Kinetics of Silicothermic Reduction of Manganese Oxide for Advanced High Strength Steel Processing

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1 Abstract

The kinetics of silicothermic reduction of manganese oxide from MnO-SiO$_2$-CaO-Al$_2$O$_3$ slags reacting with Fe-Si droplets were studied in the temperature range of 1823-1923K (1550-1650°C). The effects of initial droplet mass, initial droplet silicon content, and initial slag manganese oxide content were studied. Data obtained for 15% silicon showed agreement with control by mass transport of MnO in the slag with a mass transfer coefficient ($k_s$) of 4.0x10$^{-5}$ m/s at 1873K (1600°C). However, when this rate determining step was tested at different initial silicon contents the agreement was lost, suggesting mixed control between silicon transport in the metal and manganese oxide transport in the slag. Increasing temperature resulted in a decrease in the rate of reaction because of an increase in the favorability of SiO as a product. Significant gas generation was found during all experiments, as a result of silicon monoxide production. The ratio of silicon monoxide to silica formation was increased by factors favoring silicon transport over that of manganese, further supporting the conclusion that the reaction is under mixed control by transport of both silicon and manganese oxide.

2 Introduction

Manganese has become an important alloying element in advanced high strength steels (AHSS) with over 20wt% being proposed for certain grades of twinning induced plasticity (TWIP) steel, and values between 4-11% being of interest in third generation AHSS [1]. Reduction of manganese oxide dissolved in the slag has been proposed as a possible method of adding manganese to 2$^{\text{nd}}$ and 3$^{\text{rd}}$ generation steels in order to improve the economics of alloy addition [2] [3]. The present work seeks to advance the fundamental understanding of the kinetics and mechanism of silicothermic reduction of manganese oxide from slags.

The thermic reduction process promotes solute elements with high oxygen affinities to reduce slag components into the metal. There are two thermodynamically attainable pathways for metallic silicon to reduce manganese oxide. The reduction of manganese in the slag requires the supply of electrons from silicon, either by the formation of tetravalent silicon or, if the supply of Mn$^{2+}$ is inadequate, divalent silicon; the former results in silicon being incorporated into the slag as silicate while the latter requires the net transfer of one O$^{2-}$ ion from the slag to form SiO gas with the divalent silicon. Whilst the authors do not make any claims to the detailed mechanism, conceptually and stoichiometrically these reactions can be written as Equations 1 and 2. Bracket notation of [metal], (slag), and {gas} is used in this work. The free energies for these reactions were taken from FactSage Reaction Module and the FTDemo database [4], which take the following data from the NIST JANAF Tables [5]. At 1873K (1600°C) Equation 1 yields -103kJ/mol while Equation 2 yields -14.7kJ/mol; under standard conditions it is clear that while SiO$_2$ may be more favorable SiO can still form.

\[
\begin{align*}
[\text{Si}] + 2(\text{MnO}) & \rightleftharpoons 2[\text{Mn}] + (\text{SiO}_2) \quad \Delta G^\circ = -235733 + 70.639T \text{[J/mol]} \\
[\text{Si}] + (\text{MnO}) & \rightleftharpoons [\text{Mn}] + \{\text{SiO}\} \quad \Delta G^\circ = 186596 - 107.468T \text{[J/mol]}
\end{align*}
\]
Some of the earliest quantitative work regarding the reduction of MnO using Si in non-graphite crucibles comes from Daines and Pehlke [6]. Their work showed that manganese mass transport in the metal was the rate-limiting step, where the mass transfer coefficient ($k_m$) was equal to $7 \times 10^{-6} \text{m/s}$. The system showed significant rate enhancement with stirring, confirming mass transport control. The system underwent a two-stage reaction, the first stage faster than the second.

Shibata et al. [7] performed a series of experiments involving multiple simultaneous reactions. MnO was reduced by silicon and carbon simultaneously; the authors concluded that MnO reduction was more likely to be controlled by mass transport in the metal than the slag. They further noted that desiliconization appeared to finish within the first 300 seconds of reaction.

The work of Heo et al. [8] shows interesting correlations with CaF$_2$ addition to the slag; a ferromanganese slag reduced with metallic silicon was shown to produce a stoichiometrically balanced amount of SiO$_2$ and Mn in the presence of CaF$_2$, whereas in its absence a greater than stoichiometric quantity of silicon was consumed. These authors proposed SiO generation as the alternate manganese reduction pathway. Such a result would appear to indicate that mass transport in the slag may play a role in rate control of the system. The authors concluded that silica mass transport in the slag was controlling. However, they acknowledged the work of Sohn et al. [9] who suggested for high viscosity slags mass transport of MnO transport would be the rate controlling step.

Similar work can be found in the ferromanganese production literature; however, most of this work is directed towards understanding carbothermic reduction of manganese oxide. Early authors like Tarby and Philbrook [10] were the first to show a two-stage reaction of MnO with C, the first stage exhibiting significant gas generation and the second producing nearly no gas. The initial fast stage of reaction was proposed to be controlled by manganese transport in the slag. Daines and Pehlke [11] claimed that the reaction was under chemical reaction control at the slag-metal interface.

Pomfret and Grieveson [12] claimed that the observations of Daines and Pehlke were for the slower second stage of the reaction. Pomfret and Grieveson plotted the manganese partition over time, defined in their case as the activity of MnO in the slag ($a_{\text{MnO}}$) divided by the activity of Mn ($a_{\text{Mn}}$) in the metal, and showed that a critical ratio of $a_{\text{MnO}}/a_{\text{Mn}}$ characterized the transition from faster to slower rates. Ashizuka et al. [13] were able to demonstrate similar results to Daines and Pehlke. Xu et al. [14] used X-ray fluoroscopy techniques to observe nucleation sites for carbon monoxide along the slag-metal interface. Here it was concluded that the rate of generation of CO along the interface was the rate controlling step.

A more recent publication by Kononov et al. [15] demonstrates the importance of gaseous species in affecting the rate of manganese reduction. Different temperatures and different ratios of C/MnO were used in hydrogen, helium, and argon environments. The results indicate increasing reaction rates with increasing temperature. Further, the densest gas (argon) had the lowest CO diffusivity which was reflected in MnO reduction rates. Helium did not reduce MnO but has a higher CO diffusivity than argon, resulting in a faster rate. Hydrogen participated in the reduction and had a high CO diffusivity and so had the fastest rate of all.

Sun et al. [16] reacted slag with a carbon substrate where it generated a reduced metal product. Energy dispersive spectroscopy (EDS) revealed a manganese concentration gradient in the slag near the slag-metal boundary; such a gradient may imply that MnO transport contributes to reduction control. The rate of reduction was said to increase with increasing MnO content in the slag. Their final conclusion was that chemical or mixed-mode control may exist in the system.

From an analysis of the above literature, it would appear that there are two control steps in the carbothermic reduction of manganese oxide. The initial, fast step is controlled by MnO transport through the slag and the slower step appears to be controlled by CO production at the interface. These
conclusions, and specifically the effect of gas formation at the interface may also be relevant to silicothermic reduction should Equation 2 play a significant role.

Many reacting systems have been found to exhibit dynamic interfacial phenomena influenced by the transfer of elements across the interface [17–21] where spontaneous increases in surface area can be observed; surface area recovers as the reaction slows and nears equilibrium. Many explanations for these observations have been provided, though none have fully explained the phenomena. Most explanations incorporate an apparent decrease in surface tension [18,21] caused by one or more capillary effects: solutocapillarity based on surface active elements, electrocapillarity from charge differences, and thermocapillarity from localized temperature gradients. Surface tension decreases can manifest as dimpling, flattening, and in the most extreme case emulsification.

Previous authors have documented reaction rates associated with a wide range of reaction couples [22–24], of particular interest is the work of Rhamdhani and the aluminothermic reduction of silica. This reaction (Al/SiO₂) has a similar Gibbs energy of reaction to the current system per mole of metal solute but can only generate liquid products. Rhamdhani’s work was shown to generate a metal-slag emulsion that improved the reaction kinetics through interfacial area increase.

Possibly even more relevant to the current work, is the recent work of White and Sichen [25] where the rates of mass transfer in a stirred system of Si and CaO-SiO₂ were investigated. During the course of the reaction rapid transfer of calcium across the interface dropped the interfacial tension to a level low enough that mechanical agitation caused emulsification. Such observations imply that systems which do not normally express spontaneous emulsification may be induced to do so with stirring.

Recently, Assis et al. [26] and Spooner et al. [27] showed examples of emulsification during reactions in confocal microscopes; it should be noted that Spooner identified some issues related to the heating regimen applied during the second set of experiments. While this changed the replicability of the work of Assis, it still lead to emulsification. These authors concluded that the effect on surface tension of interfacial oxygen transfer rather than that of phosphorous is likely to be the dominant cause of emulsification. Given that reductive alloying will result in a large transfer of oxygen across the interface it is reasonable to expect that emulsification or similar surface phenomena will occur.

There is considerable disagreement in the literature regarding silicothermic reduction of manganese oxide from slag; there have been a number of different conclusions about the rate control and reaction mechanism. As it stands, no model exists to piece together the various findings. The current work is part of an ongoing study to further the collective understanding of silicothermic reduction kinetics of MnO from slag and to rationalize the apparently disparate findings in the published literature. This will be addressed firstly by collecting experimental data in the untested mid-range of silicon and manganese oxide concentrations, and secondly by analyzing not only this experimental data but that of other authors. By doing so the mechanism can be detailed and a model developed to describe changes in the rate controlling steps with changing reaction conditions. The current publication presents the first step towards this goal. Experimental data is presented and analysed for the mid-range concentrations and a tentative mechanism proposed. A subsequent publication, currently in preparation, will offer a more detailed analysis of this data on the basis of mixed control involving mass transport of silicon in the metal and manganese in the slag.

3 Experimental Procedure

3.1 Materials Usage

All ceramic components used were 99.8% alumina refractory material. Table 1 below shows the composition of all raw materials used in the experiments.
Table 1: Chemical Composition of Six Melt Species

<table>
<thead>
<tr>
<th>Component</th>
<th>Primary wt.%</th>
<th>Carbon wt.%</th>
<th>Sulfur wt.%</th>
<th>Phosphorus wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>99.9999</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Electrolytic Iron</td>
<td>99.9</td>
<td>&lt;0.0067</td>
<td>&lt;0.00143</td>
<td>--</td>
</tr>
<tr>
<td>Silica Sand</td>
<td>99.8</td>
<td>0.00605</td>
<td>0.00560</td>
<td>0.0023</td>
</tr>
<tr>
<td>Alumina Powder</td>
<td>99.5</td>
<td>0.00322</td>
<td>0.00025</td>
<td>--</td>
</tr>
<tr>
<td>Calcium Oxide Powder</td>
<td>&gt;96</td>
<td>0.1862</td>
<td>0.00671</td>
<td>0.0063</td>
</tr>
<tr>
<td>Manganese Oxide Powder</td>
<td>99</td>
<td>0.00371</td>
<td>0.00153</td>
<td>--</td>
</tr>
</tbody>
</table>

3.2 Sample Preparation

Slag samples were first prepared by pressing a 2:2:1 weight ratio of SiO$_2$:CaO:Al$_2$O$_3$ into pellets, and melting them in a platinum crucible using a resistance heated muffle furnace at 1873K (1600°C). Melts were quenched by pouring onto a steel I-beam. The shattered pieces of quenched slag were crushed and remixed; the melting/quenching/crushing procedure was repeated twice. MnO homogeneity with the pre-mixed slag was ensured in three ways: vigorous shaking of the powdered slag and MnO mixture prior to adding to the crucible, X-ray observation of the molten slag once in the furnace, and allowing for a minimum of 30 minutes homogenizing time in a liquid state once in the furnace. Owing to the X-ray opacity differences between the MnO and other slag components, it was quite clear when a slag was not homogenized; a lighter band of slag was observed on top of a darker band of MnO rich slag. ICP analysis of a blank slag, where all steps in the experimental procedure were followed except for the addition of a droplet, indicates a maximum variation in composition of ±0.5wt% MnO across the entire slag. The total mass for all slag samples was fixed at 25g; no variations in slag mass were tested during these experiments.

Metal droplets were produced by mixing appropriate quantities of silicon and iron and melting in a vacuum arc melter. The melting atmosphere contained less than 4x10$^{-10}$ atmospheres of O$_2$; droplets were melted 2-3 times for homogeneity; a total oxygen content of less than 50ppm [28] is expected.

3.3 Procedure

All reduction experiments were conducted using a vertical tube furnace heated using molybdenum disilicide elements. Reaction temperatures up to 1923K (1650°C) measured using a type-B platinum-rhodium thermocouple could be held constant within ±8K (8°C). The 8.9cm diameter alumina furnace tube was sealed using water cooled stainless steel caps at either end, fitted to allow either inert gas to flow through the furnace or to evacuate the furnace using a vacuum pump. The furnace was equipped for X-ray imaging of the slag and metal inside the crucible to allow observation of interfacial phenomena and gas bubble formation during the experiment. A diagram of the furnace setup is provided in Figure 1.
The following paragraph uses names taken from Figure 1 to better explain the stepwise procedure. An alumina crucible containing slag was placed in the cold zone of the furnace, located inside the quench collar at the base of the furnace and supported by an alumina support rod; the O-ring connections at the base were sealed. The holding cap above the furnace was removed, and a metal droplet was placed inside supported by an external neodymium magnet. The cap was attached and sealed to the dropper tube such that the droplet can fall when the magnet is removed (without unsealing the furnace). With all seals closed the system was evacuated and backfilled with argon. Thereafter, the system was continuously flushed with argon for the duration of the experiment. The crucible was raised from the bottom of the furnace into the hot zone over the course of approximately one hour to prevent thermal shock to the crucible. The hot zone temperature was uniform to approximately ±1K (1°C) for 4cm, or ±10K (10°C) for 10cm. The experiment was started by removing the magnet from the exterior of the holding cap, thus allowing the metal droplet to fall to the base of the dropper tube which was situated near the mouth of the crucible. This tube had a small hole drilled in the end, too small for a solid metal droplet to fall through but large enough for liquid metal to pass. This ensured that the metal was fully liquid prior to the start of the reaction; the length of melting was dependent on the size of the droplet. The X-ray equipment was used to determine the precise time when the metal droplet melted, moved through the hole, and entered the slag which established precise zero times for each reaction. The location of the droplet at various times is demonstrated in Figure 2. The crucible that contained both slag and metal could be quenched in less than one second by removing the support tube, which allowed for accurate end times to be established. In order to generate a concentration versus time profile for a specific set of initial conditions several of these experiments were conducted; the collection of many discrete data points allowed for the fitting of the data to a continuous curve for each initial reaction condition.
Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) was used to analyse the quenched metal droplets for manganese and silicon. Approximately 0.1g samples of metal were dissolved using a microwave digester and a solution of 3mL HCl, 2mL HNO₃, and 2mL HBF₄. Samples from the digester were then diluted to 100mL twice to get them into a measurable concentration range for the elements of interest (0-40ppm). Experimental slags were not analyzed with ICP as concentration gradients formed within the slag rendered bulk concentration measurements meaningless.

4 Results

Figure 3 through Figure 11 show the change in metallic silicon and manganese contents as a function of time for the various reaction conditions. The solid lines in these figures have been “drawn” through the data using exponential functions by the author. The dashed line shows the predicted manganese value by converting the change in wt%Si to wt%Mn using Equation 1, while the dotted line shows the same conversion using Equation 2. During the initial seconds of reaction the measured data appears to be almost entirely described by Equation 1. Beyond this time deviation can be found, where the amount of manganese reduced to the metal is less than calculated from the stoichiometry from Equation 1, implying contribution from Equation 2. A depletion of Mn²⁺ ions would improve the favorability of the SiO reaction, which may explain this behaviour. The time to achieve equilibrium for these reactions was between 240 and 360 seconds. This value is in agreement with the desiliconization data of Shibata et al. [7].
Figure 3: Concentration vs. Time Plot for the 15wt%MnO, 5wt%Si, 1.5g Droplet, and 1873K (1600°C)

Figure 4: Concentration vs. Time Plot for the 15wt%MnO, 10wt%Si, 1.5g Droplet, and 1873K (1600°C)

Figure 5: Concentration vs. Time Plot for the 10wt%MnO, 15wt%Si, 1.5g Droplet, and 1923K (1650°C)
Figure 6: Concentration vs. Time Plot for the 15wt% MnO, 15wt% Si, 0.5g Droplet, and 1873K (1600°C)

Figure 7: Concentration vs. Time Plot for the 15wt% MnO, 15wt% Si, 1.0g Droplet, and 1873K (1600°C)

Figure 8: Concentration vs. Time Plot for the 15wt% MnO, 15wt% Si, 1.5g Droplet, and 1823K (1550°C)
Visual observation of quenched slags, such as Figure 12, shows a distinct color gradient exists within the sample taken at around three minutes. Given that MnO is the only species to cause significant
pigmentation of the slag, this gradient appears to be related to manganese depletion of the slag and is not found in slags near time zero or slags that are at equilibrium. Hence it is reasonable to assume that transport of manganese oxide in the slag contributes to control of the reaction for a large portion of the reaction time. Figure 13, taken after twenty seconds of reaction, is consistently dark in both the interface and bulk slag, implying that no significant gradient exists. Figure 14 taken at twenty minutes of reaction is consistently lighter in color. In all cases gas bubbles can be observed forming along the slag-metal boundary, though each image has a different bubble shape associated with it. This is believed to be associated with how the gas bubbles evolve over time.

Note that these images have had small adjustments made to their color and contrast in order to make the changes in the slag more apparent for readers. This action has not changed the position of the MnO depleted zone. An overlay has further been added to point out key areas of interest. While only three images have been presented, similar observations by the author were found for nearly all samples.

Figure 12: Colour Gradients Surrounding the Droplet (Lower Middle of the Image) and Gas at 185 Seconds of Reaction; The Lightest Area is to the Left and Darkest to the Bottom Right

Figure 13: Negligible Color Gradients Found Surrounding the Droplet at 20 Seconds of Reaction; Note the Distinct Outline of Spherical Gas Bubbles Surrounding the Large Central Droplet
In order to quantify the correlation between color and (MnO) concentration, EDS was performed at different distances from the slag/metal interface. The data shows concentration increasing from approximately 4wt%Mn to 6wt%Mn over a 0.7mm distance in the direction perpendicular to the interface. Without a standard to reference in the SEM these values cannot be taken at face value, however their trend can, where the manganese content increases by 50%. This further reinforces the idea that manganese transport in the slag controls the reaction rate.

Based on the above qualitative evidence for mass transport control in the slag, Equation 3 was used to plot the experimental data. The mass transfer coefficients are represented as $k_s$ and $k_m$ for slag and metal respectively in units of m/s; similarly volume is given as $V_s$ or $V_m$ in m$^3$. Time is represented as ‘t’ in seconds and $A$ the interfacial area in m$^2$. The number of moles of a particular species in either the slag or metal are given as $n_s$ or $n_m$ respectively (and can have the desired species substituted); the superscripts denote whether the value is taken at equilibrium ‘e’ or at the initial composition ‘o’, and the superscript free variable is for any arbitrary time. Masses of slag or metal are represented as $m_s$ or $m_m$. Molar mass is given as capital M. Equation 3 was developed assuming control by mass transport in the slag employing a molar balance such that the equation could be written in terms of number of moles of the relevant species in the metal. Equation 4 is Equation 3 where an appropriate conversion of moles to mass has been applied.

$$-k_s t = \frac{V_s}{A} \left( \frac{n_m^e}{n_m^o + n_s^o} \right) \ln \left( \frac{n_m - n_m^e}{n_m^o - n_m^e} \right)$$

Further, in order to verify that metal transport is not the rate control, Equation 5 for metal control is shown below. Note that the significant differences are the use metal versus slag volume and the pre-logarithmic term. The molar terms in Equation 5 have been converted to mass terms in Equation 6.

$$-k_s t = \frac{V_s}{A} \left( \frac{[\text{wt\% Mn}^e] \cdot m_m^e}{M_{Mn}} + \frac{[\text{wt\% MnO}^o] \cdot m_s}{M_{MnO}} \right) \ln \left( \frac{[\text{wt\% Mn}] \cdot m_m - [\text{wt\% Mn}^e] \cdot m_m^e}{[\text{wt\% MnO}] \cdot m_s - [\text{wt\% MnO}^o] \cdot m_m^o} \right)$$

Further, this derivation includes the initial moles of manganese in the metal as part of the expression; this is a negligible non-zero value that could be assumed away, but was tracked in this expression regardless.
\[-k_m t = \frac{V_m}{A} \left( \frac{n_m^o + n_s^o - n_m^e}{n_m^o + n_s^o} \right) \ln \left( \frac{n_m - n_m^e}{n_m^o - n_m^e} \right) \]

(5)

\[-k_m t = \frac{V_m}{A} \left( \frac{\text{wt\%Mn}^o}{M_{Mn}} + \frac{\text{wt\%Mn}^o}{M_{MnO}} \right) \left( \frac{\text{wt\%Mn}^o}{M_{Mn}} + \frac{\text{wt\%Mn}^e}{M_{Mn}} \right) \ln \left( \frac{\text{wt\%Mn}^o}{M_{Mn}} + \frac{\text{wt\%Mn}^e}{M_{Mn}} \right) \]

(6)

If mass transport of manganese oxide in the slag is assumed to control the reaction rate, the change in the manganese concentration in the metal with time is given by Equation 4, whereas if mass transport in the metal controls Equation 6 would apply. This information is displayed in Table 2 for clarity.

**Table 2: Definition of Z, Y_m, and Y, Used to Plot Rate Equations**

<table>
<thead>
<tr>
<th>Z – Figures 15 to 19</th>
<th>$\frac{(\text{wt%Mn}) \ast m_m^o - (\text{wt%Mn}^e) \ast m_m^e)}{(\text{wt%Mn}^o) \ast m_m^o - (\text{wt%Mn}^e) \ast m_m^e)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y – Figure 16 (mass transfer in metal)</td>
<td>$\frac{V_m}{A} \left( \frac{\text{wt%Mn}^o}{M_{Mn}} \ast m_m^o + \frac{\text{wt%Mn}^o}{M_{MnO}} \ast m_s - (\text{wt%Mn}^e) \ast m_m^e}{\frac{\text{wt%Mn}^o}{M_{Mn}} \ast m_m^o + \frac{\text{wt%Mn}^o}{M_{MnO}} \ast m_s} \right)$</td>
</tr>
<tr>
<td>Y – Figures 15 and 17 to 19 (Slag Control)</td>
<td>$\frac{V_s}{A} \left( \frac{\text{wt%Mn}^e}{M_{Mn}} \ast m_m^e}{\frac{\text{wt%Mn}^o}{M_{Mn}} \ast m_m^o + \frac{\text{wt%Mn}^o}{M_{MnO}} \ast m_s} \right)$</td>
</tr>
</tbody>
</table>

In the current work different droplet sizes, different starting [Si], and different starting (MnO) contents have been used to alter the value of Y. The effect of temperature has also been studied. Figure 15 and Figure 16 are plotted for different droplet sizes below according to Equation 4 and Equation 6 respectively. The data plotted according to control by MnO mass transport in the slag can be fitted well to a single straight line whereas the data plotted according to metal control does not fit as well. This suggests that manganese oxide reduction is controlled by mass transport in the slag. Figure 15 shows an excellent fit of the data to a single straight line, with significant deviation only occurring following the 300 second mark. Meanwhile Figure 16 shows that the equivalent plot for mass transport in the metal appears to diverge at a much earlier time. The mass transfer coefficient $k_s$ is approximately $4.0 \times 10^{-5}$ m/s.
This result does not agree with the work of Daines and Pehlke who stated that mass transport of manganese in the metal was the rate controlling step [6]. Daines and Pehlke used much lower amounts of [Si] and (MnO) in their system, and made the bulk of their observations at times greater than the five to seven minute mark; this could explain the discrepancy. The more recent work of Heo et al. is in agreement with slag control findings, even though their claim is a silica control pathway and not manganese oxide [8].

Carrying forward the conclusion that the system is under slag mass transport control, the following figures show the results of changing initial (MnO) concentrations and initial [Si] concentrations. Figure 17 shows that changing the initial concentration of (MnO) in the system does not change the rate constant of reaction. This provides further evidence towards the idea of control by transport of manganese oxide slag. Note that as expected the $k_s$ value here is near that established in Figure 15 (approximately a ten percent difference).
Figure 17: [Mn] Concentration Data Plotted as a Function of Initial (MnO) and Time, Using Equation 4 Control by Mass Transport of MnO in the Slag; Initial Conditions 15wt%Si, Variable MnO, 1923K (1650°C), 1.5g Droplet

Figure 18 shows that by increasing the initial concentration of silicon in the metal an increase in the slope of the rate plot can be observed. This observation appears to be in contradiction to the previous evidence of mass transport control by manganese oxide in the slag, as the pre-logarithmic term is not successfully normalizing the data with changes in silicon. This finding is contradictory to the previous findings, and may imply mixed control is controlling this system.

Figure 18: [Mn] Concentration Data Plotted as a Function of Initial [Si] and Time, Using Equation 4 for Control by Mass Transport of MnO in the Slag; Initial Conditions Variable Si, 15wt%MnO, 1873K (1600°C), 1.5g Droplet

Figure 19 compares changes in temperature among reactions. Strangely, it appears as if increasing temperature may result in a decline in the rate constant. This is atypical of most systems under mass transport control, as an increase in temperature typically corresponds to an increase in the mass transfer coefficient. This anomalous change in the apparent mass transfer coefficient could be because of a shift in balance between two rate determining steps in a mixed control system or because of different levels of bubble formation on the metal surface. Further, near time zero it appears as if the higher temperature starts from a lower YlnZ than that of the lower temperatures. This may imply that a reaction occurs near time zero, without the presence of gas, corresponding well to bulk mass transfer and the increased rate constant that temperature typically brings.
One final observation from this work is the marks left by bubbles on the metal surface. Figure 20 shows a metal droplet that has been extracted from slag with large flattened areas. These appear to be gas nucleation and growth sites, where the pressure exerted by \{SiO\} manages to flatten the interface. From thermodynamic calculations silicon monoxide is the most likely gas present. This flattening is likely to happen when gas generation is at a maximum and would exert the greatest pressure on the interface. In some cases the X-ray equipment allowed for the in-situ observation of large gas bubbles in the slag, apparently breaking away from the metal. It is believed that these larger bubbles are the result of coalescence of many small bubbles into a single large bubble that can break away from the surface of the metal droplet. Unfortunately the image quality is not sufficient to measure the volume of the bubble film around the metal surface.

Meanwhile Figure 21 shows marks left by bubbles attached to the metal interface with a network of slag surrounding the sites. These circular areas of apparently clean metal show how the gas sticks directly to the metal and displaces slag around the nucleation and growth sites. This observation
provides credible evidence to the theory that a dynamic volume/area term may exist over the course of the reaction relating the ability of (MnO) to diffuse past the bubble layer and react with the metal in the slag regions; this is discussed in more detail below.

![Slag Deposit](image)

**Figure 21: Cleared Metal Surface Surrounded by Slag Deposits in a Web-Like Pattern at 2 Minutes of Reaction**

It is worth noting that none of the dynamic interfacial phenomena (flattening, roughening, or emulsification) as identified by previous workers [20,22,26] were found during the experiments. The localized flattening shown in Figure 20 is likely attributed to bubble nucleation and not surface tension breakdown. Despite exceeding the 0.1mol/m²/s interfacial oxygen transfer rate criterion proposed by Riboud and Lucas [20], the system did not exhibit interfacial breakdown; the formation of a stable bubble film around the droplet may inhibit spontaneous emulsification. This hypothesis is purely speculative, although other workers in the authors’ laboratory studying iron carbon droplets have found that when bubbles are present the interface remains remarkably stable even at high oxygen flux [29].

5 Discussion

The results presented above offer strong evidence for control by mass transport of manganese oxide in the slag. A gradient in slag pigmentation (indicative of depletion of manganese oxide close to the slag/metal interface) can be observed by visual observation. Rate plots assuming control by mass transport of MnO show remarkable consistency for a variety of droplet sizes and initial MnO concentration. Contrary to these findings changing the starting metallic silicon content of the metal disagrees with mass transport control by MnO; silicon transport in the metal may also impact the rate and control step for the reaction. The curves from Figure 3 through Figure 11 show that the concentration change of metallic manganese follows neither Equation 1 nor 2, falling somewhere in between, but that conditions likely to cause a greater deficit in the transport of Mn²⁺ to the interface relative to that of silicon will more closely follow the theoretical SiO curve.

Taken in their entirety the above observations imply some element of mixed control between silicon in the metal and manganese oxide in the slag which may explain the apparent discrepancies between different researchers [6–8]. Initial concentrations are likely to impact the dominant reaction pathway.
These findings are best summarized in Table 3 below; all MnO changes are matched with 15wt%Si droplets and all Si changes matched with 15wt%MnO slags. From Figure 3 through Figure 11 it is possible to compare the measured changes in manganese concentration to the theoretical values that would be obtained through the SiO$_2$ or SiO pathways. At a minimum, one mole of silicon will reduce one mole of manganese oxide according to Equation 2, and at a maximum one mole of silicon will reduce two moles of manganese oxide according to Equation 1. One can calculate the ‘silicon efficiency ratio’ (SER) using Equation 7, where $w_t%Mn$ represents the measured concentration of manganese, $w_t%Mn_{SiO}$ represents the concentration of manganese assuming all silicon is converted to manganese via Equation 2, and $w_t%Mn_{SiO_2}$ represents the concentration of manganese assuming all silicon becomes silica according to Equation 1; all concentrations are taken from the metal.

$$SER = 1 + \frac{w_t%Mn - w_t%Mn_{SiO}}{w_t%Mn_{SiO_2} - w_t%Mn_{SiO}}$$  \hspace{1cm} (7)

Values of SER calculated using Equation 7 are shown in Table 3 and follow the trend one would expect given the stated mechanism. High initial MnO content results in a higher initial ratio indicating that Mn$^{2+}$ flux is high and more able to oxidize the available silicon. Low initial silicon similarly results in a slower demand for Mn$^{2+}$. With the noted exception of 10wt%MnO there appears to be a slight downward trend in the efficiency with time, indicating as expected that depletion of Mn$^{2+}$ near the interfaces results in more production of SiO. The other data sets do not show observable trends. From this analysis it appears that the early stages of reaction are dominated by kinetic factors which eventually become somewhat stable and approach a ratio close to the equilibrium of the system; despite differences in the ratio near 300 seconds, eight of the nine systems (with the exception of 10wt%MnO) closely approach their expected equilibrium. The analysis shows that in order to meet the demands of the mass balance within the system the ratio of [Mn] to [Si] reacted over time must change.

**Table 3: Silicon Efficiency Ratio for Different Starting Concentrations and Over Time**

<table>
<thead>
<tr>
<th>Initial wt% Slag/Metal</th>
<th>Time (s)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>60</td>
<td>120</td>
<td>180</td>
<td>240</td>
<td>300</td>
</tr>
<tr>
<td>10%MnO</td>
<td>1.32</td>
<td>1.34</td>
<td>1.35</td>
<td>1.36</td>
<td>1.36</td>
<td>1.37</td>
</tr>
<tr>
<td>15%MnO</td>
<td>1.58</td>
<td>1.57</td>
<td>1.57</td>
<td>1.57</td>
<td>1.57</td>
<td>1.56</td>
</tr>
<tr>
<td>20%MnO</td>
<td>1.93</td>
<td>1.90</td>
<td>1.88</td>
<td>1.87</td>
<td>1.86</td>
<td>1.85</td>
</tr>
<tr>
<td>5wt%Si</td>
<td>1.94</td>
<td>1.90</td>
<td>1.87</td>
<td>1.85</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>10wt%Si</td>
<td>1.79</td>
<td>1.76</td>
<td>1.74</td>
<td>1.73</td>
<td>1.72</td>
<td>1.71</td>
</tr>
<tr>
<td>15wt%Si</td>
<td>1.62</td>
<td>1.61</td>
<td>1.61</td>
<td>1.60</td>
<td>1.60</td>
<td>1.59</td>
</tr>
</tbody>
</table>

A gas layer has been found in almost every experiment carried out. This has not been incorporated into the rate assumptions presented above and is likely also to have complicated the picture, particularly in regard to the effect of temperature on reaction rate. This result implies that mass transport of manganese oxide in the slag might not be the lone rate controlling step in this reaction. Given that all of the data for MnO differences came from droplets with 15wt% starting silicon, it is possible that at lower values of silicon the control shifts away from manganese to silicon instead. Such a result may help explain the issues authors have had explaining the reaction mechanism in the system, ranging from manganese in the metal to manganese or silicon in the slag. Given the apparent gas generation in the system, and the favourability of SiO with temperature, it is possible that higher temperatures result in more gas generation around the interface leading to blocking of the reaction pathways; this is complicated by diffusivity increases in slag with increasing temperature.
One area of concern surrounding the gas is how it affects the volume and area terms employed in any rate equation. For example, assuming that the interfacial area is the slag-metal interface is unlikely to be true if it is partially covered by gas bubbles. Figure 22 provides an illustration of how bubbles may impact the area of the reaction interface and thereby rate of reaction. The extent of the bubble layer and the volume of slag between the bubbles may change over time depending on a number of factors, such as temperature and the balance between silicon and manganese oxide transport. A gas layer would be expected to impact the interfacial area in two possible ways: first by taking up space along the interface and preventing the reaction of slag and metal in those areas, as well as forcing all transported material to funnel between the bubbles. Given the spherical geometry, the point where the neck between bubbles is at its narrowest should impact the transport more greatly than coverage of the slag-metal interface. If one considers an imaginary sphere around the metal droplet, separated by one bubble radius from the slag-metal interface this sphere would have a defined area ‘A’, occupied entirely by slag. Upon the formation of a bubble layer the area occupied by slag would drop reducing the cross-sectional area of the transport path. Assuming the spherical bubbles pack tightly in a hexagonally close packed monolayer would reduce the available transport path by 89%.

![Diagram Illustrating how Gas Generation may Affect the Diffusion Pathway and Change both Volume and Area Terms in the Rate Equation](image)

Such an assumption may help to explain what appears to be a dramatic decrease in reaction rate after the first six seconds. Close examination of the plots in Figure 3 through Figure 11 shows that the y-axis intercept at time equal to zero is always less than zero. This observation implies an early rate much faster than that evident for times greater than 6 seconds may be present. Based on the data available, it is not possible to determine the exact point at which the rate changes but if for the sake of discussion one assumes six seconds we can estimate a slope and therefore a mass transfer coefficient for this very early time period. This process is illustrated in Figure 23 as ‘$k_{s,0}$’ plotted alongside the calculated $k_s$ value from Figure 15. The mass transfer coefficient calculated based on times greater than six seconds is approximately 11% of the estimated initial slope. The authors are not claiming that the predicted initial mass transfer coefficient can be determined quantitatively but merely propose that it is of the correct order of magnitude to support the idea of blockage of transport paths by a relatively stable bubble film. The slope plotted for time less than six seconds is a very reasonable estimate; these first few seconds of reaction can account for up to 10% of the total reaction (as is the case with Figure 11).
The above findings indicate that there are two major areas for future work: derivation of a rate equation involving both manganese oxide transport from the slag and silicon transport from the metal, as well as the incorporation of the change in interfacial area with time. The interfacial area appears to change over a relatively short period of time as the result of a relatively stable bubble film, and once formed does not change much over the course of the reaction.

6 Conclusions

1. MnO mass transfer in the slag is the rate controlling step for experiments with 15wt% silicon, the mass transfer coefficient is $4.0 \times 10^{-5}$ m/s.
2. Decreasing the initial silicon content changes the rate control to mixed control by mass transport of silicon in the metal and mass transport of MnO in the slag.
3. Lowering the temperature appears to increase the reaction rate because of the decreasing favorability of SiO formation at lower temperatures.

7 Acknowledgements

The authors thank the National Science and Research Council of Canada for funding support. Special thanks to Arcelor Mittal Dofasco, US Steel Canada, Praxair, and Hatch Ltd. for their in-kind support, technical expertise, and their many helpful discussions.

8 References