Kinetic Investigations of SiMn Slags From Different Mn-sources

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Abstract

The kinetics of MnO and SiO_2 reduction were investigated for SiMn slags by using a TGA furnace between 1773 and 1923 K (1500 and 1650 °C) under CO atmospheric pressure. The charge materials were based on Assmang ore and HC FeMn Slag. Rate models for MnO and SiO_2 reduction were considered to describe the metal-producing rates, which are shown by the following equations:

$$r_{MnO} = k_{Mn} \cdot A \cdot \left(a_{MnO} - \frac{a_{Mn} \cdot p_{CO}}{K_T} \right)$$

$$r_{SiO_2} = k_{Si} \cdot A \cdot \left(a_{SiO_2} - \frac{a_{Si} \cdot p_{CO}^2}{K_T} \right)$$

The results showed that the choice of raw materials in the charge gave considerable difference to the reduction rate of MnO and SiO_2, where the highest reduction rate was found to be from charges using HC FeMn slag. The difference in the driving forces was insignificant among the SiMn slags, and the comparison of the slag viscosities was rather similar which could not explain the different reduction rates. Instead, small amount of sulfur and initial amount of iron in the charge gave implication to the enhanced reduction rates. In addition, the considered rate models were applicable to describe the reduction of MnO and SiO_2 in SiMn slags.

KeyWords

SiMn, MnO, SiO_2, Reduction, Kinetics

I. Introduction

The production of silicomanganese (SiMn) is an important process due to its contribution to the steel producing industries. It is well known that Mn as an alloying unit enhances the strength, toughness and hardness of steel products, and both Mn and Si are excellent deoxidizers which prevent porous structures [1-8]. The standard SiMn alloy typically contains approximately 70 wt% Mn, 18~20 wt% Si and 10 wt% Fe [2].

While manganese thermodynamics have been studied intensively during the past two decades [2], kinetic information in the SiMn process is however scarce. The absence of kinetic information increases the ambiguousness of the reduction mechanisms, and it is not clear how different raw materials affect the reduction of MnO and SiO_2 in the SiMn process. The metal producing reactions in the SiMn process are described by the following reactions:

$$MnO_{(l)} + C = Mn_{(l)} + CO_{(g)}$$

$$SiO_{2\,(l)} + 2C = Si_{(l)} + 2CO_{(g)}$$

Previous studies have shown that both MnO and SiO_2 reduction becomes significant above 1773 K (1500 °C) [9, 10]. The mass loss observed from a TGA furnace, which indicates MnO and SiO_2 reduction, was insignificant until 1773 K (1500 °C) but increased drastically at higher temperatures. Therefore, the present study focuses on estimating the kinetic parameters, such as activation energies and rate constants, in different SiMn slags (MnO-SiO_2-CaO-MgO-Al_2O_3) between 1773 and 1923 K (1500 and 1650 °C). The main goal is to describe the reduction rates of MnO and SiO_2 in SiMn slags from raw material Mn-sources such as Assmang ore and HC FeMn slag (High-Carbon Ferromanganese slag).

II. Theoretical Considerations

Previous studies have shown that the reduction rate of MnO in ferromanganese (FeMn) slags can be described by Eq. (1), which implies that the chemical reaction is the rate determining step [2, 11]. SiMn slags are essentially similar to FeMn slags, and the same rate expression for MnO reduction can be presumed. Assuming that SiO_2 reduction in SiMn slags is also controlled by chemical reaction, a similar rate model can be considered by Eq. (2), which was presumed and used for estimating the kinetic parameters in this work:

$$r_{MnO} = k_{MnO} \cdot A \cdot \left(a_{MnO} - \frac{a_{Mn} \cdot p_{CO}}{K_T}\right) = k_{o,MnO} \cdot A \cdot e^{-E_{MnO}/RT} \cdot \left(a_{MnO} - \frac{a_{Mn} \cdot p_{CO}}{K_{T,MnO}}\right) \quad (1)$$

$$r_{SiO_2} = k_{SiO_2} \cdot A \cdot \left(a_{SiO_2} - \frac{a_{Si} \cdot p_{CO}^2}{K_T}\right) = k_{o,SiO_2} \cdot A \cdot e^{-E_{SiO_2}/RT} \cdot \left(a_{SiO_2} - \frac{a_{Si} \cdot p_{CO}^2}{K_{T,SiO_2}}\right) \quad (2)$$

Where r (g/min) is the reduction rate, k (g/min·cm^2) is the rate constant, k_o is the pre-exponential constant, A (cm^2) is the reaction interface, E (kJ/mol) is the activation energy, R is the ideal gas constant, T (K) is the temperature, a_{MnO}, a_{SiO2} are the activity of MnO and SiO_2 in the slag phase, a_{Mn}, a_{Si} are the activity of Mn and Si in the metal phase, p_{CO} is the partial pressure of CO (g) and K_T is the equilibrium constant at temperature T.

The rate models for MnO and SiO_2 reduction also imply that the driving force for reduction, which is the difference between actual and equilibrium activities, contribute to the reduction rates. Simplified models for activities of slag (MnO, SiO_2) and metal (Mn, Si) components in their respective melts have been

recently studied and were expressed as Eqs. (3 ~ 6) [12]. These activities were derived based on FactSage 7.0 [13] and used to calculated the driving forces for MnO and SiO_2 reduction.

$$a_{MnO} = C_{MnO} \cdot \exp(0.0007576T - 123.7C_{MnO} + 30.14C_{SiO_2} + 47.84C_{MgO} + 49.54C_{CaO} - 47.96C_{Al_2O_3} + 122.8C_{MnO}^2 - 67.78C_{SiO_2}^2 - 46.32C_{MgO}^2 - 47.68C_{CaO}^2 + 22.51C_{Al_2O_3}^2 + 78.35C_{MnO}C_{CaO} + 77.56C_{MnO}C_{MgO} + 176.6C_{MnO}C_{Al_2O_3} + 101.2C_{MnO}C_{SiO_2} - 71.52C_{SiO_2}C_{CaO} - 70.58C_{SiO_2}C_{MgO} + 27.35C_{SiO_2}C_{Al_2O_3} + 46C_{SiO_2}^3 - 92.97C_{CaO}C_{MgO} + 2.44C_{CaO}^3) \quad (3)$$

$$a_{SiO_2} = C_{SiO_2} \cdot \exp(-0.0003408T + 113.8C_{MnO} - 22.79C_{SiO_2} - 51.63C_{MgO} - 52.44C_{CaO} + 36.3C_{Al_2O_3} - 119.3C_{MnO}^2 + 42.56C_{SiO_2}^2 + 32.25C_{MgO}^2 + 30.12C_{CaO}^2 - 26.26C_{Al_2O_3}^2 - 82.725C_{MnO}C_{CaO} - 82.9C_{MnO}C_{MgO} - 155.2C_{MnO}C_{Al_2O_3} - 86.98C_{MnO}C_{SiO_2} + 86.21C_{SiO_2}C_{CaO} + 86.19C_{SiO_2}C_{MgO} - 23.06C_{SiO_2}C_{Al_2O_3} - 31.26C_{SiO_2}^3 + 69.45C_{CaO}C_{MgO} + 11.29C_{CaO}^3) \quad (4)$$

$$a_{Mn} = C_{Mn} \cdot \exp(0.0005382T - 37.41C_{Mn} - 2.966C_{Si} - 0.6835C_{Fe} + 39.52C_{Mn}^2 - 1.453C_{Si}^2 - 0.5561C_{Fe}^2 + 27.48C_{Mn}C_{Si} + 38.69C_{Mn}C_{Fe} + 0.214C_{Si}C_{Fe}) \quad (5)$$

$$a_{Si} = C_{Si} \cdot \exp(0.002464T + 10.3C_{Mn} - 1.081C_{Si} + 27.52C_{Fe} - 15.49C_{Mn}^2 - 3.713C_{Si}^2 - 34.66C_{Fe}^2 + 1.324C_{Mn}C_{Si} - 47.01C_{Mn}C_{Fe} - 9.127C_{Si}C_{Fe}) \quad (6)$$

Where C_{MnO}, C_{SiO2}, C_{CaO}, C_{MgO}, C_{Al2O3} are the mass fraction of MnO, SiO_2, CaO, MgO, Al_2O_3 in the slag phase, and C_{Mn}, C_{Si}, C_{Fe}, C_C are the mass fraction of Mn, Si, Fe, C in the metal phase, respectively.

III. Experimental Procedures

The focus of this work was to study the reaction rates and to estimate the kinetic parameters of MnO and SiO_2 reduction in SiMn slags. The characterization and preparation of SiMn charges, the TGA furnace and the experimental conditions are described in the following sub-sections.

A. *Raw materials preparation*

Three different SiMn charges based on Assmang ore and HC FeMn slag were used in this work. The composition of raw materials and the charge compositions are shown in Tables 1 and 2, respectively. The raw materials were analyzed by SINTEF (MOLAB) [14], and the particle sizes were between 0.6 ~ 1.6 mm. The amount of each raw material was considered to aim at approximately 40 wt % SiO_2 and 5 wt % MnO in slag and 18 wt % Si in metal phase, which is close to the thermodynamic equilibrium at 1873 K (1600 °C) [2]. The raw materials in each charge type were added as layers into the graphite crucibles (36 mm outer diameter, 30 mm inner diameter, 70 mm height and 61 mm deep) with the low melting materials at the top and the carbon at the bottom.

Table 1. Chemical compositions of raw materials

Material	MnO	MnO_2	SiO_2	Fe_2O_3	CaO	MgO	Al_2O_3	S	C	CO_2	H_2O	Total [wt%]
Assmang	32.69	33.22	5.77	15.06	6.26	1.1	0.26	0.16	0.27	3.52	1.55	99.86
Quartz	0.14	-	93.85	-	0.09	0.05	1.19	-	-	-	-	95.32
HCS*	35.23	-	25.45	-	18.45	7.53	12.3	0.46	0.46	-	2.2	102.08
Coke	0.04	-	5.6	0.86	0.42	0.22	2.79	0.4	87.68	-	15.5	113.51

* HCS: High Carbon FeMn Slag

106

Table 2. Charge compositions based on Assmang ore and HC FeMn slag

Charge	Assmang	Quartz	HCS	Coke	Total [g]	C+M/A***
As**	7	1.94	-	2.2	11.14	12.22
As/HCS	4	1.69	4	2.5	12.19	2.56
HCS	-	1.46	10	3	14.46	2.08

** As: Assmang Ore

*** C+M/A: $CaO+MgO/Al_2O_3$

B. *TGA furnace and experimental conditions*

The experiments were conducted by using a TGA furnace, which is schematically shown in Figure 1. The furnace can endure temperatures up to 1973 K (1700 °C) and the maximum heating rate is up to 25 K/min. A mass balance is installed at the top and a Molybdenum (Mo)-wire was used to suspend the graphite crucible inside the furnace chamber. A B-type thermocouple was placed 1cm beneath the graphite crucible to measure the temperatures.

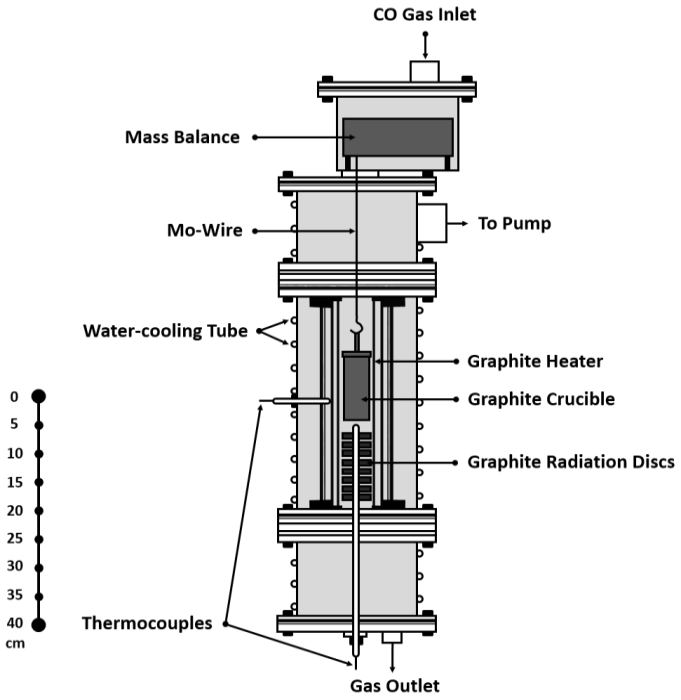

Fig. 1 – Schematic of the TGA furnace

The heating of the furnace was programed to follow a temperature schedule which is described in Figure 2. Initially, the furnace was rapidly heated up to 1473 K (1200 °C) (+25 K/min) and held for 30 minutes to secure complete degree of pre-reduction [2]. Then, further heating (+4.5 K/min) was done and stopped at temperatures between 1773 and 1923 K (1500 and 1650 °C). This temperature profile was considered to simulate the industrial furnace process. 16 experiments for each charge type with a temperature difference of 10 K (10 °C) were conducted between 1773 and 1923 K (1500 and 1650 °C).

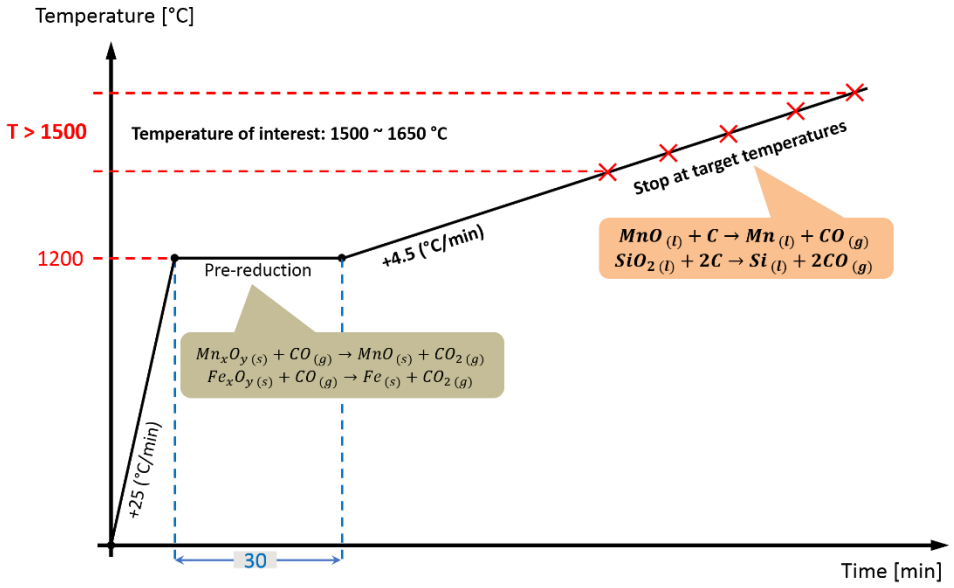

Fig. 2 – Temperature schedule

All experiments were conducted in CO atmospheric pressure (0.5 l/min CO) to simulate the industrial environment, and the mass change data were logged every 5 seconds. Lastly, charge samples were prepared by mounting epoxy to be further analyzed.

The charge samples were ground, polished and analyzed by an EPMA (Electron Probe Micro Analyzer): JEOL JXA-8500F. More than 5 random points in the slag phase were analyzed for each phase, and the corresponding metal compositions were calculated based on the average slag composition. As the metal analyses are more uncertain than the slag analyses, the slag analyses were used to estimate the amount of MnO and SiO_2 reduction.

IV. Results and Discussions

The objective of this study was to empirically find kinetic parameters and evaluate the presumed rate models for MnO and SiO_2 reduction in SiMn slags between 1773 and 1923 K (1500 and 1650 °C). The results of the following aspects are described and discussed in sub-sections: TGA results, Slag/Metal composition, Arrhenius plots and Rate models.

A. *TGA results and Slag/Metal composition*

The main information from the TGA furnace is the mass change of the charge materials during the experimental condition. Figure 3 describes the average TGA results of 16 experiments for each charge type between 1773 to 1923 K (1200 to 1650 °C). Note that a complete degree of pre-reduction was assumed at 1473 K (1200 °C) and used as a new reference point for further reduction of MnO and SiO_2.

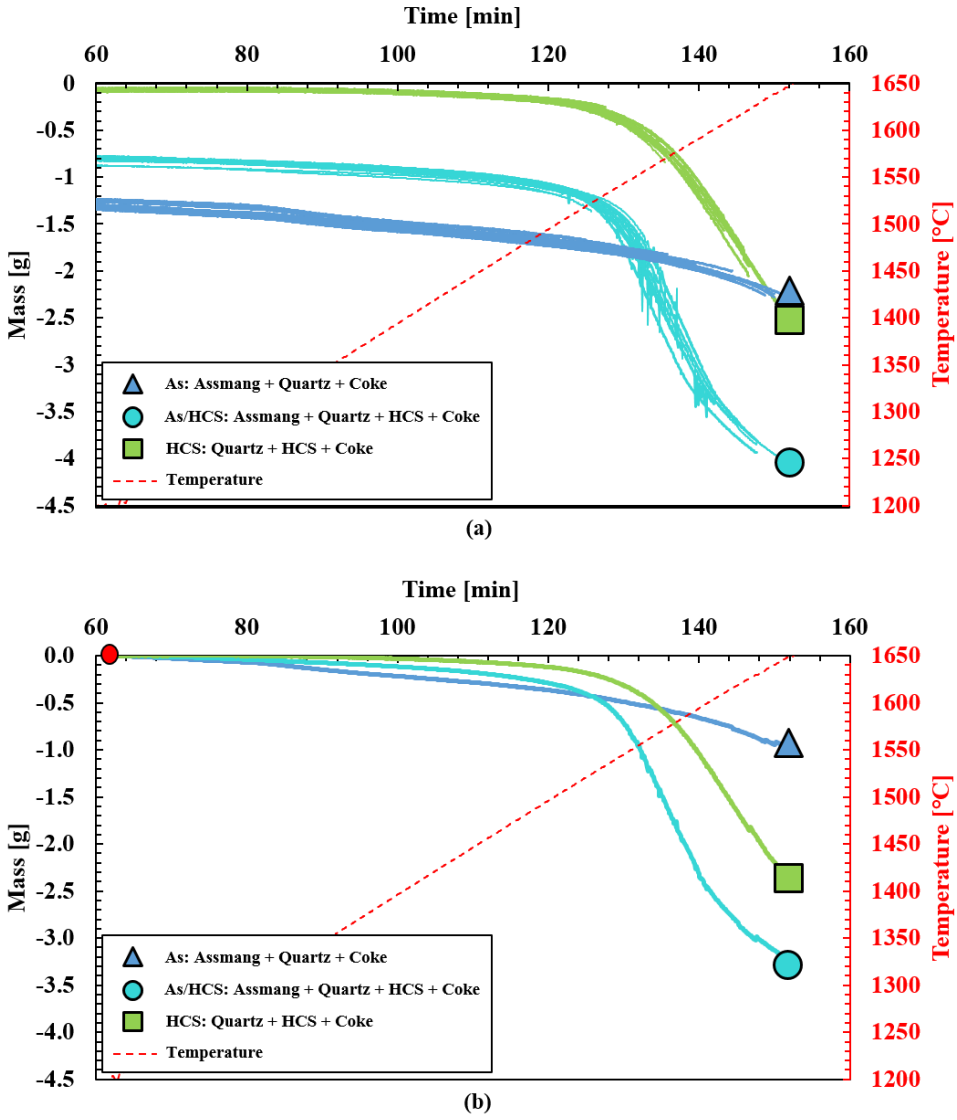

Fig. 3 – TGA results: 16 experiments for each charge type (a), and the average mass changes with a new reference point (red circle) at 1473 K (1200 °C) (b)

The mass change for all charge types below 1773 K (1500 °C) were insignificant, which indicated low degree of MnO and SiO_2 reduction. However, the mass changes increased at higher temperatures, and the reduction rates of MnO and SiO_2 seem to accelerate above 1773 K (1500 °C), especially for the two charges with HC FeMn slags, "As/HCS" and "HCS".

While a drastic change in both "As/HCS" and "HCS" was observed, the same result was not seen in "As", where no HC FeMn slag was used, even until 1923 K (1650 °C). The lower mass change of "As" indicates lower degree of MnO and SiO_2 reduction compared to "As/HCS" and "HCS", and also resembles the mass changes previously seen in FeMn charges [9]. The reduction of "As" seems linear and progressive between 1473 and 1873 K (1200 and 1600 °C). Nevertheless, the TGA result does not describes the reduction degrees of MnO and SiO_2 separately. To determine the reduction degrees of MnO and SiO_2, quantitative slag and metal composition is required.

The average chemical compositions of slag and the corresponding calculated metal with their respective activities (slag: a_{MnO} and a_{SiO2}, metal: a_{Mn}/K_T and a_{Si}/K_T) between 1773 and 1923 K (1500 to 1650 °C) in 3 different charge types are shown in Table 3. The different reduction degrees of MnO in the 3 charges were clearly observed from Table 3 between 1773 and 1923 K (1500 to 1650 °C). The MnO content in "As" drops from approximately 51 to 46 wt %, which indicated a low degree of MnO reduction. On the other hand, considerable amount of MnO reduction can be observed from "As/HCS" and "HCS". The changes in MnO amount were approximately from 41 to 5 wt % and from 32 to 7 wt % in "As/HCS" and "HCS", respectively. In addition, the a_{MnO} showed good accordance of the changing amount of MnO. While the decrease of a_{MnO} in "As" was insignificant, it was clear in "As/HCS" and "HCS". For the two latter cases, the a_{MnO} was approximately 0.2 at 1773 K (1500 °C) and gradually decreased near to 0 at 1923 K (1650 °C), which also indicates the higher reduction degree of MnO.

Table 4 describes the slag composition in absolute amount (g), where the amount of each slag and metal component were calculated assuming constant amount of unreducible oxides, CaO, MgO and Al_2O_3, for each temperature. Note that the amount of MnO and SiO_2 at 1473 K (1200 °C) was also calculated assuming complete degree of pre-reduction to use as a reference point.

Table 4 shows the clear change of slag (MnO, SiO_2) and metal (Mn, Si) between 1773 to 1923 K (1500 to 1650 °C). The amount of MnO and SiO_2 decreases gradually with increasing temperature, and the amount of Mn and Si increases accordingly. To compare the reduction extent of MnO and SiO_2 from the initial slag composition (calculated slag composition at 1473 K), simple Eqs. (7, 8) were used to describe the reduction degrees in a scale of 0 ~ 1. Figure 4 shows the MnO and SiO_2 reduction degrees of the 3 different charges.

$$Reduction\ Degree_{(MnO)} = \frac{Produced\ Mn\ [g]}{Initial\ MnO\ [g]} \times \frac{70.97\ [^{g\ MnO}/_{mol}]}{54.94\ [^{g\ Mn}/_{mol}]} \quad (7)$$

$$Reduction\ Degree_{(SiO_2)} = \frac{Produced\ Si\ [g]}{Initial\ SiO_2\ [g]} \times \frac{60.08\ [^{g\ SiO_2}/_{mol}]}{28.09\ [^{g\ Si}/_{mol}]} \quad (8)$$

185 Table 3. Relative amount of slag and metal compositions with their respective activities for 3 different
186 charges between 1773 and 1923 K (1500 and 1650 °C)

Charge-Temp.	Slag (EPMA) [wt %]								Metal (Calculated) [wt %]					
	MnO	SiO_2	CaO	MgO	Al_2O_3	a_{MnO}	a_{SiO2}	C+M/A	Mn	Si	Fe	C	a_{Mn}/K_T	a_{Si}/K_T
As-1500	50.6	39.1	7.6	1.2	0.5	0.152	0.285	17.2	54.6	4.3	35.9	5.2	0.0037	0.1280
1510	49.3	40.5	7.7	1.3	0.7	0.137	0.339	13.7	55.9	2.0	35.9	6.2	0.0035	0.0378
1520	51.3	37.9	7.2	1.3	0.5	0.171	0.237	16.0	54.4	7.4	34.0	4.2	0.0030	0.1914
1530	50.5	38.8	7.7	1.2	0.5	0.160	0.269	16.4	55.2	5.8	34.3	4.6	0.0029	0.0994
1540	51.4	37.4	8.4	0.7	0.7	0.181	0.218	13.3	55.0	8.8	32.6	3.5	0.0026	0.1598
1550	50.1	38.7	8.3	0.8	0.7	0.165	0.258	12.7	56.4	7.4	32.2	4.1	0.0025	0.0915
1560	50.8	37.9	7.5	1.4	0.5	0.177	0.229	16.3	55.8	8.7	31.7	3.8	0.0021	0.1026
1570	49.0	39.7	7.7	1.3	0.5	0.155	0.289	16.6	57.6	6.7	31.3	4.5	0.0021	0.0504
1580	49.4	39.0	8.6	0.7	0.8	0.165	0.261	11.7	57.5	8.1	30.6	3.9	0.0019	0.0543
1590	50.1	38.2	8.9	0.8	0.7	0.179	0.230	13.4	57.1	9.4	30.1	3.4	0.0017	0.0587
1600	49.1	38.7	8.9	0.7	0.9	0.173	0.243	11.1	58.3	9.7	28.6	3.5	0.0016	0.0511
1610	48.4	38.8	9.1	0.7	0.8	0.173	0.240	12.5	59.1	10.4	27.3	3.2	0.0015	0.0479
1620	48.7	37.7	9.4	0.7	0.9	0.193	0.198	11.0	59.2	12.3	25.8	2.7	0.0013	0.0581
1630	46.1	40.5	8.0	1.4	0.8	0.154	0.289	11.6	60.8	9.9	25.6	3.6	0.0013	0.0311
1640	45.7	40.1	9.3	1.4	0.8	0.162	0.263	13.3	61.1	11.3	24.3	3.3	0.0011	0.0339
1650	48.1	37.3	7.5	1.3	0.7	0.208	0.175	12.0	59.6	13.5	24.2	2.8	0.0009	0.0443
As/HCS-1500	40.5	35.1	12.3	3.8	5.2	0.210	0.107	3.1	50.0	10.7	36.5	2.9	0.0031	0.6101
1510	39.8	35.4	12.2	3.5	5.8	0.204	0.111	2.7	52.7	10.6	33.8	3.0	0.0030	0.4818
1520	39.1	36.6	12.0	3.9	5.6	0.184	0.135	2.9	54.5	5.2	35.6	4.7	0.0032	0.1010
1530	39.1	35.7	12.1	3.7	4.9	0.200	0.113	3.3	54.6	10.5	31.8	3.1	0.0026	0.2934
1540	38.3	36.8	12.2	3.9	5.0	0.182	0.135	3.2	56.8	6.4	32.4	4.4	0.0028	0.0904
1550	34.1	39.0	13.2	3.7	6.3	0.143	0.168	2.7	64.8	6.5	24.1	4.6	0.0029	0.0734
1560	29.5	40.4	14.4	4.0	6.7	0.115	0.182	2.7	68.4	8.9	18.7	3.9	0.0027	0.1021
1570	24.0	41.8	16.2	4.3	8.0	0.087	0.187	2.6	70.2	11.1	15.3	3.4	0.0024	0.1244
1580	19.7	44.1	18.3	5.2	8.8	0.062	0.227	2.7	72.0	10.3	14.1	3.7	0.0023	0.0838
1590	17.2	44.2	19.2	5.2	9.2	0.054	0.212	2.7	71.8	11.6	13.2	3.4	0.0020	0.0882
1600	12.7	43.8	21.6	6.2	10.4	0.039	0.174	2.7	71.3	13.9	12.0	2.9	0.0016	0.1094
1610	12.3	45.4	21.2	6.0	10.7	0.035	0.213	2.6	72.2	12.4	12.1	3.2	0.0016	0.0682
1620	10.9	44.6	22.5	6.4	11.5	0.032	0.183	2.5	71.6	13.7	11.7	3.0	0.0014	0.0710
1630	6.8	45.5	24.2	6.7	12.4	0.018	0.181	2.5	71.8	14.1	11.1	2.9	0.0013	0.0637
1640	6.8	44.0	24.9	7.2	12.8	0.020	0.147	2.5	71.0	15.2	11.0	2.8	0.0011	0.0651
1650	4.9	43.9	26.5	7.1	13.8	0.014	0.136	2.4	70.9	15.7	10.7	2.8	0.0010	0.0591
HCS-1500	31.7	34.5	15.4	4.9	9.4	0.171	0.076	2.2	27.3	30.1	36.2	6.4	0.0005	-
1510	31.7	34.2	15.8	5.0	9.7	0.176	0.072	2.2	29.7	32.4	27.2	10.7	0.0002	-
1520	31.5	34.1	15.9	5.1	9.7	0.178	0.069	2.2	35.5	32.1	22.2	10.2	0.0002	-
1530	30.8	33.8	15.8	5.2	10.0	0.179	0.064	2.1	43.8	31.5	15.0	9.6	0.0001	-
1540	31.7	34.4	15.8	5.5	9.2	0.177	0.074	2.3	28.6	30.7	33.2	7.6	0.0002	-
1550	30.6	35.8	16.1	5.6	9.5	0.155	0.092	2.3	58.6	0.1	34.5	6.9	0.0027	-
1560	30.0	35.7	16.3	5.8	9.7	0.154	0.090	2.3	63.9	8.8	23.5	3.9	0.0025	0.1012
1570	27.6	35.6	16.9	5.8	10.0	0.143	0.080	2.3	68.5	18.9	10.1	2.5	0.0013	0.5175
1580	24.1	38.8	17.3	5.5	11.3	0.098	0.124	2.0	82.1	3.4	8.2	6.3	0.0028	0.0126
1590	23.7	38.4	17.5	5.8	11.4	0.100	0.116	2.1	80.5	7.0	7.6	5.0	0.0025	0.0302
1600	21.2	38.8	18.5	6.2	11.5	0.086	0.114	2.2	79.9	10.4	5.9	3.9	0.0021	0.0507
1610	17.1	40.1	19.4	6.3	12.9	0.061	0.124	2.0	80.8	10.8	4.6	3.8	0.0019	0.0444
1620	14.3	40.8	21.3	6.8	13.3	0.047	0.127	2.1	80.8	11.6	4.0	3.7	0.0017	0.0423
1630	11.6	41.5	22.9	7.1	13.9	0.035	0.130	2.2	80.8	12.1	3.6	3.6	0.0016	0.0385
1640	9.2	40.2	23.6	7.8	15.3	0.028	0.097	2.0	77.7	16.4	3.2	2.9	0.0010	0.0694
1650	7.1	40.2	25.5	7.8	15.9	0.021	0.092	2.1	77.3	17.0	3.0	2.8	0.0009	0.0657

187

188 Table 4. Calculated absolute amount of slag and metal for 3 different charges at 1473 K (1200 °C) and
189 between 1773 and 1923 K (1500 and 1650 °C)

Charge-Temp.	Slag [g]						Metal [g]	
	MnO	SiO_2	CaO	MgO	Al_2O_3	Total	Mn	Si
As-1200	4.2	2.3				7.1	-	-
As-1500	2.8	2.1				5.4	1.12	0.09
1510	2.7	2.2				5.5	1.15	0.04
1520	2.7	2.0				5.2	1.18	0.16
1530	2.7	2.1				5.3	1.19	0.13
1540	2.6	1.9				5.0	1.25	0.20
1550	2.5	2.0				5.0	1.30	0.17
1560	2.5	1.9				5.0	1.31	0.20
1570	2.4	2.0	0.44	0.08	0.04	5.0	1.36	0.16
1580	2.4	1.9				4.9	1.39	0.20
1590	2.4	1.8				4.8	1.40	0.23
1600	2.3	1.8				4.6	1.50	0.25
1610	2.1	1.7				4.4	1.60	0.28
1620	2.0	1.6				4.1	1.70	0.35
1630	1.9	1.7				4.2	1.76	0.29
1640	1.8	1.6				4.0	1.86	0.34
1650	1.9	1.4				3.8	1.82	0.41
As/HCS-1200	3.8	2.9				8.5	-	-
As/HCS-1500	3.0	2.6				7.5	0.58	0.12
1510	2.9	2.6				7.4	0.66	0.13
1520	3.0	2.8				7.6	0.65	0.06
1530	2.9	2.6				7.3	0.73	0.14
1540	2.8	2.7				7.4	0.74	0.08
1550	2.3	2.7				6.8	1.14	0.11
1560	1.8	2.5				6.1	1.54	0.20
1570	1.3	2.2	0.98	0.34	0.52	5.4	1.94	0.31
1580	1.0	2.2				5.1	2.16	0.31
1590	0.8	2.1				4.8	2.30	0.37
1600	0.5	1.9				4.2	2.52	0.49
1610	0.5	2.0				4.3	2.52	0.43
1620	0.5	1.8				4.1	2.59	0.49
1630	0.3	1.8				3.9	2.73	0.54
1640	0.3	1.6				3.7	2.74	0.59
1650	0.2	1.6				3.6	2.80	0.62
HCS-1200	3.7	4.0				11.5	-	-
HCS-1500	3.6	3.9				11.2	0.07	0.08
1510	3.5	3.8				11.1	0.10	0.11
1520	3.5	3.7				11.0	0.15	0.13
1530	3.3	3.6				10.7	0.27	0.20
1540	3.6	3.9				11.2	0.08	0.09
1550	3.5	4.0				11.3	0.16	0.00
1560	3.3	4.0				11.1	0.25	0.03
1570	2.8	3.7	1.82	0.74	1.23	10.3	0.63	0.17
1580	2.5	4.0				10.2	0.93	0.04
1590	2.4	3.9				10.0	0.99	0.09
1600	2.0	3.7				9.5	1.27	0.16
1610	1.5	3.6				8.9	1.65	0.22
1620	1.2	3.5				8.5	1.89	0.27
1630	0.9	3.4				8.1	2.10	0.31
1640	0.7	3.0				7.5	2.30	0.48
1650	0.5	3.0				7.2	2.43	0.53

The MnO and SiO_2 reduction degrees of 3 different charges are clearly described in Figure 4. The solid lines represents the reduction degree of MnO and the dotted line the reduction degree of SiO_2. "As/HCS" showed the highest reduction of MnO and SiO_2 compared to its initial amount at 1473 K (1200 °C). On the other hand, the reduction of MnO and SiO_2 in "As" was both relatively slower and lower than "As/HCS".

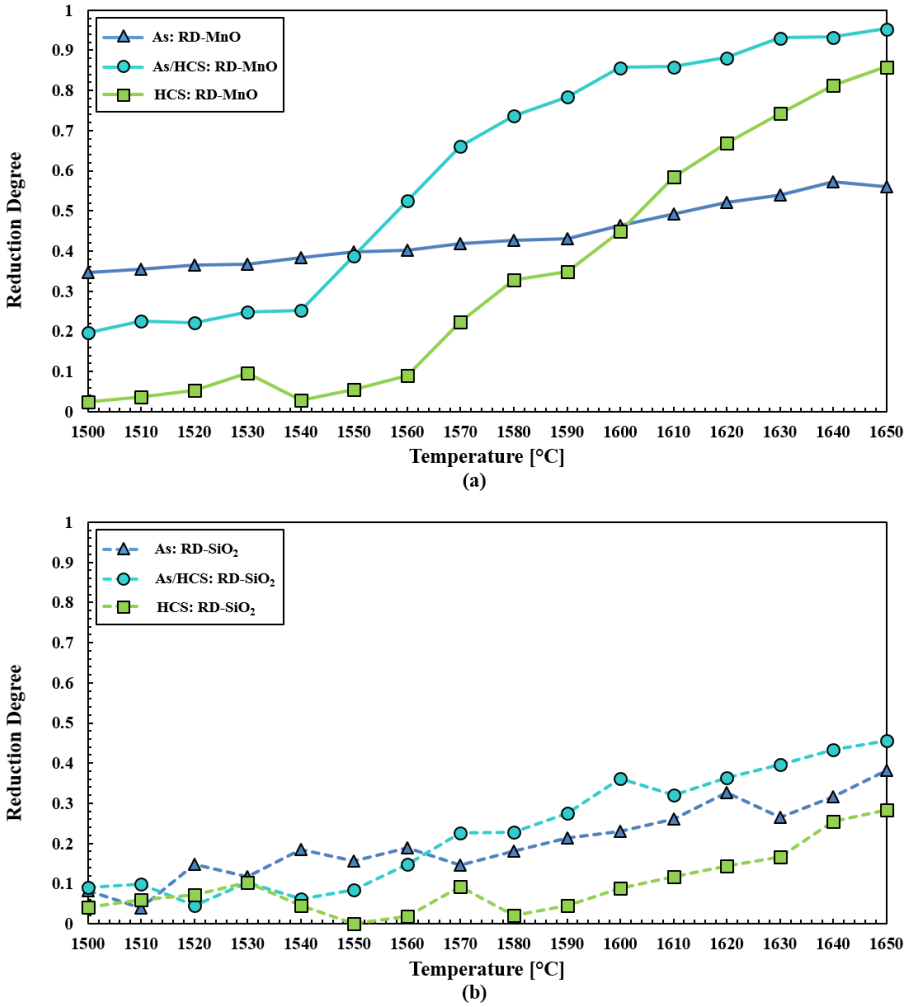

Fig. 4 – The reduction degrees of MnO (a) and SiO_2 (b) for 3 different charge between 1773 and 1923 K (1500 and 1650 °C)

In addition, the a_{MnO} at 1773 K (1500 °C) was the highest in "As/HCS" and lowest in "As", which gives implications of the different reduction degree of MnO. However, the a_{MnO} difference of the 3 different charges were not significant and thus the difference in the driving force is also assumed to be low. This implies that the rate constants should be a factor which is more comparable between the different reduction rates.

B. *Arrhenius plots and Rate models*

The Arrhenius plots for MnO and SiO_2 reduction of the 3 charges have been estimated based on the rates obtained by the TGA results and EPMA analyses. Figure 5 describes the Arrhenius plots of MnO and SiO_2 reduction of the 3 charges. In addition, Table 5 summarizes the activation energies and pre-exponential constants estimated of the 3 different slags between 1773 to 1923 K (1500 and 1650 °C).

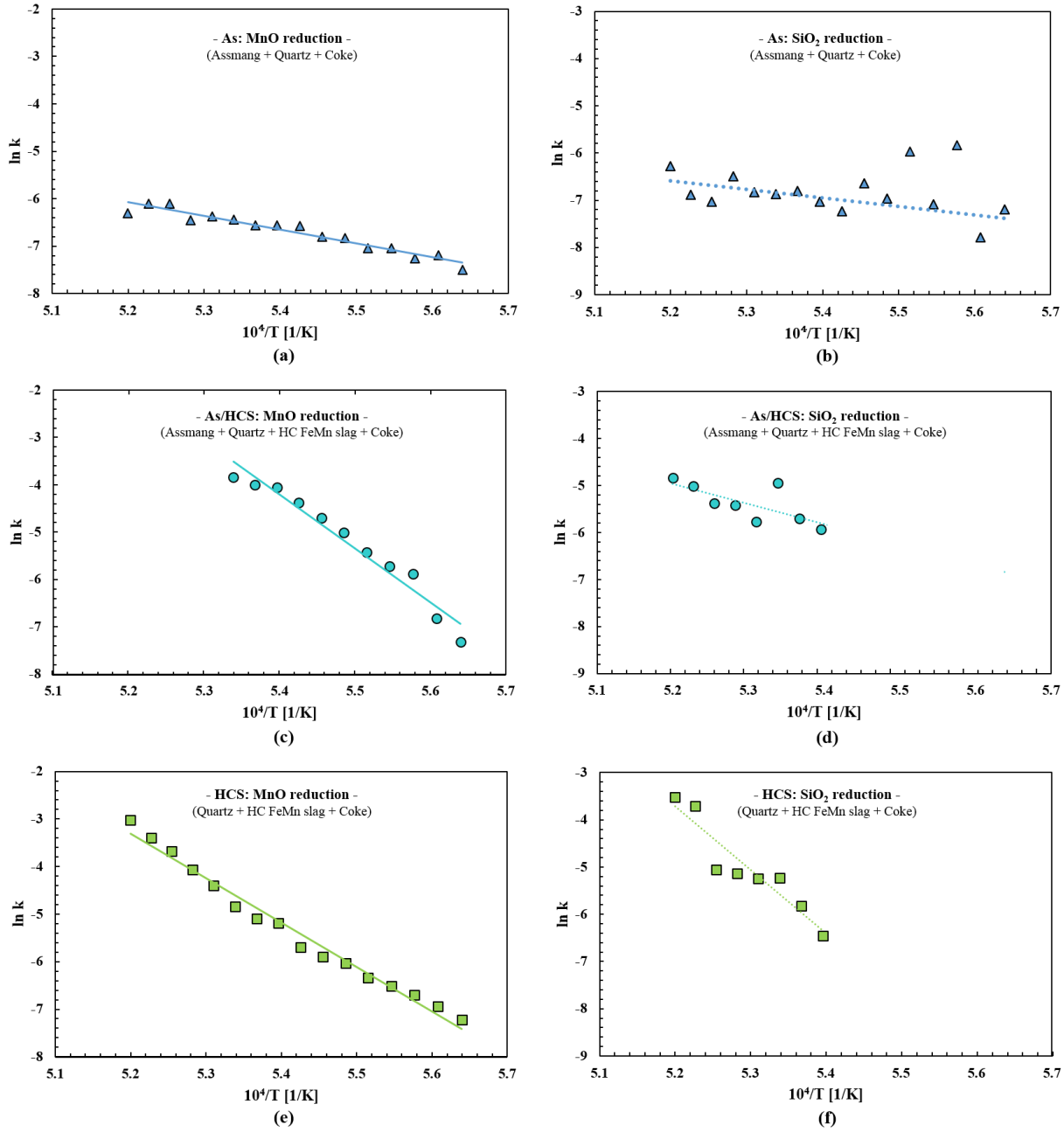

Fig. 5 – Arrhenius plots of MnO reduction (a, c, e) and SiO_2 reduction (b, d, f) between 1773 to 1923 K (1500 and 1650 °C)

Table 5. Summary of the activation energies and pre-exponential constants of the 3 different charges between 1773 and 1923 K (1500 and 1650 °C)

Charge	MnO Reduction	
	Ea [kJ/mol]	k_O [g/min · cm^2]
As	~ 250	9.66×10^{3}
As/HCS	~ 920	1.62×10^{24}
HCS	~ 780	5.87×10^{19}
Charge	SiO_2 Reduction	
	Ea [kJ/mol]	k_O [g/min · cm^2]
As	~ 160	3.04×10^{0}
As/HCS	~ 870	5.92×10^{21}
HCS	~ 1130	6.61×10^{28}

For both MnO and SiO_2 reduction, the estimated activation energies of "As/HCS" and "HCS" were high, while this was not the case for "As". The difference in activation energies implies that the choice of raw material for the charge can have significant impact regarding kinetics. Comparing "As" with "As/HCS" and "HCS", it seems that HC FeMn Slag as raw material in the charge is necessary to obtain significant reduction of MnO and SiO_2. In addition, the considerably lower temperature dependency and rate constant of "As" compared to "As/HCS" and "HCS" also implies that MnO and SiO_2 reduction is hindered by kinetic factors such as viscosity and amount of trace elements.

The viscosities of the 3 charges between 1773 to 1923 K (1500 to 1650 °C), which were obtained by using FactSage 7.0 [13], are described in Figure 6. The increasing viscosities despite of increasing temperature in "As/HCS" and "HCS" indicates changing slag composition due to MnO reduction. On the other hand, the viscosity does not seem to explain the lower reduction degree in "As", which shows the lowest viscosity compared to the other cases. The C+M/A ratio of "As" from Table 3 was around 12.5, which is considerably higher than "As/HCS" and "HCS". This implies that other kinetic factors are prevalent regarding the reduction rate rather than the slag viscosity.

The initial amount of sulfur in slag at 1473 K (1200 °C) of the 3 different charges are shown in Table 6. Sulfur is known to behave as a strong surface-active specie for most metals [15], and the initial amount of sulfur in the charges seems to give the explanation of the different reduction rates observed. "As", which was the lowest reduction rate, had the least amount of sulfur among the charges. The sulfur content was about twice in "As/HCS" and more in "HCS". This implies that the amount of sulfur affects the kinetics more than the slag viscosity. This is in an accordance with recent observations where the initial sulfur content in the charge strongly affected the reduction rates of MnO and SiO_2 [10, 16].

The rate constants are also compared with the different amount of initial sulfur in Figure 7. There seems to be an optimal amount of sulfur regarding reduction rate. "HCS" had more sulfur content than "As/HCS" but the reduction rate was slower. Similar results were observed from a recent study using synthetic raw materials [17]. However, it is not clear whether the sulfur content gave the relatively slower reduction rate in "HCS" than "As/HCS". The Mn-source for "HCS" was only HC FeMn slag, which lacks iron, and previous studies have shown that initial amount of iron leads to MnO reduction by dissolved carbon in the metal [18].

It can be a combined effect of sulfur and initial iron in the case of "As/HCS", but further experiments are required to see which contribution is more.

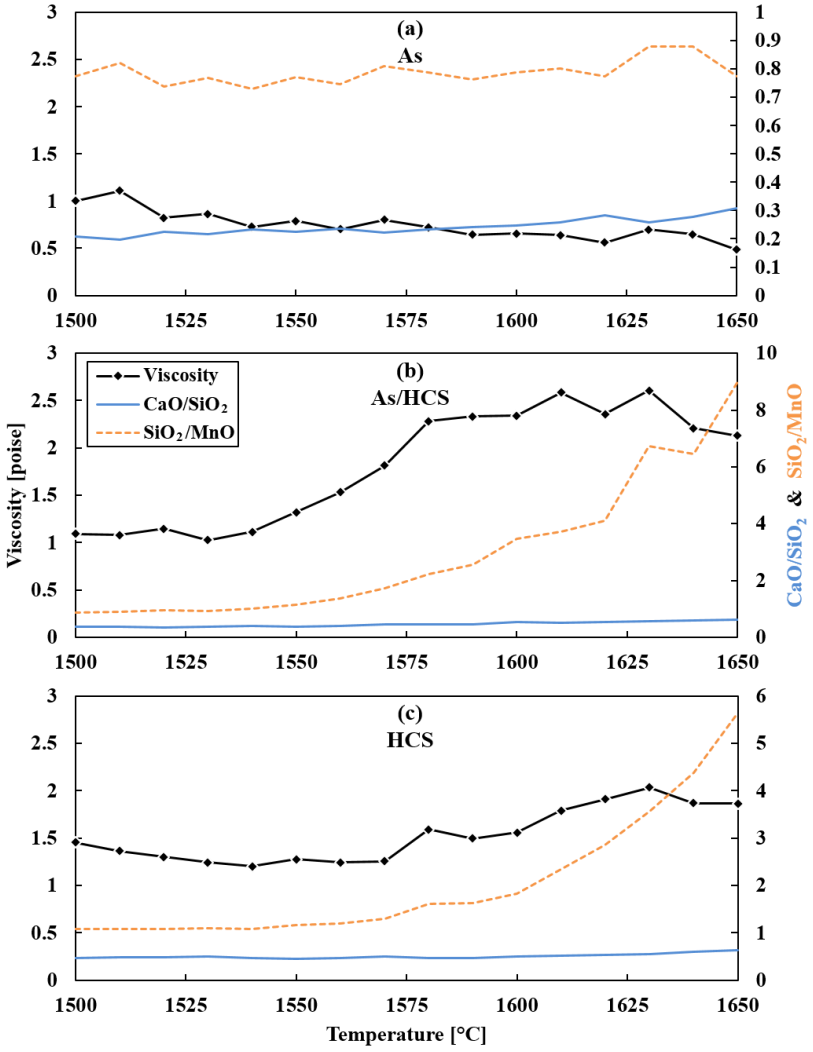

Fig. 6 – Viscosities of "As" (a), "As/HCS" (b) and "HCS" (c) compared with CaO/SiO_2 and SiO_2/MnO ratio between 1773 to 1923 K (1500 and 1650 °C)

Table 6. Initial sulfur content of different charge types (wt % S in coke not included)

Charge type	Slag Composition at 1200 °C [wt %]					
	MnO	SiO_2	CaO	MgO	Al_2O_3	S
As	59.33	32.74	6.23	1.11	0.60	0.16
As/HCS	44.45	34.03	11.48	4.00	6.04	0.29
HCS	32.84	34.15	15.84	6.47	10.71	0.39

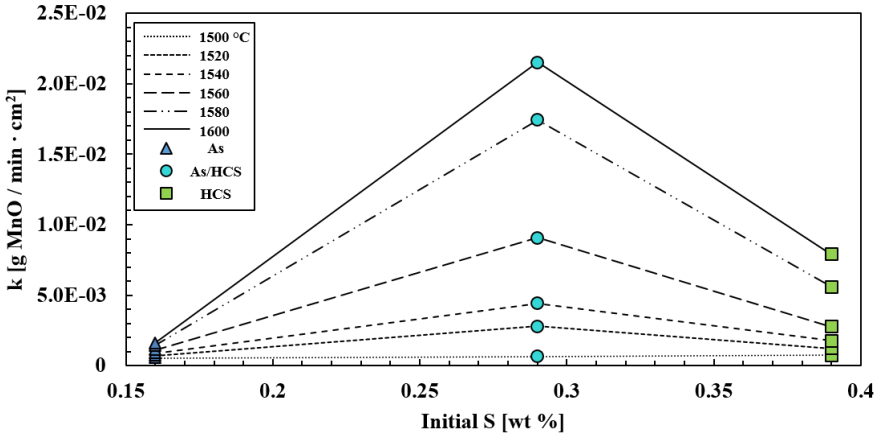

Fig. 7 – Rate constants compare with initial sulfur amount at different temperatures

Based on the parameters estimated on Table 4, the reduction rates of MnO and SiO_2 in SiMn slags can be described by using the rate models, Eqs. (1, 2). The comparisons between the rate models and experimentally measured slag components (MnO and SiO_2) are shown in Figure 8. Note that the parameters which describes the best fit for the 3 charges were applied to the rate models (approximately 2 % error in the raw material analyses).

The comparison shows that the presumed rate models, which were based on FeMn slags in this study, are fairly applicable as well as in SiMn slags. The solid and dotted lines, which describe the relative amount of MnO and SiO_2 from the rate models, showed good match with the measured amount between 1773 to 1923 K (1500 and 1650 °C). Regardless of the reduction extent, the rate models were able to describe the reduction of MnO and SiO_2 in different SiMn slags

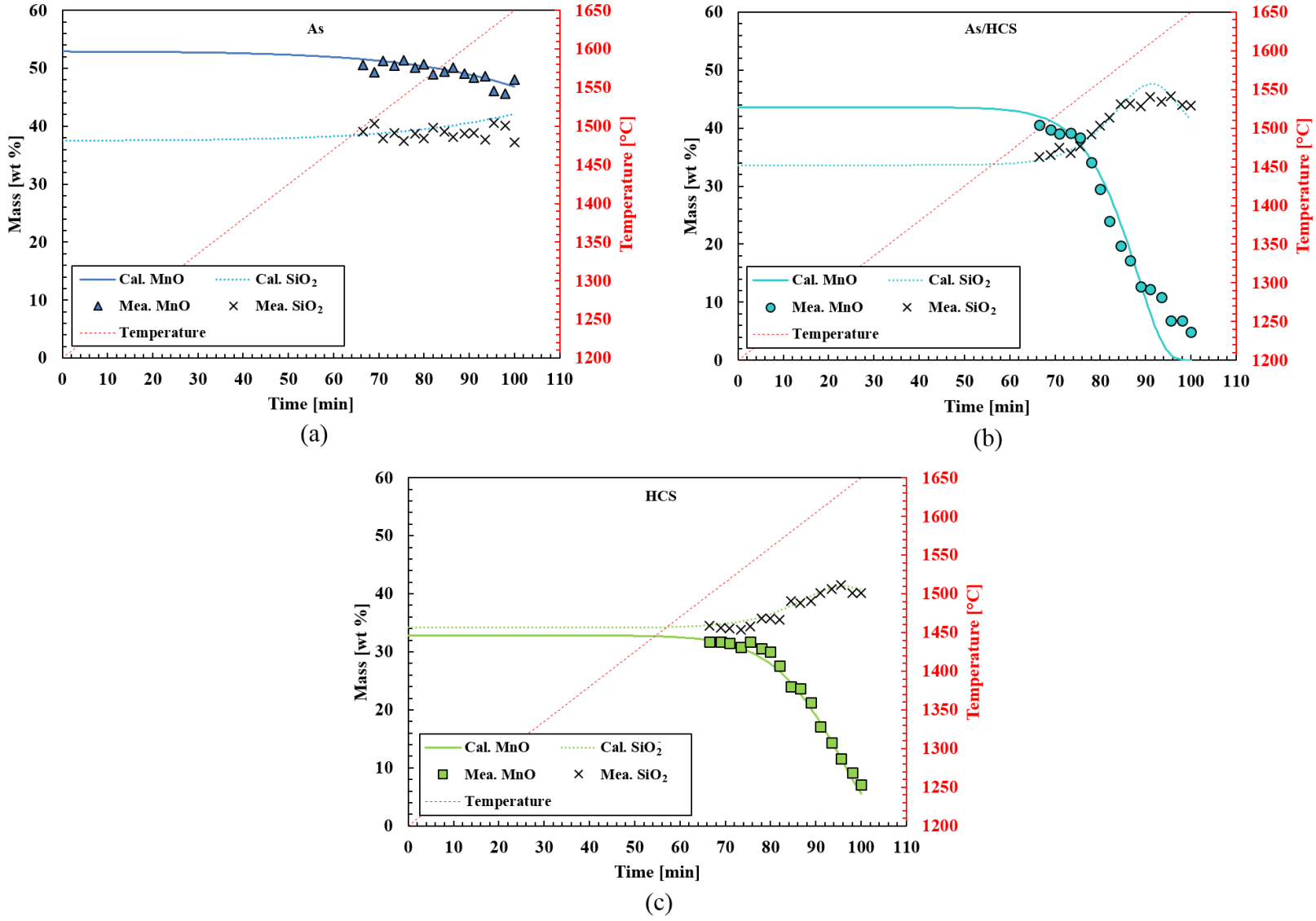

Fig. 8 – The MnO and SiO_2 reduction obtained by using the rate models (solid and dotted lines) and the experimentally measured (symbols) for charges "As" (a), "As/HCS" (b) and "HCS" (c) between 1773 to 1923 K (1500 and 1650 °C)

V. Conclusion

The focus of this study was to estimate the kinetic parameters and evaluate the presumed rate models for MnO and SiO_2 reduction in SiMn slags. TGA results showed that most of the MnO and SiO_2 reduction starts to occur above 1773 K (1500 °C), and the charge "As/HCS" (Assmang + Quartz + HC FeMn Slag + Coke) had the fastest and highest reduction. On the other hand, "As" (Assmang + Quartz + Coke) showed the slowest and lowest reduction even up to 1923 K (1650 °C). The small difference of a_{MnO} among different slags in this case does not necessary explains the different reduction rates.

However, significant difference in kinetic parameters were estimated between "As" with "As/HCS" and "HCS" (High-carbon slag + Quartz + Coke), which implied influence from viscosity and amount of trace elements regarding the reduction rate. Comparison of viscosity showed that the different reduction rates were more affected by the small amounts of sulfur rather than the slag basicity. The effect of sulfur increasing the reduction rate was observed but further experiments are required to isolate both effects from sulfur and initial amount of iron. The presumed rate models were able to describe the reduction of MnO and SiO_2 for the different SiMn slags.

Acknowledgments

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