_2O_3 in the slag is significant (i.e., if the dissolved Fe_2O_3 from the WOB has not reached equilibrium with the metal to form FeO), then the rate of CO evolution as the stored oxygen reacts with carbon in the metal droplets may be sufficient enough to cause slopping.

APPLICATION OF RESULTS

Lance height, oxygen flow rate, hot metal silicon content and the foamability of the slag are among the many factors that can affect the slopping behavior of the slag during oxygen steelmaking. This study focuses on developing a fundamental understanding of the decarburization reaction during oxygen steelmaking and slopping at the early stages of the blow.

In particular, the effect of the FeO content in the slag on the rate of decarburization was studied according to the conditions present with and without WOB additions to the furnace. In addition, the foamability of the slag was measured by Jung and Fruehan using the conditions representative of the first 50 percent of the blow.¹⁰ In the following section, the results are applied to oxygen steelmaking, and strategies for recycling the WOBs into the BOF while avoiding slopping are presented.

Effect of FeO Content in the Slag and Temperature on Decarburization

The primary function of the oxygen steelmaking process is to decarburize the metal bath. Four stages characterize the decarburization during this process.¹¹

During the first stage, the oxygen lance is kept relatively high above the bath, creating a "soft blow." Silicon, manganese and iron from the metal are oxidized to SiO_2 , MnO and FeO and enter the slag. The rate of decarburization is slow during this time, and a large buildup of FeO and SiO_2 is present in the slag.

At approximately 20 percent into the blow, the oxygen lance is lowered and the decarburization rate is accelerated considerably as metal droplets become entrained in the slag and carbon is oxidized by FeO in the slag. The results from the present study show that under certain conditions, the metal droplets themselves become emulsified within the slag-metal-gas mixture, which

leads to extremely fast rates of decarburization or CO generation.

During the second stage, the FeO content of the slag decreases considerably (Figure 11). Upon reaching the third stage of decarburization, steady-state is achieved and the rate is governed by the oxygen flow rate. In the final stage, the decarburization rate decreases significantly because the carbon content of the metal bath was low, and the rate was controlled by mass transfer of C. The excess oxygen oxidizes the iron to FeO .

The early stages of the blow can be critical to slopping. Reports show that if the FeO content of the slag is too high before ignition (when the lance is lowered and decarburization accelerates), then the reaction between FeO and carbon from the metal droplets during the second stage of decarburization becomes violent. Slopping is likely to occur.¹²

The results of the present study indicate that a critical temperature exists for a given FeO content, at which point the rate of reaction (2) increases by, and up to, an order of magnitude. This critical temperature decreases as the FeO content of the slag increases (Figure 9). Therefore, the hypothesis has been made that the higher the FeO content of the slag before ignition, the more likely the critical temperature will be reached and ignition will occur earlier (Figure 11).

According to Ispat Inland, the temperature of the metal might increase from about 1,300 to 1,370°C during the first stage of the blow. (The slag temperature might be even higher, but is not well-defined.)¹ At 1,370°C, the rate of decarburization or CO evolution is much faster for a slag containing 30 weight percent FeO than that for a slag containing 20 weight percent FeO . Because the rate is faster for the higher FeO containing slag, the expectation remains that the FeO content will decrease more rapidly after ignition (Figure 11). Therefore, the potential for slopping

might increase with the increase of retained FeO in the slag before ignition.

Reports show that slopping is more frequent when WOBs or heavily oxidized scrap are charged into the furnace at the beginning of the blow.^{1,13} This might be caused by large increases in the retained FeO in the slag, as both the FeO from the WOBs and/or oxidized scrap, as well as the iron oxidized to FeO from the metal by the oxygen lance, report to the slag (Figure 11). Therefore, in order to use WOBs or heavily oxidized scrap in the BOF and limit slopping, new practices must be developed to avoid large increases in the retained FeO in the slag before ignition when the slag basicity and temperature are low.

Effect of the Foaming Properties of the Slag on Slopping

According to the present hypothesis, slopping occurs when excessive CO evolution goes into a highly foamable slag. The work

Figure 11 A diagram is shown of the hypothesized path of the FeO content of the slag during the blow from (a) 0 to 100 percent time and (b) 10 to 30 percent time. I represents normal operation, and II represents the effect of WOB or heavily oxidized scrap additions at the beginning of the blow.

in this article dealt primarily with the rate of CO evolution by reduction of FeO in the slag by carbon in metal droplets.

Jung and Fruehan examined the foaming as an adjunct to the present work.¹⁰ Based on their work and previous studies, Jung and Fruehan found that the foaming in the composition range of interest increases with decreasing basicity and temperature. The foamability defined by the foam index, Σ , of selected slag compositions is shown in Table IV.

Table IV is based on the results of Jung and Fruehan. The temperature dependence of Σ was calculated from the following relation developed by Oztürk and Fruehan:¹⁴

$$\Sigma = 1.78 \times 10^{-5} \exp [16,797/T] \quad \text{.....(9)}$$

As illustrated in Table IV, at a given temperature, Σ varies by a factor of 2 as the basicity changes by 0.2. This might not seem to be a large variation, but it could be enough to significantly increase the potential for slopping, especially if ignition occurs at a lower temperature and basicity because the FeO content of the slag is high from WOB additions. For example, from the present work, the rate of CO generation accelerates at approximately 1,360 and 1,400°C for 30 and 20 weight percent FeO, respectively, and for a basicity of 1.2. For these two conditions, Σ varies between 0.7 and 0.51. If the basicity was only 1, Σ would increase by a factor of 2. Therefore, in order to avoid

slopping when using WOBs, new strategies for their addition must be considered. These methods are discussed in the following section.

Recommendations

Based on the current understanding of the decarburization reaction and slag foaming, practices can be used that reduce the possibility of slopping. These include altering the timing of the WOB additions or varying the blowing practice. In terms of WOB addition, the following are recommended:

- (1) Add the WOBs continuously rather than in large batches to avoid excessive FeO buildup in the slag.
- (2) Add the WOBs after ignition when the FeO has decreased and the temperature and basicity of the slag are higher.

In terms of the blowing practice, the following are recommended:

- (1) If WOBs are added at the beginning of the blow, reduce the time that the lance height is kept high to maintain an FeO level similar to normal practice.
- (2) At the critical condition or ignition point (approximately 25 percent of the blow), reduce the oxygen blowing rate by 20 percent for two to three minutes to reduce the CO evolution.

These recommendations are intended for plants that recycle or plan to recycle WOBs into the BOF. These recommendations might need to be adjusted depending on individual practices.

CONCLUSIONS

The goal of this research was to determine the mechanisms influencing the slopping behavior of the slag during oxygen steelmaking, primarily at the early stages of the blow when WOBs are and are not used. From this study, the following was determined:

- (1) The oxygen potential of the slag has a significant influence on the behavior of the Fe-C-S droplets as they react with FeO in the slag. At 1,440°C, the droplet remained intact while reacting with slags containing < 10 weight percent FeO, and the rate was defined by reaction (3). At higher FeO contents, the droplet was observed to become emulsified within the slag. The large increase in surface area caused by emulsification is believed to have caused the increase in rate by one to two orders of magnitude when increasing the FeO content from 5 to 20 weight percent.
- (2) The effect of temperature on the rate of reaction (2) was studied for slags containing 10 to 30 weight percent FeO from 1,370 to 1,490°C. Findings show that a critical temperature was reached for each FeO concentration at the point where the rate increased dramatically. The cause for the increase was not determined. However, the belief exists that the surface tension and viscosity of the slag or metal and the diffusivity of the Fe^{2+} and O^{2-} ions in the slag may have contributed to this large increase in reaction rate with relatively small increases in temperature.
- (3) The rate of reaction (2) was found to be faster for slags that contained Fe_2O_3 than for those without. The increase may have occurred because of an increase in oxygen potential of the slag, which influenced emulsification of the droplet.
- (4) The results of this study were applied to the oxygen steelmaking process and slopping behavior at the early stages of the blow. From this, methods for recycling WOBs into the BOF while avoiding slopping were developed.

ACKNOWLEDGMENTS

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Table IV Variation of the Foam Index, Σ , With Basicity and Temperature for a Slag Containing 20 Weight Percent FeO and 10 Weight Percent MgO

Basicity (%CaO/%SiO ₂)	1,300°C	1,350°C	1,400°C
1.0	2.12	1.53	1.12
1.2	.97	.70	.51
1.4	.58	.42	.31

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References

1. "Waste Oxides in the BOF," *CISR-CMU Meeting*, October 25, 1995, Pittsburgh, PA.
2. E.W. Mulholland, G.S.F. Hazeldan and M.W. Davies, "Visualization of Slag-Metal Reactions by X-ray Fluorescence: Decarburization in Basic Oxygen Steelmaking," *JISI*, September 1973, p. 632.
3. H. Gaye and P.V. Riboud, "Oxidation Kinetics of Iron Alloy Drops in Oxidizing Slags," *Metallurgy Transactions B*, Vol. 813, September 1977, p. 409.
4. T. Gare and G.S.F. Hazeldan, "Basic Oxygen Steelmaking: Decarburization of Binary Fe-C Droplets and Ternary Fe-C-X Droplets in Ferruginous Slags," *Ironmaking and Steelmaking*, No. 4, 1981, p. 169.
5. D.J. Min and R.J. Fruehan, "Rate of Reduction of FeO in Slag by Fe-C Drops," *Metallurgy Transactions B*, Vol. 23B, February 1992, p. 29.
6. G.G. Krishna-Murthy, Y. Sawada and J.F. Elliott, "Reduction of FeO Dissolved in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ Slags by Fe-C Droplets," *Ironmaking and Steelmaking*, Vol. 20, No. 3, 1993, p. 179.
7. G.G. Krishna-Murthy, A. Hasham and U.B. Pal, "Removal of FeO During Foaming of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-FeO}$ Slags by Low Carbon-Iron Melts," *ISIJ*, Vol. 34, No. 5, 1994, p. 408.
8. G.G. Krishna-Murthy, A. Hasham and U.B. Pal, "Reduction Rates of FeO in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-X}$ Slags by Fe-C Droplets," *Ironmaking and Steelmaking*, Vol. 20, No. 3, 1993, p. 191.
9. R.J. Fruehan, ed., "The Making, Shaping and Treating of Steel," 11th Edition, *Steelmaking and Refining Volume*, The AISE Steel Foundation, 1998, p. 134.
10. S. Jung and R.J. Fruehan, "Foaming Characteristics of BOF Slags," unpublished.
11. H.W. Meyer, "Oxygen Steelmaking: Its Control and Future," *JISI*, June 1969, p. 781.
12. H.W. Meyer, D.A. Dukelow and M.M. Fischer, "Static and Dynamic Control of the Basic Oxygen Process," *Journal of Metals*, June 1964, p. 501.
13. X. Zhang, U.S. Steel Research, personal communication, May 1999.
14. R.J. Fruehan and B. Ozturk, "Communication: Effect of Temperature on Slag Foaming," *Metallurgy Transactions B*, Vol. 26B, October 1995, p. 1,086.

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Appendix C

Critical aspects of recycling waste oxides in steelmaking

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ABSTRACT

The US steel industry produces over three millions of waste oxide dusts per year which can be used as valuable resources by directly recycling them into steelmaking processes. This paper examines a number of critical issues for recycling into the OSM converter, recycling of EAF dust in an EAF, and recycling of EAF-AOD dusts in stainless steel production. Specifically the reasons for increased slopping when recycling is carried out in OSM and methods to reduce slopping are discussed. For EAF the impact of recycling on energy, productivity and Zn content of the dust is examined. The recovery of Cr and Ni for recycling stainless steelmaking dusts is estimated.

The decarburization reaction in steelmaking can occur by the direct reaction (1) or indirectly by FeO in slag by reactions (2) and (3).

Industrial data indicates that when WOBs are used the FeO content of the slag in the first 50% of the blow is higher than normal (1). This excessive FeO in the slag can be viewed as stored oxygen which when it reaction rate with carbon dissolved in iron generates excessive amounts of CO. Also, if this occurs early in the process the slag temperature and basicity are low which increases the foamability of the slag contributing to the increased probability of slopping.

Recently Molloseau and Fruehan (2) investigated the rate of reaction (3) under conditions representative of the first half of the oxygen blowing period in OSM. In the experiments, iron carbon drops were reacted in a slag with a basicity $\left(\frac{\% \text{CaO}}{\% \text{SiO}_2} \right)$ of 1.2 and FeO contents ranging from 3 to 35%. The experimental apparatus is shown in Figure (1) and the details are given elsewhere (2). The rate was determined by measuring the volume of CO generated. In addition, the reaction was examined using x-ray fluoroscopy. Typical rate results are shown in Figure (2). The interesting and previously unreported phenomena found was that there is a critical FeO content and temperature at which the rate increased dramatically. This is shown in Figure (3) for 1440°C. The dashed line is the rate for low FeO contents in which the overall rate of reaction is controlled by the intermediate reaction step for reaction (3) between CO₂ and carbon in iron (4) followed by the slag-gas reaction (5)

Reaction (4) was previously found to be the rate controlling reaction for low FeO contents (<8% FeO) (4).

The x-ray fluoroscopy experiments indicated that below the critical FeO content and temperature the metal droplet remained as a single spherical drop. Above the critical conditions the metal drop emulsified as shown schematically in Figure (4). As seen after about 10 seconds the drop coalesced. Consequently, this phenomena would not have been found by simply examining the slag-metal system after the experiment without x-ray fluoroscopy. It is hypothesized that slopping can occur if this critical condition for the fast rate occurs before the slag has low foamability.

In a coordinated study, Jung and Fruehan (3) examined the foamability of slags representative of those present during the first 60% of the blowing period in OSM. They measured the foam index (Σ) which can be defined by (6)

$$V_f = \Sigma Q \quad (6)$$

where V_f is the volume of foam and Q is the gas flow rate or in OSM the rate of CO generation. The results indicate that the foam index decreases significantly during the blow due to increasing basicity and FeO content of the slag and increasing temperature. The foamability, as indicated by the foam index, is a factor of four higher at about 17% than at 50% of the blow. Consequently, the foam height for a given decarburization or CO generation rate is higher during the early stage of the blow as shown for a hypothetical 200 tonne furnace in Figure (5).

When WOBs are used the FeO content of the slag is higher in the early stages and, consequently, the critical conditions for fast decarburization occur sooner. Also, the decrease in FeO is faster also leading to increased CO generation. This is shown schematically in Figure (6) as a plot of FeO versus blowing time with WOBs (II) and without WOBs (I). It is interesting to note that when highly oxidized (rusty) scrap is used slopping also increases for the same reason.

Based on this understanding that when using WOBs the following recommendations are made.

1. Add the WOBs continuously to avoid excessive FeO build up in the slag or after the critical condition for increased decarburization rate have been obtained.
2. If WOBs are added at the beginning, reduce the time the lance is in the high position to avoid excessive FeO in the slag.
3. At the critical condition, at about 25% of the blow, reduce the oxygen flow rate by 20% for 3-4 minutes to avoid excessive CO generation.

Recycle of EAF Dusts

Recycling of EAF dusts has been carried out for decades. Due to the need to reduce the iron and other reducible oxides in the dust the energy requirement and, consequently, the productivity can be significantly affected. Also, the method of addition can affect the process and costs. The EAF dusts can be added as a batch in large bags (super sacks) or injected into the melt. Injection can cause additional amounts of dust by the dusts being entrained in the off gases prior to melting or reacting. Typical injection costs are \$2 to 3 per tonne of injected dust.

The composition of EAF dusts has been extensively studied (6). The composition depends on the charge materials and process details. For example the use of galvanized scrap increases the Zn content, of DRI/HBI increases the amount of iron oxide, and lime injection the CaO content of the dust. A typical dust composition is given in Table (I).

Table I – Typical EAF dust composition for scrap melting and no recycle			
ZnO	28%	CaO	12%
Fe ₂ O ₃	37%	MgO	5%
PbO	2.1%	Na ₂ O	1.8%
MnO	4.0%		

The effect of using the dust listed in Table (I) on energy and productivity was computed. The base case is for a 100% scrap in a charge requiring 400 kwh/tonne, a 60 minute tap to tap time with power on for 45 minutes while tapping 150 tonnes and a slag with 25% FeO and a basicity of two. As seen in Figure (7) energy consumption increases and productivity decreases with dust recycle.

With recycling on subsequent heats the dust load and Zn content of the dust will increase. For 12.5 kg of dust for a normal scrap charge and 10 kg of the dust is recycled each heat the Zn content and amount of dust will increase as shown in Figure (8). After about 4 to 5 heats the Zn content and dust amount reach a steady state values of about 50% and 18 kg respectively. In this case, 8 kg of dust must be disposed of for each heat or a reduction of 37.5%. However, with the high Zn content the dust could possibly be sold to produce fertilizer or zinc metal. If more of the dust is recycled the dust generation rate and it's Zn content increases. For example, for 2% recycle 26.5 kg of dust per tonne is generated but only 6.5 kg per tonne containing 61% Zn must be disposed of or sold.

Recycling of Stainless Steelmaking Dusts

The EAF and AOD in stainless steelmaking generate considerable amounts of waste oxides which contain chromium and nickel. Therefore, in addition to avoiding the dust disposal problem, these materials will add valuable chromium and nickel to the steel, if they are recycled. Most of the nickel (>90%) will enter the metal but some of the chromium will remain as an oxide in the slag phase. Also, Cr₂O₃ or CrO are relatively stable oxides and it may be difficult to reduce them. The recycling of EAF-AOD dusts is currently under investigation. The preliminary experiments have centered on the recovery of Cr from these materials.

In normal EAF melting of stainless steel the chromium distribution between slag and metal was controlled by Fe-FeO equilibrium.

However, due to forming considerations recently stainless steel producers add silicon as ferrosilicon or other materials to reduce chromium oxide out of the slag in order to keep the slag liquid and $\underline{Si} - (SiO_2)$ is determining the chromium distribution.

In the present work, 200 grams of an Fe – 14.7% Cr – 7% Ni – 1.29% Si melt was equilibrated with 60 grams of a 43% CaO – 35% SiO₂ – 6% Al₂O₃ – 2% FeO – 3.7% Cr₂O₃ slag. To this, 87 g of a WOB whose composition is listed in Table (II) was added. Samples of the metal were taken and analyzed for Cr and Si, the results are given in Figure (9). Iron and chromium were reduced out of the WOB and the final metal weight was 233 grams.

Table II – Composition of Stainless Steel WOB			
FeO	23%	CaO	8.9%
Fe ₂ O ₃	12.8%	SiO ₂	9.2%
Cr ₂ O ₃	9.2%	Fe	11%
NiO	1%	MgO	3%
C	14%		

As seen in Figure (9) the reduction rate was relatively fast. Based on a mass balance all of the chromium in the dust was reduced. The silicon and carbon also reduced much of the iron oxide. As a side note, the reaction of carbon with iron oxide which produces CO caused the slag to foam extensively. Whereas the results are very preliminary, it appears that the chromium in the WOBs can be recovered and the WOBs can also promote foaming.

CONCLUSIONS

Waste oxides collected from the off gases in iron and steelmaking processes contain valuable steelmaking ingredients. One way to reclaim the useful components is by direct recycling into the steelmaking process. The recycling of dusts from OSM and the blast furnace in the steelmaking converter, EAF dusts recycled in the EAF and of stainless steelmaking EAF and AOD dusts in the EAF have been discussed.

Recycling of BF-OSM dusts in the BOF can be accomplished without excessive slopping by the timing of the addition or of altering the blowing practice. EAF dusts can be recycled with minimum increase in energy consumption while building up the zinc in the dust to acceptable levels for sale. Stainless steelmaking dusts from the EAF and AOD can provide valuable chromium and nickel to the metal with minimal loss to the

slag. These recycling processes do require extra care and control but can reduce disposal costs and provide valuable materials for steelmaking.

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REFERENCES

1. C. Molloseau and R. J. Fruehan, 2000 Steelmaking Conference Proceedings ISS, Pittsburgh PA, 2000, pp. 303-313.
2. C. Molloseau and R. J. Fruehan, submitted to Metall. & Materials Transactions B.
3. S. Jung and R. J. Fruehan, to be published Trans ISIJ, 2000.
4. DJ Min and R. J. Fruehan, Metall. Trans. B, Vol. 23B, 1992, p. 29.
5. K. Ito and R. J. Fruehan, Metall. Trans. B, Vol. 20B, 1989, p. 509.
6. The EPRI Center for Materials Production, "Minimizing Electric Arc Furnace Dust Generation", CMP Report 96-1A, Pittsburgh PA.

Figure 1. Apparatus for measuring rate of reaction of Fe-C drops in OSM slags.

Figure 2. Typical results for rate of reaction of Fe-C drops in OSM slags.

Figure 3. Rate of reaction versus FeO content in the slag at 1440°C.

Figure 4. Schematic diagram illustrating emulsification of Fe-C drops in slags with high FeO contents.

Figure 5. Foam height for a given decarburization rate during different stages of the process.

Figure 6. Schematic diagram illustrating the FeO content of the slag in OSM with (II) and without (I) waste oxides addition.

Figure 7. Effect of EAF dust recycling on energy consumption and productivity.

Figure 3. The dust generation rate and Zn content with continuous recycle at 40%.

Figure 9. Rate of reduction of chromium oxide in WOBs by silicon in the metal.

Appendix D

Foaming Characteristics of BOF Slags

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Slag foaming measurements were carried out for BOF type slags that exist during the first half of the blowing period in order to better understand slopping of slag. The foam index (Σ) decreases with increasing FeO up to about 20 % FeO content and is almost constant for FeO from 20 to 32 % FeO. This is believed to be because above about 25 % FeO, the viscosity is nearly constant. The foam index shows a minimum value at basicity $[(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)]$ of 1.4 at 1713 K; it increases at higher basicities due to the precipitates such as 2CaOSiO_2 or $(\text{Fe,Mg})\text{O}$ which stabilizes the foam. The effect of TiO_2 and MgO on foam index was also evaluated. An empirical equation for the foam index obtained by the previous researchers was applied to the present experimental results. The foaming during the first half of the blowing in BOF process was described based on the empirical relationship and the foam height was estimated for a BOS converter as a function of decarburization rate.

KEY WORDS: slopping; BOF Slags; foam index; viscosity of slags; bubble size.

1. Introduction

Slopping remains one of the major concerns in oxygen steelmaking (OSM). Slopping results from excessive amounts of gas being generated in a highly foamable slag. Most of the previous work on foaming has been done for limited conditions, primarily relevant to iron smelting. For example, FeO contents were less than 5 % in a limited temperature range. For steelmaking slags most measurements have been for latter in the process, close to tap conditions. These conditions do not reflect those present during the first part of oxygen steelmaking (OSM) when slopping occurs. Therefore, it is important to understand the fundamental features of slag foaming occurring during the first half of the blow in the BOF process.

In recent investigations on slag foaming in the metallurgical processes, foams were often generated and maintained at steady state by using a constant rate of production of gas bubbles. Zhang and Fruehan¹⁾ injected argon gas into liquid slag contained in an cylindrical alumina crucible at 1773 K through an alumina nozzle (1.75 mm I.D.) and examined foaming by a X-ray video technique. The results showed that the whole foam column was composed of polyhedron shaped bubbles, and no initial transitional spherical bubbles could be seen. In studying the kinetics of the reaction between FeO in the slag and carbon in the liquid iron, Zhang and Fruehan¹⁾ observed foams dominated by spherical bubbles of much smaller size using the same X-ray video technique. The later type of foam was much more stable than that observed by Jiang and Fruehan,²⁾ although the slag compositions and temperatures were almost identical in both experiments. The more stable foam resulted from smaller bubbles generated by the chemical reaction.

The dynamic measurement of foamability was first pro-

posed by Bikerman³⁾ in which an equilibrium between formation and collapse of the foam was established by the generated gas bubbles of definite size at a constant rate. The unit of “foaminess” was defined as the foam index (Σ), given by

$$\Sigma = \frac{V_f}{Q_g} \quad (1)$$

where V_f is the volume of the foam at steady state and Q_g is the gas flow rate. The parameter Σ has the unit of the time and can be roughly interpreted as the average traveling time of gas in the foamed liquid. Bikerman³⁾ found that Σ is independent of the amount of the liquid and the cross-sectional area of the cylindrical container.

In the study of slag foams, Ito and Fruehan⁴⁾ modified Bikerman's definition of the dynamic measurement of foam stability and referred to it as the foam index,

$$\Sigma = \frac{\Delta h}{\Delta v} = \frac{\Delta H_f}{\Delta v_s} = \frac{H_f}{v_s} \quad (2)$$

where h is the height of the foam layer at steady state, H_f is the foam height defined as the difference of the level of foamed liquid surface to the level of the liquid at rest, v is the linear gas velocity in the foam and v_s the superficial gas velocity which is defined by,

$$v_s = \frac{Q_g}{A} \quad (3)$$

Here A is the cross-sectional area of the container. Ito and Fruehan⁴⁾ also showed that the measured foam index is independent of the size of the container above a certain

size when the effect of the container is negligible. They measured the foam index for a slag of composition $\text{CaO}/\text{SiO}_2=0.67$; $\text{FeO}=30\%$ at 1573 K in four different sized crucibles (diameter: 25, 32, 38, 50 mm). The results showed that foam indexes obtained were the same for all the crucibles greater than that of the 32 mm diameter. They also showed that in a $\text{CaO}-\text{SiO}_2-\text{FeO}$ system, Σ decreased with increasing basicity up to 1.22 at 1673 K. When CaO/SiO_2 was greater than 1.22, Σ increased due to the presence of second-phase particles (CaO or 2CaOSiO_2). Second-phase particles have a large effect on foam stability because they increase the bulk viscosity of the slag. Jiang and Fruehan²⁾ also conducted a larger scale experiment for their slags at 1773 K in which the diameter of the crucible was 92 mm; Their results for the same slag at the same temperature were similar.

It has been shown that the foam index is closely related to the physical properties of the liquid slag by dimensional analysis.^{1,2)} In a recent study, Zhang and Fruehan¹⁾ measured the foam index for the bath-smelting type of slags ($\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{FeO}$) with small bubbles generated by argon gas injection through the nozzle of multiple small orifices. An improved correlation was obtained by using more accurate data for the slag viscosity, density, surface tension, and bubble diameter in the dimensional analysis. The correlation developed is expressed by

$$\Sigma = 115 \frac{\mu^{1.2}}{\sigma^{0.2} \rho D_b^{0.9}} \quad (4)$$

where Σ is the foam index (sec), μ is the viscosity (N s/m^2), σ is the surface tension (N/m), ρ is the density (kg/m^3), and D_b is the bubble diameter (m).

It is the objective of this research to understand the fundamental features of slag foaming for $\text{CaO}-\text{SiO}_2-\text{FeO}-\text{MgO}$ slags relevant to steelmaking processes during the first half of the blowing in the converter. Also Ti is often in blast furnace hot metal which enters the slag. Therefore the effect of TiO_2 on slag foaming was examined. The effect of MgO was also measured. Another focus of this research is to confirm if the correlation recently developed by Zhang and Fruehan¹⁾ can be applied to the BOF slags.

2. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. An electric resistance furnace with a 150-mm hot zone length was used for the experiments to establish an isothermal condition. The slag sample weighed about 150 g, which corresponded to a slag depth of about 4 cm for a crucible diameter of 4.5 cm. This slag depth is sufficient to eliminate the effect of the amount of the liquid on foaming, as indicated by Bikerman.³⁾ It took about 30–60 min to take each set of measurements during which the dissolution of MgO from the crucible resulted in the final slag composition containing 6–22% MgO. The argon gas was introduced into the molten slag through a pure iron pipe with a knife edged nozzle (2.1-mm ID, 3.2-mm OD) which was placed about 0.5–1.0 mm above the bottom of the crucible. When the foam height reached a stable level, the surface position of the slag was detected with an electric probe

Fig. 1. Schematic diagram of the experimental apparatus.

Fig. 2. Foam height of $\text{CaO}-\text{SiO}_2-\text{FeO}-\text{MgO}$ slags as a function of superficial gas velocity at 1713 K.

made of a pure iron rod. In the present study, the foam height was measured as the difference between the top foam surface position and the liquid slag position at rest. In order to obtain an accurate value for the foam index, a series of measurements at various gas flow rates were conducted for each slag composition studied, and the foam index was determined from the slope of the line in a foam height vs. superficial gas velocity plot, as shown in Fig. 2.

The master slag composed of CaO , SiO_2 , and MgO was pre-melted in a MgO crucible using an induction furnace. CaO , SiO_2 , and FeO was added to the master slag to adjust the slag compositions for actual experiments. FeO was prepared by sintering Fe_2O_3 powder in an iron crucible under Ar gas atmosphere at 1573 K for about 12 hr. After the measurement was finished, the slag samples were chemically analyzed.

3. Results and Discussions

3.1. Bubble Size

It has been pointed out that the foam stability of liquid

depends not only on its physical properties but also on the bubble size.⁵⁾ In foams produced in the present foaming experiment, the following relationship between the volume of bubbles (V_B), bubble frequency (f), the gas flow rate (V_g) can be deduced by Eq. (5).

$$V_B = V_g / f \quad (5)$$

Assuming that bubbles are perfect spheres, Eq. (5) can be rewritten as follows.

$$D_b = \left(\frac{6V_g}{\pi \cdot f} \right)^{1/3} \quad (6)$$

As indicated in Eq. (6), the equivalent spherical bubble diameter (D_b) can be calculated by measuring the bubble frequency (f) at a given gas flow rate. Figure 3 shows the measured bubble diameter as a function of gas flow rate. Bubble frequency measurements, which were obtained using a pressure transducer installed between the gas flow controller and the gas lance in Fig. 1 which would indicate when a bubble was released. The measured bubble diameter is larger than that calculated from the equation proposed by Sano *et al.*⁶⁾ shown as a straight line. In the calculation of

Fig. 3. The relationship between mean bubble size and gas flowrate at 1713 K.

bubble diameters using Sano's equation,⁶⁾ the surface tension and density values of the slag system designated by CSFM-4 in Table 1 were used. Because the consideration of viscosity effect on the bubble size was not taken into in Sano's equation, there may be some discrepancy between the measured bubble size and the calculated one. Compared to the average bubble diameter (about 12 mm) measured by Ito and Fruehan⁴⁾ for CaO-SiO₂-FeO-Al₂O₃ system, the average bubble diameter for the CaO-SiO₂-FeO-MgO slag system shows higher values (about 17 mm). A second reason might be resulted from the difference of the shape of the nozzle tips used in the present work and in the experiment performed by Ito and Fruehan.⁴⁾ While the gas lance in the work by Ito and Fruehan⁴⁾ was made of stainless pipe with knife edged nozzle (O.D.=2.1 mm), the lance in the present research was made of iron pipe with flat edged nozzle. According to the research by Sano *et al.*,⁶⁾ the bubbles produced through flat edged nozzle may be larger than those through knife edged nozzle because the bottom part of the bubble sticking to the flat edged nozzle may expand to the external surface of the nozzle tips.

3.2. The Effect of FeO Content on Foam Index

The experimental results for determining foam index (Σ) along with the analytical results for the slag compositions are presented in Table 1. Σ is plotted in Fig. 4 as a function of FeO content. It is indicated that the foam index Σ decreases with increasing FeO up to about 20% FeO content. This phenomena was also observed for bath smelting slag systems (CaO/SiO₂=1 and 1.25) measured by Jiang and Fruehan²⁾ and for Nippon steel's bath smelting slag.²⁾ Jiang and Fruehan²⁾ attributed the higher foaming index observed for the lower basicity slag (CaO/SiO₂=1) to the fact that viscosities for the bath smelting slags are higher. One interesting point found in the measurement by Jiang and Fruehan²⁾ is that a maximum foaming index occurred at around 2% FeO. From their experimental observations, it is concluded that CaO-SiO₂ slags do not foam when no FeO is present in the slag, because it is too viscous to foam significantly. That is, the slags with low FeO contents have a high melting point and viscosity, and no true foam is formed due to the channeling of the gas bubbles through

Table 1. BOF Slag Foaming Measurement for CaO-SiO₂-FeO-MgO_{ox} system.

Sample No.	Temp (K)	Basicity (C/S ratio)	%CaO	%SiO ₂	%FeO	%MgO	%TiO ₂	Foam Index	Density (g/cm ³)	Surface tension (N/m)	Viscosity (N·s/m ²)
CSFM-01	1673	0.93	29.61	31.95	20.47	17.97		1.10	2.922	0.509	0.293
CSFM-03	1713	1.0	34.78	33.76	22.52	8.94		0.59	2.958	0.502	0.270
CSFM-04	1713	1.1	37.39	35.57	20.87	6.17		0.53	2.936	0.493	0.291
CSFM-05	1713	1.1	30.96	29.39	24.16	15.69		0.54	2.978	0.527	0.226
CSFM-06	1713	1.1	29.11	27.73	31.52	11.64		0.68	3.093	0.524	0.221
CSFM-07	1713	0.93	30.00	32.13	18.09	17.78		0.57	2.892	0.511	0.248
CSFM-08	1713	0.86	28.67	33.42	17.57	20.34		0.87	2.874	0.510	0.250
CSFM-09	1713	0.61	23.02	37.73	15.23	24.02		0.98	2.824	0.497	0.283
CSFM-10	1713	0.42	17.21	40.99	13.68	28.12		1.70	2.786	0.489	0.309
CSFM-11	1823	1.0	34.08	32.77	15.11	18.04		0.50	2.851	0.516	0.213
CSFM-12	1773	0.93	29.12	31.32	20.96	18.60		0.75	2.925	0.525	0.178
CSFM-13	1713	1.0	38.18	38.94	10.24	12.38		0.37	2.784	0.486	0.310
CSFM-14	1713	1.0	28.07	27.53	27.98	14.10		0.87	3.045	0.524	0.220
CSFM-21	1713	1.0	31.67	31.73	17.68	15.95	2.66	0.87	2.905	0.507	0.239
CSFM-22	1713	1.0	29.31	29.05	18.48	16.61	4.96	1.1	2.936	0.510	0.219
CSFM-23	1713	1.0	27.95	27.63	19.37	16.44	7.17	1.2	2.964	0.510	0.207
CSFM-24	1713	1.0	27.01	26.55	20.15	16.47	9.44	1.4	2.987	0.510	0.196

Fig. 4. The change of the foam index for CaO-SiO₂-FeO-MgO_{sat} slags as a function of FeO content at 1713 K.

Fig. 5. The relationship between the viscosity of slag and FeO contents at 1713 K.

the slag layer. This phenomena has also been observed in the previous research about the addition effect of P₂O₅ on foaming of CaO-SiO₂ slags by Cooper and Kitchener.⁷ They have shown that foaming is absent with binary CaO-SiO₂ melts but is marked when P₂O₅ in the range of 0 to 1.8 % is added to melts containing more than 50 % of SiO₂.

The tendency in Fig. 4 can be explained on the basis of Fig. 5 plotting viscosity as a function of FeO content. The viscosities of both bath smelting slags and BOF slags decrease with increasing FeO content. In Fig. 5, the viscosities of the slags were estimated using Urbain's model⁸ based on the slag compositions shown in Table 1. From the result in Fig. 5, it is believed that the decrease of viscosity is the major contributor to foam instability of slags.

The apparent result for the bath smelting slags and BOF slag is that foam index Σ decreases with increasing the FeO content up to about 20 % FeO. However, the foam index Σ is almost constant with increasing FeO content higher than 20 % FeO in the slag. As indicated in Fig. 5, the viscosity does not decrease significantly above 25 % FeO which is the most likely reason for the foam index being constant.

Fig. 6. The change of foam index Σ with basicity index $((\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3))$ of the CaO-SiO₂-FeO-MgO_{sat} slags at 1713 K.

3.3. The Effect of Slag Basicity on Foam Index

Figure 6 shows the foam index for CaO-SiO₂-FeO-MgO slags at 1713 K as a function of basicity index defined as $(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$ in weight percent. The foam index decreases with increasing $(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$ up to 1.4, which is expected to be the liquidus composition. In general the surface tension increases and viscosity decreases with increasing basicity. Therefore, low surface tension and high viscosity is expected to favor the stability of slag foam. However, the foam index increases with increasing basicity when the basicity index is higher than 1.4. A similar tendency can be seen in the data of foam index measured by Ito and Fruehan⁴ for CaO-SiO₂-FeO-Al₂O₃ slag system. The critical basicity indexes reaching the minimum foam index are about 1.20 at 1573 K and 1.22 at 1673 K, which correspond to the liquidus temperature of CaO-SiO₂-FeO-Al₂O₃ slag system. They⁴ reported that this is because solid particles such as 2CaOSiO₂ precipitate at higher CaO contents, and the particles significantly increase foam stability. The similar finding can be seen in other previous research.⁷ When SiO₂ is low and CaO high, the slags may crystallize at the steelmaking temperatures, the crystallizing substance being in most cases the orthosilicate Ca₂SiO₄, as can be confirmed in the CaO-SiO₂-FeO phase diagram.⁹ From the CaO-SiO₂-FeO phase diagram, even basic slags are not saturated with CaO, but rather with Ca₂SiO₄ or, in some cases, with 3CaOSiO₂. If the slag is high enough in magnesia content as in the present slags saturated with MgO, magnesiowustite[(Fe,Mg)O] may be the phase which crystallizes first. Therefore, the increase of foam index caused by the precipitation of second-phase particles may be due to the role of the particles like 2CaOSiO₂ or (Fe,Mg)O which increase the bulk viscosity. Of course, high viscosity is required both to stop the drainage of the liquid from the thin films separating the bubbles in foams and the coalescence of bubbles approaching each other in gas bubbles. It should be noted that precipitated second phase particles which are smaller than the foam bubbles stabilize the foam. The increase in the bulk viscosity reduces the slag foam bubble drainage rate.

Fig. 7. The change of the foam index for CaO-SiO₂-FeO-MgO_m slags as a function of TiO₂ content at 1713 K.

However, large pieces of undissolved lime do not stabilize the foam.

The slight difference of the basicity index for the minimum foam index between CaO-SiO₂-FeO-Al₂O₃ and CaO-SiO₂-FeO-MgO slag may be attributable to the fact that MgO and Al₂O₃ are regarded as basic and acidic oxide, respectively. CaO and MgO are being dealt with as the same oxide for convenience in defining basicity index in Fig. 6. The minimum is actually the liquidus composition and therefore is not necessarily related to the basicity.

3.4. The Effect of TiO₂ Content on Foam Index

Figure 7 shows the effect of TiO₂ on the foam index for the BOF slags. As the content of TiO₂ increases, the experimentally measured foam index increases. According to the previous research,¹⁰⁾ TiO₂ increases the viscosity and lowers the surface tension of FeO just as SiO₂ does. However, it was pointed out that TiO₂ was not a networkbuilder because Ti⁴⁺ cations are too large. It is known that TiO₂ introduced in an acid silicate melt lowers its viscosity in the same manner as CaO or FeO. From the experimental tendency in Fig. 7, it may therefore be speculated that TiO₂ added combines with MgO dissolved from the crucible wall to form 2MgOTiO₂ ($T_m = 1756^\circ\text{C}$) precipitates. In reality, the calculation of predicted foam index based on several models which do not take the presence of precipitates into consideration. Although the viscosity in the calculation decreased along with the increase of TiO₂ content, the actual viscosity affected by the formation of precipitates may increase, which is believed to be the crucial reason for the increase of foam index observed in Fig. 7.

3.5. The Effect of MgO on Foam Index

Figure 8 shows the influence of MgO content on the foaming behavior for a 35%CaO-35%SiO₂-30%FeO slag to which a proper amount of MgO was added for each measurement. In order to facilitate the control of MgO content, an Fe crucible was used for the slag container for these measurements. It is shown that the foam index decreases with increasing MgO additions. In Fig. 8, the foam index obtained for 28CaO-28SiO₂-28FeO-14MgO_m slag is in relatively good agreement with the results at lower MgO

Fig. 8. The change of the foam index for CaO-SiO₂-FeO-MgO_m slags as a function of MgO content at 1713 K.

Fig. 9. The temperature dependence of the foam index for CaO-SiO₂-FeO-MgO slag.

contents measured using an iron crucible. The tendency in Fig. 8 has been reported by Ren *et al.*¹¹⁾ who reported a reduction in foaming intensity with increasing MgO contents at 1623 K for basic compositions (CaO/SiO₂ ≥ 1).

3.6. The Effect of Temperature on Foam Index

Figure 9 shows the temperature dependence of the foam index for a 35%CaO-35%SiO₂-30%FeO-10%MgO slag. It is indicated that the logarithm of foam index decreases with increasing temperature in the temperature range of 1673 to 1823 K. Generally since the temperature coefficient for surface tension¹²⁾ is positive and that for viscosity¹³⁾ is negative, decreasing temperature would favor the increase of the foam index. From the data in Fig. 9, the temperature dependence of the foam index can be expressed by Eq. (7).

$$\log \Sigma = \frac{6610}{T} - 3.90 \quad (7)$$

The temperature dependence given by Eq. (7) can be used to predict the foam index at other temperature for the slag and experimental conditions employed in this study. From

Fig. 10. The result of the dimensional analysis considering the effect of the bubble size. $N_2 = \Sigma \mu g / \sigma$, $Mo = \mu^4 g / \sigma^3 \rho$, and $Ar = \rho^2 D_b^3 g / \mu^2$

Eq. (7), the apparent activation energy for the decay of the foam can be estimated to be 126.5 kJ/mol. For this value, Ito and Fruehan⁴⁾ obtained 160 kJ/mol as the activation energy for the decay of the foam for 35%CaO–35%SiO₂–30%FeO slag in the temperature range of 1 523 to 1 673 K. And Ozturk and Fruehan¹⁴⁾ reported the value of 139.6 kJ/mol as the apparent activation value for foam decay for 48%CaO–32%SiO₂–10%FeO–10%Al₂O₃ slag in the temperature range of 1 723 to 1 873 K. It was found that there was no significant difference between the activation energy for the foam decay and that for the viscous flow in the case of both present result and their results.^{4,14)}

3.7. Application of the Existing Correlation to the Present Experimental Results

It has been proved that the foam index for bath smelting slags by Ito and Fruehan,¹⁵⁾ Jiang and Fruehan²⁾ and ladle slags by Roth *et al.*¹⁶⁾ has the quantitative relationship with the slag physical properties. According to the previous research,¹⁾ it is obvious that the foam stability of slags are affected by viscosity, surface tension, density, and the average bubble diameter. For the case where the bubbles were produced by injecting gas from an orifice, the average bubble diameter can be estimated by the viscosity, surface tension, nozzle geometry, and gas flow rate or simply measured as in the present study. One of the objectives of this research is to confirm if the experimentally determined foam indexes in the present work agree with those calculated by the equation derived by Zhang and Fruehan.¹⁾

Zhang and Fruehan¹⁾ described the following equation which reflects the dependence of the foam index on the viscosity, surface tension, density, and the average bubble diameter by the dimensional analysis. The estimation of the slag properties is given in Appendix. As can be seen in Fig. 10, the correlation (4) developed by Zhang and Fruehan predicts the foam index for BOF slags during the first half

Fig. 11. The calculated foam index for CaO–SiO₂–FeO–MgO slag during the course of the blowing time in the BOS process.

Table 2. The slag composition in the BOS process defined approximately during the first half of the blowing.

stage in the entire blowing time	Temperature(K)	CaO/SiO ₂	mass% FeO	mass% MgO
17%	1633	0.8	35	2
33%	1693	1.2	32	4
50%	1753	1.5	23	6

of the blowing reasonably enough. Equation (4) indicates that viscosity is the most important physical properties in determining foam index with surface tension, density, and bubble size also being important. That is, the foam stability increases with increasing viscosity and decreasing the bubble size, surface tension and density of slags, as was previously mentioned. In applying Eq. (4) to the present results, the average measured value in Fig. 3 was used to estimate the size of the bubbles produced by injecting gases through an orifice into liquid slags.

4. Foaming in Steelmaking Process

Understanding slag foaming in the converter is crucial not only for the prevention of slopping but also for the control of the reactions occurring in the BOS process. The slag foaming in the BOS process can be estimated using the foaming index formula previously derived as a function of the physical properties of BOS slags. Based on the estimated foam index, the foam height in the converter during the first half of the blowing can be calculated using the following Eq. (8) derived by Ito and Fruehan.¹⁵⁾ Here V_g^* is a superficial gas velocity and h^* height before foaming begins.

$$h = \Sigma (V_g^2 - V_g^{*2}) + h^* \dots \dots \dots (8)$$

Figure 11 shows the estimated foam index for CaO–SiO₂–FeO–MgO slags as a function of the blowing time quantified by percentage with respect to the entire processing time in BOS process. The three slag compositions were selected to simulate the stages 1, 2, and 3 which correspond to the 17 % stage, 33 % stage, and 50 % stage of the entire blowing time in the BOS operation, respectively based on the real process data supplied by Inland Steel

Table A1. Recommended values for partial molar volume $\bar{V}$ of various slag constituents at 1773 K.¹⁹⁾

Constituent	CaO	SiO ₂	FeO	MgO	TiO ₂
$\bar{V}$, cm ³ mol ⁻¹	20.7	19.55+7.966 X_{SiO_2}	15.8	16.1	24.0

 Table A2. Recommended values for partial surface tension $\bar{\sigma}$ of various slag constituents at 1773 K.¹⁹⁾

Constituent	CaO	SiO ₂	FeO	MgO	TiO ₂
$\bar{\sigma}$, mNm ⁻¹	625	260	645	635	360

tension, and viscosity. The uncertainties vary according to the physical property being estimated so that experimental uncertainties are about $\pm 2\%$ for density, about $\pm 10\%$, and about $\pm 25\%$ for viscosity measurements. It is unreasonable to expect any predictive model to produce data which are more accurate than those obtained experimentally, for the models use experimental results to derive values for the various partial molar parameters.

An additive method for the estimation of densities in alloys and slags has been widely used. In this method, the molar volume V , can be obtained from Eqs. (A-1) and (A-2) below where M , x , and $\bar{V}$ are the molecular weight, mole fraction, and the partial molar volume, respectively, and the subscripts 1, 2, and 3 denote the various oxide constituents of the slag.

$$\rho = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{V} \quad \text{.....(A-1)}$$

$$V = x_1 \bar{V}_1 + x_2 \bar{V}_2 + x_3 \bar{V}_3 \quad \text{.....(A-2)}$$

The partial molar volume is usually assumed to be equal to the molar volume of the pure component V° .¹⁹⁾ The recommended values for V° for the various oxides at 1773 K are given in Table A1. In order to calculate the values for the molar volume of CaO, SiO₂, FeO, MgO, and TiO₂ based on those obtained in Table A1, 0.01% K⁻¹ was used as the temperature dependence of the molar volume.¹⁹⁾

Methods for estimating the surface tension of slags based on the addition of the partial molar contributions $\bar{\sigma}$ of the individual constituents have been reported by Appen *et al.*,²⁰⁾ Boni and Derge²¹⁾ and Popel.²²⁾ All these methods make use of Eq. (A-3)

$$\sigma = x_1 \bar{\sigma}_1 + x_2 \bar{\sigma}_2 + x_3 \bar{\sigma}_3 \quad \text{.....(A-3)}$$

where the subscripts 1, 2, 3, etc., denote the various slag constituents. Values of $\bar{\sigma}_i$ are often taken to be the surface tension of the pure component σ° . This method of estimating the surface tension works well for certain slag mixtures but breaks down when surface-active constituents, such as P₂O₅, are present. Surface-active components migrate preferentially to the surface and cause a sharp decrease in the surface tension and only very small concentrations are required to cause an appreciable decrease in σ . The recommended values for σ° for the various oxides at 1773 K are given in Table A2. In order to calculate the values for the surface tension of CaO, SiO₂, FeO, MgO, and TiO₂ based on those shown in Table A2, 0.15 mNm⁻¹ K⁻¹ was applied as the temperature dependence of the surface tension ($d\sigma/dT$) of the present slag system.¹⁹⁾

Several models exist for the estimation of viscosities of

 Table A3. Equations for B -parameters in Urbain model for viscosity.

B_i	$B_i = a_i + b_i \alpha + c_i \alpha^2$
B_0	$13.8 + 39.9355\alpha - 44.049\alpha^2$
B_1	$30.481 - 117.1505\alpha + 129.9978\alpha^2$
B_2	$-40.9429 + 234.0486\alpha - 300.04\alpha^2$
B_3	$60.7619 - 153.976\alpha + 211.1616\alpha^2$

slags based on their chemical composition. The applicability of these models has been reviewed and it was concluded that the models developed by Urbain *et al.*⁸⁾ and Riboud *et al.*¹⁸⁾ were in closer agreement with the experimentally measured viscosities than the others. However, it was found that the Urbain model gives a slightly better fit than the Riboud model. In the present study, Urbain's model was used for the estimation of slag viscosities. Both of these models use the Frenkel equation, as given in Eq. (A-4), where A and B are viscosity parameters, T is the temperature K, and μ is in N m⁻² s,

$$\mu = A \cdot T \cdot \exp(B/T) \quad \text{.....(A-4)}$$

In this model the parameters A and B are calculated by dividing the slag constituents into three categories.

$$\text{glass former: } x_G = x_{\text{SiO}_2} + x_{\text{P}_2\text{O}_5} \quad \text{.....(A-5)}$$

$$\text{modifier: } x_M = x_{\text{CaO}} + x_{\text{MgO}} + x_{\text{FeO}} + 2x_{\text{TiO}_2} + x_{\text{K}_2\text{O}} + 3x_{\text{CaF}_2} + x_{\text{MnO}} + 2x_{\text{ZnO}} \quad \text{.....(A-6)}$$

$$\text{amphoterics: } x_A = x_{\text{Al}_2\text{O}_3} + x_{\text{Fe}_2\text{O}_3} + x_{\text{B}_2\text{O}_3} \quad \text{.....(A-7)}$$

The normalized values x_G^* , x_M^* , and x_A^* are obtained by dividing the mole fractions, x_G , x_M , and x_A by the term $(1 + 2x_{\text{CaF}_2} + 0.5x_{\text{FeO}_3} + x_{\text{TiO}_2} + x_{\text{ZnO}_2})$.

$$x_G^* = \frac{x_G}{1 + 2x_{\text{CaF}_2} + 0.5x_{\text{FeO}_3} + x_{\text{TiO}_2} + x_{\text{ZnO}_2}} \quad \text{.....(A-8)}$$

$$x_M^* = \frac{x_M}{1 + 2x_{\text{CaF}_2} + 0.5x_{\text{FeO}_3} + x_{\text{TiO}_2} + x_{\text{ZnO}_2}} \quad \text{.....(A-9)}$$

$$x_A^* = \frac{x_A}{1 + 2x_{\text{CaF}_2} + 0.5x_{\text{FeO}_3} + x_{\text{TiO}_2} + x_{\text{ZnO}_2}} \quad \text{.....(A-10)}$$

Urbain proposed that the parameter B was influenced both by the ratio α and by x_G^* . The parameter B can be expressed in the form of Eq. (A-12) where B_1 , B_2 , and B_3 can be obtained by Eq. (A-13).

$$\alpha = \frac{x_M^*}{x_M^* + x_A^*} \quad \text{.....(A-11)}$$

$$B = B_0 + B_1 x_G^* + B_2 (x_G^*)^2 + B_3 (x_G^*)^3 \quad \text{.....(A-12)}$$

$$B_i = a_i + b_i \alpha + c_i \alpha^2 \quad \text{.....(A-13)}$$

B_0 , B_1 , B_2 , and B_3 can be calculated from the equations listed in Table A3 and these parameters are then introduced into Eq. (A-12) to calculate B .

The parameter A can be calculated from B by Eq. (A-14) and the viscosity of the slag (in N m⁻² s) can then be determined by using Eq. (A-15).

$$-\ln A = 0.2693B + 11.6725 \quad \text{.....(A-14)}$$

$$\mu = 0.1[AT \exp(10^3 B/T)] \quad \text{.....(A-15)}$$

Fig. 12. The expected foam height of BOF slag during the first half of the blowing as a function of the decarburization rate.

Company. Because BOF slags usually contain 6 to 8% MgO at the end of the BOS operation, the MgO content in Table 2 was approximately defined by the solubility of MgO.¹⁷⁾ It was indicated that the MgO content of just a few percent intensifies the foaming action of acidic and neutral slags.¹⁸⁾ The predicted foam index decreases as the BOS operation proceed in the range of 0.8 to 1.5 which corresponds to the basicity change of BOF slags by the addition of burnt lime (CaO) during the blowing in BOS process. From the point of view of the only physical properties of the BOF slags studied, the slopping can be predicted at the initial stage where the slag composition lies in the low basicity, high FeO content, and low temperature.

Figure 12 shows the expected foam height of the slags during the first half of the blowing in the BOS process. The foam height was calculated for a 200-ton converter (Diameter=6.0m) as a function of decarburization rate under the assumption that the CO gas generated by the decarburization reaction dominated the superficial gas velocity in the vessel. During the first half of the blowing, the change of stage 1 to stage 2 led to larger decrease of foam height than that of stage 2 to stage 3. This figure indicates why slopping occurs during the first 50% of the blow.

5. Summary and Conclusions

Slag foaming was qualitatively investigated for BOF type slag during the first half of the blowing period in the process in order to improve our understanding on slopping. The foam index Σ decreases up to about 20% FeO content. This is believed to be due to the effect of viscosity which decreases as FeO content increases. At FeO contents higher than 20% FeO, foam index is almost constant. In a CaO-SiO₂-FeO-MgO_{sat} system, the foam index decreases with increasing basicity up to 1.4 at 1713 K; when (CaO+MgO)/(SiO₂+Al₂O₃) was greater than 1.4, foam index increased due to the precipitates like 2CaOSiO₂ or (Fe,Mg)O. As the content of TiO₂ increases, the experimentally measured foam index increases. It is expected that TiO₂ added combines with MgO from the crucible wall or the slag to form 2MgOTiO₂ ($T_m=2029$ K) precipitate. It is indicated that the logarithm of foam index decreases with

increasing temperature in the temperature range of 1673 to 1823 K for 35%CaO-35%SiO₂-30%FeO-10%MgO slag. This is primarily because the foam index is inversely proportional to viscosity the foam index decreases and the temperature coefficient for viscosity is negative. The foam index decreases with increasing MgO additions to 35CaO-35SiO₂-30FeO slag.

The correlation developed by Zhang and Fruehan predicts the foam index for the present BOF slags during the first half of the blowing reasonably well. The measured foam indexes are slightly larger than those calculated. This may be because the uncertainty in viscosity estimation for BOF slags is relatively larger than that for bath smelting slags and ladle slags based on Urbain's model. The foam height was estimated for a 200-ton converter (Diameter=6.0m) as a function of decarburization rate. The calculations indicate that slopping is more likely early in the blow if the decarburization rate is high.

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REFERENCES

- 1) Y. Zhang and R. J. Fruehan: *Metall. Trans. B*, 26B (1995), 813.
- 2) R. Jiang and R. J. Fruehan: *Metall. Trans. B*, 22B (1991), 481.
- 3) J. J. Bikerman: *Trans. Faraday Soc.*, 34 (1938), 634.
- 4) K. Ito and R. J. Fruehan: *Metall. Trans. B*, 20B (1989), 509.
- 5) S. Hara, M. Ikuta, M. Kitamura, and M. Ogino: *Tetsu-to-Hagané*, 69 (1983), 152.
- 6) M. Sano, K. Mori, and T. Sato: *Tetsu-to-Hagané*, 63 (1977), 2308.
- 7) C. F. Cooper and J. A. Kitchener: *J. Iron Steel Inst.*, 193 (1959), 48.
- 8) K. Urbain: *Steel Res.*, 58 (1987), 111.
- 9) Verein Deutscher Eisenhüttenleute (VDEh): *SLAG ATLAS*, 2nd Ed., Verlag Stahleisen GmbH, Düsseldorf, (1995), 126.
- 10) P. Kozakevitch: *J. Met.*, 21 (1969), 57.
- 11) J. Ren, M. Westholt, and K. Koch: *Steel Res.*, 65 (1994), 213.
- 12) Y. Kawai, K. Mori, H. Shiraishi, and N. Yamada: *Tetsu-to-Hagané*, 62 (1976), 53.
- 13) P. Kozakevitch: *Rev. Metall.*, 46 (1949), 572.
- 14) B. Ozturk and R. J. Fruehan: *Metall. Trans. B*, 26B (1995), 1086.
- 15) K. Ito and R. J. Fruehan: *Metall. Trans. B*, 20B (1989), 515.
- 16) R. E. Roth, R. Jiang, and R. J. Fruehan: *Trans. ISS*, 19 (1992), Nov, 55.
- 17) G. Trömel, K. Koch, W. Fix, and N. Großkurth: *Arch. Eisenhüttenwes.*, 40 (1969), 969.
- 18) P. V. Riboud, Y. Roux, L. D. Lucas and H. Gaye: *Fachber. Huttenprax. Metallweiterverarb.*, (1981), 859.
- 19) K. C. Mills and B. J. Keene: *Int. Mater. Rev.*, 32 (1-2) (1987), 105.
- 20) A. A. Appen, K. A. Shishkov, and S. S. Kayalova: *Zh. Fiz. Khim.*, 46 (1952), 909.
- 21) E. Boni and G. Derge: *J. Met.*, 8 (1956), 53.
- 22) S. I. Popel: *Metallurgicheskie shlaki i primeneniye ih v stroit el'stve*, (Metallurgical slags and their use in building), Akad. Stroit i Arkhitekt, SSSR, Ural'sk Filial, (1962), 97-127.

Appendix. Estimation of Physical Properties

In order to estimate the foam index using Eq. (7), it is necessary to estimate slag properties. Due to the experimental difficulties at high temperatures, accurate measurement of the physical properties of slags in many cases has not been made. Therefore, models were developed to estimate the values for the properties such as density, surface

Appendix E

Foamability of Stainless Steelmaking Slags in an EAF

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Key Words: stainless steelmaking slags, foam index, chrome oxide reduction

ABSTRACT

The possible causes for the poor foamability of stainless steelmaking slags were examined in this research. Specifically the foam index of a simulated stainless steelmaking slag containing " Cr_2O_3 " (CrO and Cr_2O_3) was measured and the rate at which carbon reacts with Cr_2O_3 , CrO , and FeO was also measured. The experimental results show that the foam index of stainless steelmaking slags is comparable to carbon steelmaking slags provided that the amount of solid chrome oxide particles or complexes is not excessive. However, the experimental results demonstrate that the reaction rate of carbon with CrO or Cr_2O_3 dissolved in the slag and hence the generation of CO is significantly slower than for the reaction rate of carbon with FeO dissolved in slags. Therefore, the lack of FeO in stainless steelmaking slags is a primary reason for the poor foamability. Also, exploratory research indicates that waste oxides containing carbon and iron oxide produces high rates of CO evolution and consequently could improve foaming.

INTRODUCTION

Slag foaming is beneficial in EAF steelmaking since the foam shields the refractories from the arc, lowers electrode consumption, stabilizes the arc, and insulates the melt from the atmosphere. Stainless steelmakers report that the foamability of their slags is poor compared to carbon steelmaking slags. The poor foamability is due to either a low gas generation rate from reactions taking place in the slag or the slag having a low foam index.

The foam index is a parameter that quantifies the ability of a slag to generate foam from either an injected gas or a gas that is generated within the slag or metal. The corresponding mathematical definition of the foam index (Σ) is given by equation (1).

$$\Sigma = \frac{H_f}{V_g^s} \quad (1)$$

In equation (1), H_f indicates the foam height, and V_g^s is the superficial gas velocity defined in equation (2).

$$V_g^s = \frac{Q}{A} \quad (2)$$

In the preceding expression, Q is the gas flow rate, and A represents the crucible or vessel cross sectional area.

The first objective of this research was to measure the foam index of a stainless steelmaking slag and, more specifically, to measure the effect of chrome oxide on the foam index since this oxide is a major difference between stainless and carbon steelmaking slags. Additionally, chrome oxide has a low solubility in slag systems with a high basicity as shown in Figure 1¹. When the solubility limit for chrome oxide is exceeded, second phase precipitates form that increase the bulk viscosity of the slag. The bulk viscosity is the viscosity of a mixture of liquid and solid particles. Ito and Fruehan showed that these second phase particles increase the foam index of the CaO-FeO-SiO₂ slag system². To account for the second phase precipitates effect on the bulk viscosity, Ito and Fruehan used equation (3)².

$$\mu = \mu_o(1 + 5.5\xi) \quad (3)$$

In the equation above, μ is the bulk viscosity, μ_o is the viscosity of the pure liquid, and ξ is the volume fraction of solid particles. Equation (3) is valid for all slags with small amounts of second phase precipitates present.

Figure 1: Chromium oxide contents of melts saturated with a spinel phase as a function of melt basicity for melts of the system CaO-MgO-CrO_x-SiO₂. (Wt% Cr₂O₃)*=Total chromium oxide in liquid calculated as Cr₂O₃. From Pretorius thesis

Later, Zhang and Fruehan³ correlated the foam index to the slag's physical properties, as shown in equation (4). This expression demonstrates the importance of the viscosity to the foam index.

$$\Sigma = 115 \frac{\mu^{1.2}}{\gamma^2 \rho D^9} \quad (4)$$

In equation (4), D is the bubble diameter, μ represents the slag's bulk viscosity, and γ equals the slag's surface tension. However, the second phase solid particles become detrimental to the foamability when their size is large compared to the bubble diameter; as a result, equation (4) becomes void. Therefore, if the chrome oxide content greatly exceeds the solubility limit of the slag; then, a considerable amount of oversized solid chrome oxide particles or complexes would form and lower the foam index, thus possibly explaining the poor foamability of stainless steelmaking slags.

The objective to measure the effect of chrome oxide on the foam index was complicated by the fact that chrome oxide exists predominately as Cr_2O_3 in slags that are in equilibrium with air but as CrO , i.e. Cr^{+2} , in reducing conditions such as slags in equilibrium with iron melts. The precise distribution of chrome oxide between CrO and Cr_2O_3 depends on the slag basicity and oxygen potential. In this research, the oxygen potential was set by the slag-metal equilibrium; i.e. Cr in the metal and CrO in the slag. Later in the paper, the equilibrium oxygen potential is shown to be very low which favors CrO . This is important to the foam index measurement because CrO has a higher solubility than Cr_2O_3 in slags.

Instead of having a poor foam index, possibly the lack of sufficient gas generation from different slag oxide/carbon reactions could explain the cause for stainless steelmaking slag's poor foaming. For instance, the FeO and " Cr_2O_3 " content is very different between stainless and carbon steelmaking slags; the stainless steelmaking slags are very low in FeO but high in " Cr_2O_3 ". Therefore, if the rate of reaction (5) is significantly greater than the rate of reaction (6) or (7); then, the generation rate of CO could limit the foaming of stainless steelmaking slags.

The rates of CO generation were determined by measuring the rate of pressure increase inside a sealed reaction chamber, which is known as the CVPI technique (Constant Volume Pressure Increase). Since Waste Oxide Briquettes (WOBs) contain a considerable amount of C , FeO , and Fe_2O_3 , their impact on gas generation and slag foaming was also examined with the CVPI technique.

EXPERIMENTAL

Foam Index Experiment-Figure 2 shows a cutaway view of the experimental apparatus used to measure the effect of " Cr_2O_3 " on the foam index of a $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ slag system. Prior to heatup, 150g of a master slag was prepared by weighing each component to an accuracy of 0.1g. Table I details the master slag composition. Next, 29g of metal composed of 80% Fe -20% Cr was placed into an MgO crucible. Then, the master slag was packed into the same MgO crucible and heated to 1550°C in a sealed argon environment. A Mo wire, sleeved in an alumina lance, was lowered into the molten slag. Next, the argon was shutoff, and another alumina lance, used to inject the argon, was lowered to the bottom of the MgO crucible and raised 2 cm which was more than four times the height of the Fe-Cr metal that had been placed into the MgO crucible. This step

prevented the Fe-Cr metal from being ejected into the molten slag by the argon, creating an emulsified mixture. Then, the argon flow was resumed and injected into the molten slag. After the foam stabilized, a Pt wire, sleeved in an alumina lance, was slowly lowered until it just touched the slag surface and completed an electric circuit. The slag foam height was measured at four different argon flow rates. After measuring the foam height at the fourth argon flow rate, Cr_2O_3 pellets were added with a mullite drop tube. The Cr and Cr_2O_3 pellets were allowed to equilibrate for twenty minutes, which included five minutes of stirring with argon. Finally, the foam heights were measured with the same method described above. The procedure of adding a known amount of Cr_2O_3 to the slag and measuring the corresponding foam height was repeated until the supply of Cr_2O_3 pellets was exhausted which occurred at a Cr_2O_3 content of 15.6%. At this point the test was terminated. The foam index measurement experiment was repeated two more times. Both experiments were terminated after the slag foaming ceased which occurred when the Cr_2O_3 content exceeded 20%.

Table I: Master Slag Composition for the Foam Index Experiments

Component	Weight %
MgO	12
CaO	41
SiO_2	41
Al_2O_3	6

Figure 2: Foam Index Experimental Setup

CVPI Experiment -The Constant Volume Pressure Increase (CVPI) technique was used to measure the rate at which CO was generated from reactions (5) through (7) as well as the gas generated from WOBs. Prior to these individual experiments, 1kg of a master slag was prepared by weighing each component to an accuracy of 0.1g. Table II lists the slag composition, and Figure 3 shows a cutaway view of the experimental apparatus. The experimental setup is similar to that used by Sarma et al⁴.

The first CVPI experiment was conducted to measure the rate of FeO reduction. 180g of the master slag was packed into an MgO crucible and heated to 1550°C in a sealed argon environment. After heatup, 12 g of FeO was added to the slag, and the slag was stirred. Next, an alumina lance and graphite disc assembly was lowered until it was just above the molten slag, and the argon used for purging was shutoff. At this point, the experimental apparatus was calibrated by injecting 120ml of argon into the furnace tube with a syringe. The subsequent pressure increase in the furnace tube was measured with a pressure transducer. The data collected by the pressure transducer generated a calibration curve that converted the change in pressure to the moles of gas. Finally, the argon injected during calibration was vented, and the experiment commenced when the graphite disc, which had a surface area of 6.1 cm², was lowered and submerged completely into the slag. This phase of the experiment was completed when the measured pressure approached the maximum calibration pressure by raising the graphite disc from the slag. An additional 5.8g of FeO was added to the slag, the slag was stirred, and the graphite was lowered into the slag once again. The FeO CVPI experiment was terminated when the maximum calibration pressure was reached.

Table II: Master Slag Composition for the CVPI Experiments

Component	Weight %
MgO	12
CaO	42.5
SiO ₂	42.5
Al ₂ O ₃	3

A second CVPI experiment measured the rate of Cr₂O₃ reduction. The experimental procedure was identical to the previous experiment except that Cr₂O₃ was added to the slag instead of FeO, 5.5g of Cr₂O₃ were added initially and 5.7g were added later.

A third CVPI experiment measured the rate of reduction of “Cr₂O₃”. An Fe/Cr melt was placed into the MgO crucible prior to loading the master slag so the Cr and Cr₂O₃ pellets could equilibrate to the stable Cr₂O₃/CrO mixture. This experiment also had two phases: 5.4g of Cr₂O₃ pellets were loaded initially, and 5.7g of Cr₂O₃ pellets were loaded later.

Finally, a CVPI experiment measured the gas generated by three WOBs individually: WOB #1, 17.7g, WOB #2, 3.4g, and WOB #3, 7.0g. Since the WOBs contained carbon, iron oxides, and chrome oxides that were in physical contact, they could not be present in the furnace during heatup. Instead, the furnace was heated up with a dummy lance/WOB assembly; the dummy WOB was a chunk of master slag with nearly the same volume as the actual WOB. After calibration, the dummy lance/ WOB assembly was replaced with a real lance/WOB assembly that was immersed immediately into the liquid slag, and the test commenced. The furnace tube was vented when the maximum calibration pressure was reached. The sequence of pressurizing and venting the furnace tube was continued until the WOB reactions slowed down; at this point the test was concluded. Table III shows the WOB composition.

RESULTS AND DISCUSSION

Foam Index-The foam height versus superficial gas velocity is plotted in Figure 4 for two typical measurements; the foam index equals the slope of the line that best fits the data collected. The measured foam

indexes versus “Cr₂O₃” concentrations are plotted in Figure 5. These numbers are comparable to the foam indexes measured by Jung and Fruehan⁵ and Ito and Fruehan² for other slag systems.

Table III: WOB Composition

Component	Weight %
Al ₂ O ₃	1.28
Cr ₂ O ₃	9.15
NiO	1.84
SiO ₂	6.13
MnO	2.35
MgO	2.82
CaO	8.91
FeO	23.28
Fe ₂ O ₃	12.80
C	14.15
Cr	2.59
Fe	10.93
Other	3.77

Figure 3: CVPI Experimental Setup

Since the Cr and Cr₂O₃ pellets were allowed to equilibrate for at least twenty minutes, including five minutes of Argon stirring, equilibrium is assumed to have been achieved between the Cr and (“Cr₂O₃”). Since equilibrium existed, the slag Po₂ can be calculated from thermodynamic relations. The Fe/Cr metal can be approximated as an ideal solution, so a_{cr} is equivalent to 0.2 in Equation (9). Furthermore, assume the chromium oxide was composed entirely of CrO, and the slag was saturated with CrO. Using the ΔG°_R of reaction (8)⁶, the

preceding approximation and two assumptions, the P_{O_2} turns out to be on the order of 10^{-13} atmospheres, and this oxygen potential approximates the oxygen potential in an EAF where the chrome oxide consists mostly of CrO. The P_{O_2} would be lower if the slag was not saturated with CrO.

$$\Delta G^\circ_R = -334,218 + 63.81T$$

$$K_{eq} = \frac{(a_{CrO})}{(a_{Cr})(P_{O_2})^{0.5}} \quad (9)$$

Figure 4: Foam height of slag versus superficial gas velocity for two “Cr₂O₃” concentrations.

Figure 6 illustrates the proposed ideal relationship between the foam index and second phase precipitates as described in the introduction. The slag has a baseline foam index when it is liquid. The foam index should increase when “Cr₂O₃” precipitates form since the slag’s bulk viscosity increases. The foam index eventually reaches a maximum value and then decreases with additional “Cr₂O₃” because the size of the solid chrome oxide precipitates becomes excessive and detrimental to the slag’s foamability. There is modest agreement between the ideal relationship in Figure 6 and the measured relationship in Figure 5. The scatter of the data in Figure 5 could be due to the high rate of deterioration of the alumina lance that injected the argon. The high deterioration rate would result in the argon being injected into the slag at different depths from experiment to experiment. Regardless, there was no evidence in this research that chromium oxide is responsible for the poor foamability of stainless steelmaking slags provided, of course, that the slag composition does not excessively exceed the “Cr₂O₃” content of the slag’s liquidus composition. In other words, the data shows that the “Cr₂O₃” content should be kept lower than 16% for the slag composition, temperature, and oxygen potential used in this research. In industry, the “Cr₂O₃” content is lowered by adding ferrosilicon to the slag.

Figure 5: Measured relationship between the foam index and the “Cr₂O₃” content. The line represents one possible best-fit curve.

Figure 6: Ideal Relationship between the foam index and second phase particles

Rate Of FeO And “Cr₂O₃” Reduction -The results of the CVPI experiments, shown in Figures 7 and 8, clearly demonstrate that the CO production rate is faster for FeO reduction than for chrome oxide reduction, note the scales are different in these two figures. Figure 8 shows three trials in which CO is generated: 180g of master slag with 3% “Cr₂O₃” present, 180g of master slag with 3% Cr₂O₃ present, and 180g of master slag only. Since the rate of CO generated from the slag with no Cr₂O₃ present is for all intents and purposes identical to the remaining two trials, then it seems probable that the CO is generated from other sources of oxygen contained in the master slag. The sources of oxygen could be FeO or even the reduction of SiO₂ by carbon. In any event the amount of CO generated is small. Therefore, the reaction rates of equation (6) and (7) must be very slow. The same phenomenon was measured when the slag contained 6% “Cr₂O₃” and 6% Cr₂O₃.

The observation that iron oxide reduction is faster than chrome oxide reduction agrees with the result obtained when the FeO and “Cr₂O₃” reduction rates are calculated using a model developed by Sarma et al⁴ and then comparing the two calculated rates to each other. Only CrO reduction will be considered in the following discussion since the majority of the “Cr₂O₃” is CrO and the Cr₂O₃ reduction sequence is complex. Sarma et al⁴ identified the following steps as potentially rate limiting during iron oxide reduction:

.. Diffusion of FeO from the bulk of the slag to the slag- gas interface.

2. Reduction of FeO at the slag- gas interface. The reduction reaction is given by equation (10). The reaction rate of equation (10) was developed by Belton et al^{7,8,9} and is shown in equation (11).

$$\text{Rate} = k_{\text{SG}}(p_{\text{a}_0}^{\text{SG}} - p_{\text{CO}_2}^{\text{SG}})$$

where, k_{SG} =rate constant for the dissociation of CO_2
 a_0 =ratio of p_{CO_2} to p_{CO}

3. Diffusion of CO_2 from the slag- gas interface to the gas- carbon interface. The rate is given by equation (12).

$$J_{\text{CO}_2} = \frac{m_g}{RT}(p_{\text{CO}_2}^{\text{SG}} - p_{\text{CO}_2}^{\text{GC}})$$

where, J_{CO_2} =flux of CO_2
 m_g =average mass transfer coefficient of CO_2 between the two interfaces

4. Oxidation of the graphite. The oxidation reaction is shown in equation (13). The corresponding reaction rate is given by equation (14).

$$\text{Rate} = k_{\text{GC}}(p_{\text{CO}_2}^{\text{GC}} - p_{\text{CO}_2}^{\text{e}}) \quad (14)$$

where, k_{GC} =rate constant for reaction (13)
 $p_{\text{CO}_2}^{\text{e}}$ =equilibrium CO_2 pressure for reaction (13)

The steps potentially limiting CrO reduction are similar. However reaction (10) must be modified to show CrO reduction occurring at the slag- gas interface, this is done in reaction (15).

Assuming the CrO and FeO transport rates through the slag are high and reactions (11) and (15) occur quickly, i.e. reactions (11) and (15) remain in equilibrium, then the rate limiting steps are steps 3) and 4) for both FeO and CrO reduction. Therefore, the overall reduction rate can be expressed in terms of the two limiting steps and is given by equation (16).

Figure 7: Rate of CO generated from the reduction of FeO by graphite.

Figure 8: Comparison of CO Generation Rates

$$\text{Rate} = \frac{1}{\frac{1}{k_{GC}} + \frac{RT}{m_g}} (p_{\text{CO}_2}^{\text{SG}} - p_{\text{CO}_2}^{\text{GC}})$$

where, $p_{\text{CO}_2}^{\text{SG}}$ =equilibrium CO_2 pressure at the slag-gas interface

$p_{\text{CO}_2}^{\text{GC}}$ =equilibrium CO_2 pressure at the gas-carbon interface

k_{GC} =gas-carbon rate constant in equation (14)

R =universal gas constant

T =temperature

m_g =average gas phase mass transfer coefficient in equation (12)

Next, the FeO and CrO reduction rates are compared in equation (17); k_{GC} , R , T , and m_g from equation (16) are eliminated since these values are equivalent for both CrO and FeO reduction.

$$\frac{\text{FeO Reduction Rate}}{\text{CrO Reduction Rate}} = \frac{(p_{\text{CO}_2\text{FeO}}^{\text{SG}} - p_{\text{CO}_2}^{\text{GC}})}{(p_{\text{CO}_2\text{CrO}}^{\text{SG}} - p_{\text{CO}_2}^{\text{GC}})} \quad (17)$$

The $p_{\text{CO}_2\text{FeO}}^{\text{SG}}$ is calculated from the equilibrium constant, equation (18), and the ΔG^*_R , equation (19), of reaction (10).

$$K_{eq} = \frac{(a_{\text{Fe}})(p_{\text{CO}_2\text{FeO}}^{\text{SG}})}{(\gamma_{\text{FeO}})(X_{\text{FeO}})(p_{\text{CO}})}$$

where, a_{Fe} =activity of Fe, equals 1

X_{FeO} =FeO mole fraction, equals .05 for 6% FeO content

γ_{FeO} =FeO activity coefficient, approximately equals 2 for 6% FeO content

p_{CO} =CO pressure, approximately equals 1 atmosphere

$$\Delta G^*_R = -55400 + 44T$$

The resulting $p_{\text{CO}_2\text{FeO}}^{\text{SG}}$ equals 1.9×10^{-2} atmospheres.

Similarly, the $p_{\text{CO}_2\text{CrO}}^{\text{SG}}$ is calculated from the ΔG^*_R , equation (21), and the equilibrium constant, equation (20), of reaction (15).

$$K_{eq} = \frac{(a_{cr})(p_{CO_2CrO}^{SG})}{(g_{CrO})(X_{CrO})(p_{CO})}$$

where, a_{cr} =activity of chromium, equals .2

γ_{CrO} =CrO activity coefficient, approximately equals 2.64 for 6% "Cr₂O₃" content¹⁰

X_{CrO} =CrO mole fraction, equals .036 for 6% "Cr₂O₃" content

p_{CO} =CO pressure, approximately equal to 1 atmosphere

$$\Delta G_R^* = 51800 + 23T \quad (21)$$

The resulting $p_{CO_2CrO}^{SG}$ equals 1×10^{-3} atmospheres.

The $p_{CO_2}^{GC}$ of reaction (13) in a carbon saturated system is essentially zero atmospheres. Therefore, the ratio given by equation (17) equals nineteen after inputting the calculated $p_{CO_2FeO}^{SG}$, $p_{CO_2CrO}^{SG}$, and $p_{CO_2}^{GC}$ values; thus Sarma's model predicts that FeO reduction would be much faster than CrO reduction.

The reduction rate of FeO and CrO can also be examined using the results of Story et al¹¹ who investigated the oxidation rate of carbon by CO₂, equation (13), in detail. At high temperatures, like 1550°C, the oxidation rate of carbon is controlled by the diffusion of CO₂ through the porous graphite and the oxidation reaction itself near the surface. These two steps acting in series are known as limited mixed control. For limited mixed control the k_{GC} term in equation (14) is expressed as:

$$k_{GC} = \frac{k_{lm}}{RT}$$

where, k_{lm} =rate constant for limited mixed control

A value of 60 cm/sec for k_{lm} can be extrapolated from the work of Story et al¹¹. As a result, k_{GC} equals 4×10^{-4} moles/cm²-atm-sec in this example. Finally, the calculated reduction rate, equation (14), equals 7.6×10^{-6} moles/cm²-sec with 6% FeO content. For comparison, the measured reaction rate in Figure 7 is 6×10^{-6} mol/cm² sec. The calculated rate and measured rate are in very good agreement. The minor difference between the two rates must be due, at least partly, to steps 1), 2), and 3) listed by Sarma et al⁴.

After substituting the same k_{GC} value, 4×10^{-4} moles/cm²-atm-sec, and the $p_{CO_2CrO}^{SG}$ calculated previously, 1×10^{-3} atmospheres, into equation (14), the calculated CrO reduction rate equals 4×10^{-7} moles/cm²-sec. This value is essentially zero and is therefore in good agreement with the measured reduction rate. This implies that the oxidation of carbon by CO₂ could be controlling the overall rate of equation (7). However, there is no information on the CrO reduction rate at the slag-gas interface, step 2 in Sarma et al's⁴ model. Therefore, this step may also control the overall rate of equation (7).

Estimation of Foam Height from CO Generation -Even more important than the CO generation rate itself, was the impact of the CO generation rate on the foam height. An approximate measurement of the maximum

foam height achieved during each CVPI experiment was recorded on the lance/graphite assembly. Specifically, both the slag and foam discolored the lance; this length of lance is denoted as H_f in Figure 3. The maximum foam height achieved during the FeO experiment was nearly four times greater than the height achieved during either chrome oxide experiment.

Gas Generation and Foaming Due to WOB Additions -Since this research provides evidence that a lack of gas generation is a cause for the poor foamability of stainless steelmaking slags; then, the addition of WOBs could provide the necessary carbon and iron oxides to generate an adequate amount of CO for foaming. The rate of gas generated by the WOBs was faster than for either FeO or chrome oxide reduction. Figure 9 shows the gas generation rate for WOB #2, the results for WOB #1 and #3 were similar. The substantial increase in the gas generation rate was due to the WOBs containing Fe_2O_3 which was shown to have a faster reduction rate to FeO than FeO to Fe by Fruehan¹², the WOBs containing coke which was proven to reduce iron oxides at a faster rate than graphite in the same paper by Fruehan¹², and diffusion not limiting the reduction rates since the iron oxides and carbon were in direct contact probably throughout the experiment.

Figure 9: Rate of CO generated by WOB #2.

Sarma's work predicts that the FeO reduction rate should be faster when the FeO is a separate phase like in a WOB compared to when the FeO is in solution. Since the a_{FeO} in equation (18) for a WOB is unity, the resulting $p_{CO_2FeO}^{SG}$ equals 0.2 atmospheres. The larger $p_{CO_2FeO}^{SG}$ creates a greater driving force in rate equation (16) and therefore, the FeO reduction rate should be faster in a WOB than when the FeO is in solution.

The foam height measurements, H_f , generated from the reduction of the WOBs were greater than the foam height generated from either the reduction of Cr_2O_3 or " Cr_2O_3 " but less than the foam height generated from the reduction of FeO. This is probably because the WOBs generated their gas at or near the slag surface and therefore could not cause as much foaming. However, based on the gas generation rate shown in Figure 9, WOB additions would be expected to generate good foaming.

CONCLUSIONS

The findings of this research are:

- 1) There is no evidence that chrome oxide reduces the foam index until the " Cr_2O_3 " content excessively exceeds the solubility limit of the slag. The critical " Cr_2O_3 " content depends on the temperature, slag basicity, and oxygen potential.
- 2) The rate of FeO reduction with carbon is much faster than chrome oxide reduction and corresponds with a higher rate of CO generation, which consequently generates more foam.
- 3) Slag foaming in stainless steel production can be induced with WOB additions that contain both iron oxides and carbon.

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REFERENCES

- 1 E.B. Pretorius: PhD thesis, "Activity-Composition Relations of Chromium Oxide in Silicate Melts," The Pennsylvania State University, 1989.
- 2 K. Ito and R. J. Fruehan, "Study on the Foaming of $\text{CaO-SiO}_2\text{-FeO}$ Slags: Part I. Foaming Parameters and Experimental Results," Metallurgical Transactions B, Vol. 20B, August 1989, pp. 509-514.
- 3 Y. Zhang and R. J. Fruehan, "Effect of the Bubble Size and Chemical Reactions on Slag Foaming," Metallurgical Transactions B, Vol. 26B, August 1995, pp. 803-812.
- 4 B. Sarma: PhD thesis, "Reduction of FeO from Smelting Slags by Solid Carbon," Carnegie Mellon University, Pittsburgh, PA, 1992.
- 5 S. Jung and R. J. Fruehan, unpublished research, Carnegie Mellon University, Pittsburgh, PA May, 1999.
- 6 N. Y. Toker, L. S. Darken, and A. Muan, "Equilibrium Phase Relations and Thermodynamics for the Cr-O System in the Temperature Range from 1500°C to 1825°C ," Metallurgical Transactions B, Vol. 22B, April 1991, pp. 225-232.
- 7 Y. Sasaki, S. Hara, D. R. Gaskell, and G. R. Belton, "Isotope Exchange Studies of the Rate of Dissociation of CO_2 on Liquid Iron Oxides and CaO-Saturated Calcium Ferrites," Metallurgical Transactions B, Vol. 15B, September 1984, pp. 563-571.
- 8 S. K. El-Rahaiby, Y. Sasaki, D. R. Gaskell, and G. R. Belton, "Interfacial Rates of Reaction of CO_2 with Liquid Iron Silicates, Silica-Saturated Manganese Silicates, and Some Calcium Iron Silicates," Metallurgical Transactions B, Vol. 17B, June 1986, pp. 307-316.
- 9 S. Sun: PhD thesis, University of Newcastle, Australia.
- 10 E. B. Pretorius and A. Muan, "Activity-Composition Relations of Chromium Oxide in Silicate Melts at 1500°C under Strongly Reducing Conditions," J. Am. Ceram. Soc., Vol. 75, No. 6, June 1992, pp. 1364-1377.

11. S. R. Story and R. J. Fruehan, "Kinetics of Oxidation of Carbonaceous Materials by CO_2 and H_2O between 1300°C and 1500°C ," Metallurgical Transactions B, Vol. 31B, February 2000, pp. 43-54.
12. R. J. Fruehan, "The Rate of Reduction of Iron Oxides by Carbon," Metallurgical Transactions B, Vol. 8B, June 1977, pp. 279-286.