DISSOLUTION OF QUARTZ IN MN-SLAGS DURING PRODUCTION OF SIMN ALLOY

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ABSTRACT

Silicomanganese (SiMn), containing approximately 16-30% Si, is produced in submerged arc furnaces using various Mn sources and quartz as the primary raw materials, along with fluxes and reductants. In the high-temperature zone known as the coke bed, a silica-rich slag is formed. SiMn is produced through the reduction of SiO_2 from the slag. Dissolution of quartz into slags with different compositions, the primary slag formed from the Mn sources and flux before any MnO reduction occurred, representing conditions at the top of the coke bed, and dissolution of quartz into a partially reduced slag to simulate conditions inside the coke bed has been investigated. Experimental investigations were carried out to study the dissolution of quartz particles of varying sizes, 5 mm and 25 mm in synthetic slags with different compositions at temperatures between 1400 °C and 1600 °C, with varying holding times. Observed results are compared with liquidus compositions and equilibrium phases for original and formed slags. Particle size has been shown to be of little importance for the dissolution. Quartz dissolved more easily in slag at top of the coke bed than slag in the coke bed. Complete dissolution was observed after 30 minutes at 1600 °C in all cases, but not after 0 minutes.

INTRODUCTION

Manganese ferroalloys are essential functional additives in steel production, they are produced in two main qualities: High Carbon Ferromanganese (HCFeMn) and Silicomanganese (SiMn), with the main difference being the higher Si-content in SiMn. Globally, around 4 million tonnes of High Carbon Ferromanganese (HCFeMn) and around 16.6 million tonnes of Silicomanganese (SiMn) were produced in 2022. Several different grades are produced. For standard SiMn the analyses are in the range 65-68 % Mn, 1.5-3 % C and 12.5-21% Si.

The major part of SiMn is produced by carbothermic reduction of oxides in large electric Submerged Arc Furnaces (SAF) of 10-45 MW as illustrated in Figure 1.

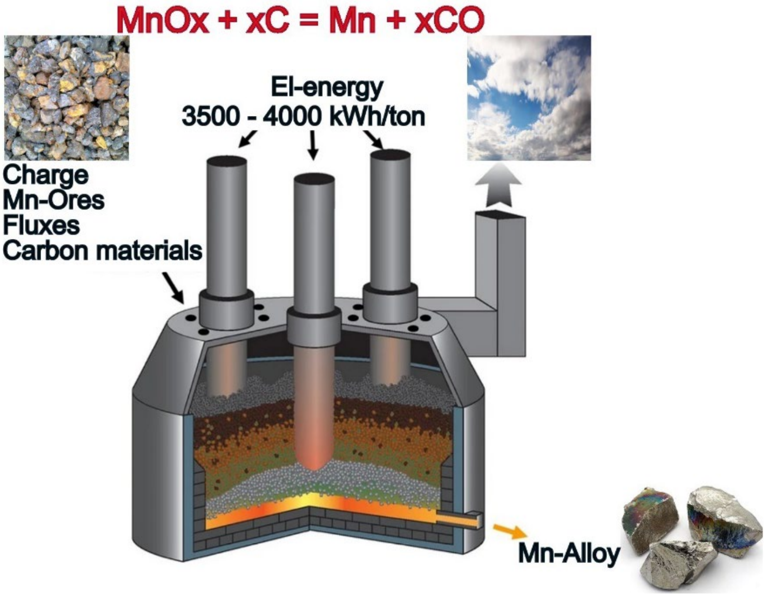


FIG 1 – Overview of Mn-alloy production (Olsen, Tangstad and Lindstad, 2007).

Manganese ores and HCFeMn slags are the main Mn sources and quartz the main Si source. Fluxes as dolomite and limestone are added to adjust the properties of the final slag. Several carbon sources are used as reductant, coke is most common. Raw materials are fed at room temperature to the top of the furnace. Slag and alloy are tapped out at the furnace bottom, at around 1500 °C. Reduction of Mn-oxides produces a CO/CO_2 gas mixture that leaves at the top of the charge mixture. The process and reactions were extensively studied and described by Olsen, Tangstad and Lindstad (2007).

During the production of silicomanganese alloys, the submerged arc furnace can be divided into two main reaction zones (Olsen, Tangstad and Lindstad, 2007). Their existences have been confirmed by excavation of industrial furnaces of Mn-alloys (Ringdalen and Ksiazek, 2018; Olsen and Tangstad, 2004; Nordbø, Øvrelid and Gridset, 2021). In the upper part of the furnace, the prereduction zone, the raw materials are solid, and reductions take place by gas-solid reactions. In the lower part of the furnace, the coke bed, slag, and metal are liquid. Here heat is generated by ohmic resistance in solid coke. Most of the supplied energy is consumed here, and the final reduction of MnO to Mn and of SiO_2 to Si takes place in this zone by the following main reactions.

$$(MnO) + C = \underline{Mn} + CO_{(g)} \qquad (1)$$
$$(SiO_2) + 2C = \underline{Si} + 2CO_{(g)} \qquad (2)$$
$$2(MnO) + \underline{Si} = 2\underline{Mn} + (SiO_2) \qquad (3)$$

At the top of the coke bed, the initial slag is formed by melting and reduction of the Mn sources and dissolution of the fluxes. When the viscosity of the slag is low enough, it will drain into the coke bed. The temperature where this is achieved defines the temperature at the top of the coke bed and influences the temperature in the coke bed (Olsen, Tangstad and Lindstad, 2007). The type of Mn sources and their composition as well type of fluxes and reductants affects melting and reduction at the top of the coke bed (Ringdalen, Tangstad and Brynjulfsen, 2015).

In SiMn-production, quartz is added to obtain high enough SiO_2 content in the slag, typically 38-44 %, to have high enough SiO_2 activity in the slag to obtain the required Si-content in the alloy. Composition of the charge mixture vary with the Mn source used and targeted product composition. Its MnO content is normally so high that during melting it will first form a MnO containing liquid slag in equilibrium with solid MnO, or MnO-containing phase (Ringdalen, Gaal, Tangstad and Ostrovski, 2010). This will be present until MnO in the solid-liquid mixture have been reduced to a MnO content where there are no solid equilibrium phase present at the given temperature. Slag with around 10 % MnO is tapped out at around 1600 °C at the bottom of the furnace. Quartz transforms during heating to other SiO_2 polymorphs and is at the top of the coke bed, where the temperature is 1200-1600 °C, present as cristobalite or amorphous silica or a mixture of these (Ringdalen, 2014). SiO_2 will here dissolve in the primary slag formed from MnO sources and fluxes with a $MnO-SiO_2$ content of the primary slag as illustrated in Figure 2.

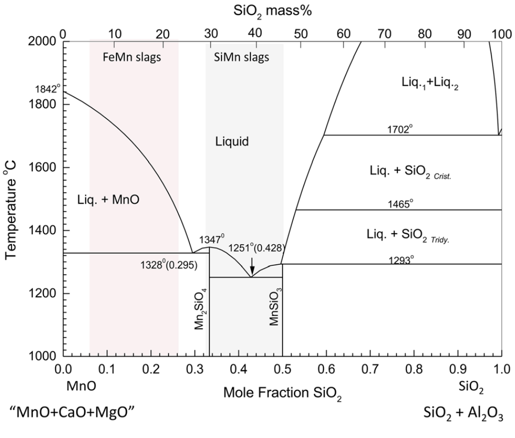


FIG 2 – $MnO-SiO_2$ phase diagram indicating the primary slag in FeMn and SiMn production (Tangstad et al, 2021).

Dissolution rate of SiO_2 into the slag will, as described by Tangstad et al (2021), affect the reduction to SiMn-alloy according to two main scenarios: if SiO_2 dissolves fast and simultaneously with solid

MnO, the reduction will be from the average charge composition. If dissolution of SiO_2 is slower, this will determine the composition of the liquid slag and reduction of SiO_2 to Si is determined by SiO_2 dissolution in the primary Mn-slag. In small-scale experiments where Mn sources and quartz particles up to 2 cm were mixed, SiO_2 was found to dissolve in the slag from Mn sources at temperatures below 1400 °C (Tangstad et al, 2021; Kim, 2018). In contrast, Maroufi and coworkers (2014) found that the dissolution rate of SiO_2 in Mn slags was determined by mass transfer of silica in the slag. The experiments were conducted at 1400-1500 °C, using an industrial tap slag with 15% MnO and 45% SiO_2. The SiO_2 source was fused silica, either as a crucible in static experiments with 1 g of slag or as a rotating rod in dynamic experiments with 130 grams of slag. Undissolved quartz has, as shown in Figure 3, been found in the coke bed in industrial excavations (Ringdalen and Ksiazek, 2018) while no quartz was observed in the coke bed in other (Ringdalen and Ksiazek, 2018; Norbø, Øvrelid and Gridset, 2021). Similarly, quartz has been observed in the coke bed in some pilot experiments with SiMn-production, while not seen in most (Ringdalen and Tangstad, 2013; Ringdalen and Solheim, 2018). If large amounts are present, it will strongly affect the electrical current paths and coke bed temperature.

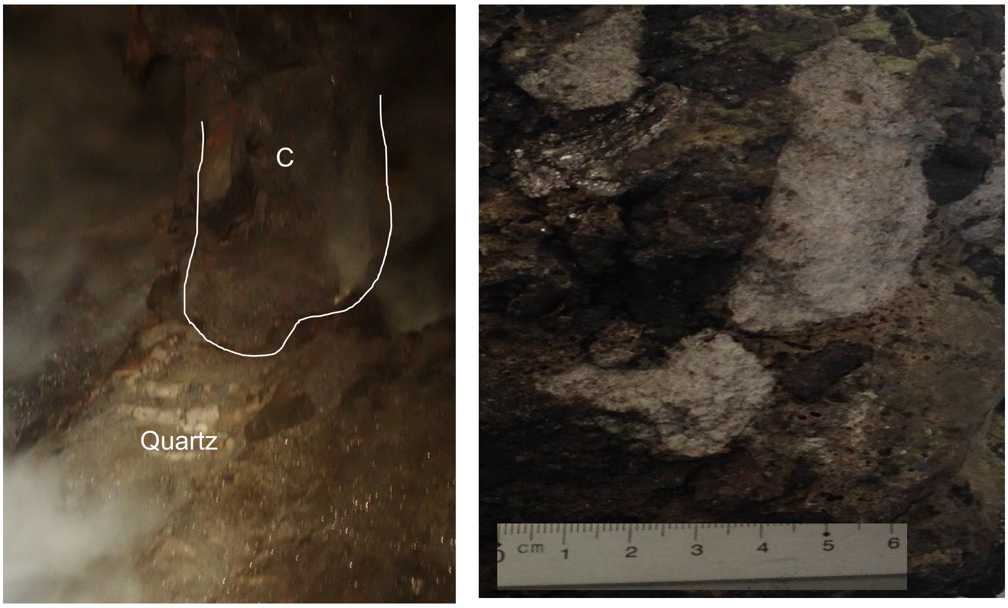


FIG 3 – Quartz in coke bed from excavation of SiMn furnace at Glencore *(*Ringdalen and Ksiazek, 2018). Position of layers of quartz in coke bed below electrode C to the left and quartz pieces in the coke bed to the right.

Effect of different parameters on dissolution of quartz in Mn-slag under various conditions as well as its effect on industrial furnace operation seems from this not to be clear and requires further investigations.

In the current study, dissolution of quartz in primary slag at the top of the coke bed and partly reduced slag in the coke bed has been compared for two different particle sizes of quartz. The basis was a slag from a charge mixture with Comilog ore, quartz and limestone earlier used in small scale reduction experiments (Larssen, 2017; Canaguier and Tangstad, 2020). Based on this slag, two different slag compositions were investigated. In both slags % SiO_2 was around 75 % of target, simulating the situation when not all SiO_2 had been dissolved into the slag. One of the slags had the original MnO content simulating the situation at the top of the coke bed with simultaneous melting of Mn-ore and dissolution of quartz. The other slag contained around 15 % MnO, simulating the situation in the coke bed when MnO is partly reduced and when there still is undissolved quartz present. The value 15 % is taken from measurements of %MnO in slag in pilot scale experiments (Ringdalen and Solheim, 2018). In industrial furnaces the slag content is expected to be lower. To allow investigations of near industrial particle sizes of quartz, the experiments were run in a graphite crucible with diameter of 11.8 cm heated in an induction furnace.

EXPERIMENTAL

In the dissolution experiments, quartz in two different size fractions were dropped into preheated synthetic slags with two different compositions, one simulating quartz dissolution at the top of the coke bed, and the other simulating quartz dissolution in the coke bed during SiMn production. Compositions of the two slags used in the experiments were based on a charge mixture of Comilog, ore, quartz and limestone used in earlier experiments (Larssen, 2017; Canaguier and Tangstad, 2020) and with a composition given in Table 1.

TABLE 1 – Composition of charge mixture of Comilog ore, quartz and limestone used as basis for calculations of slag compositions (Canaguier and Tangstad, 2020).

MnO [wt%]	SiO_2 [wt%]	CaO [wt%]	MgO [wt%]	Al_2O_3 [wt%]
49.81	31.36	13.58	0.3	4.95

This composition was used to simulate the slag at the top of the coke bed. To simulate the slag in the coke bed, MnO content was adjusted to 15 %, maintaining the same ratio between the other oxides. Additionally, for both slags, the percentage of SiO_2 was adjusted to 75 % of the calculated value to simulate the dissolution of remaining SiO_2, with the MgO content excluded. The composition was then normalised to 100 %. The calculated slag compositions are given in Table 2. Synthetic slags with these compositions were prepared from powders of pure oxides MnO, SiO_2, CaO, and Al_2O_3 from VWR chemicals. These powders were mixed, melted in a graphite crucible heated to 1700 °C in an induction furnace, cooled down and crushed to 20 – 25 mm pieces. EPMA analysis of the synthetic slag showed that it was homogenous, only phases formed during solidification, and no undissolved particles were observed. The composition of the synthetic slag was determined by XRF at an independent laboratory (Nemko Norlab). As shown in Table 2, the synthetic slag has a composition close to the planned one. This also confirms that slags with high MnO content can be produced in a graphite crucible without reduction of MnO.

TABLE 2 – Composition of the planned and the produced slags for the dissolution of quartz experiments.

Slag	MnO [wt%]	SiO_2 [wt%]	CaO [wt%]	Al_2O_3 [wt%]
Slag 1 planned	54.22	25.60	14.78	5.39
Slag 1 produced	54.05	26.58	15.12	5.54
Slag 2 planned	15.00	47.54	27.45	10.01
Slag 2 produced	15.12	48.71	25.84	10.04

Quartz pieces for the dissolution experiments were Snekkevik quartz provided by Eramet Norway with typical composition given in Table 3. The quartz particles had, as seen in the EPMA picture in Figure 4, small inclusions of minerals containing either Fe or Mg, K rich silicates, mainly along the grain boundaries.

TABLE 3 – Typical composition of Snekkevik quartz used in the dissolution experiments (Larssen, 2017).

MnO [wt%]	SiO_2 [wt%]	CaO [wt%]	MgO [wt%]	Al_2O_3 [wt%]	K_2O [wt%]
0.36	94.13	3.4	0.06	0.61	0.14

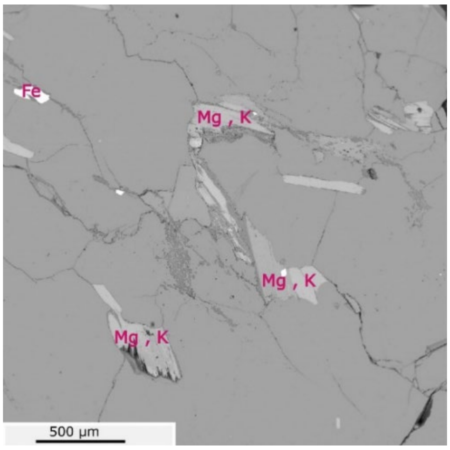


FIG 4 – The untreated quartz used for dissolution experiments contained inclusions of minerals such as Mg, K and Fe along grain boundaries as observed in the EPMA image.

The quartz was crushed and screened to make two different particle sizes: 5 mm and 25 mm, which were used to investigate effect of particle size in the dissolution experiments. 5 mm particles were made by screening at 5 mm and 6.5 mm, and 25 mm particles by screening at 20 mm and 30 mm.

The experiments were conducted in a 75-kW induction furnace produced by Inductotherm with a frequency of 2500 kHz. The materials were placed in an inner graphite crucible, 11.5 cm in diameter and 40 cm high with a closed bottom, open top and no gas purging. Temperatures were measured with a type C thermocouple placed at the crucible bottom. This was also used to control the heating of the furnace. Temperature at the top of the molten slag was assumed to be the same as the measured temperatures at the bottom of the crucible. Stirring of the liquid slag due to induction was assumed to cancel out the large temperature gradient normally found in this apparatus. Experimental temperatures have due to this some uncertainties. The same furnace and crucible were used both for production of synthetic slag and for dissolution experiments. Set-up for dissolution experiments is shown in Figure 5.

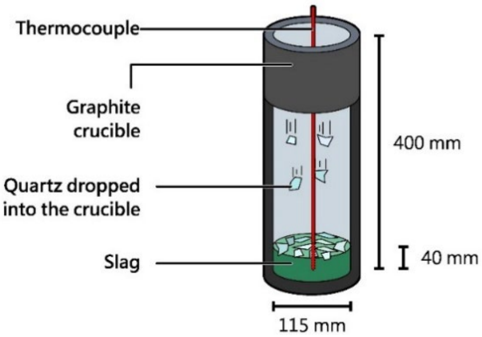


FIG 5 – Crucible used for production of synthetic slag and for dissolution experiments, here illustrating set-up for dissolution experiments.

In the dissolution experiments, the crucible was initially filled with either 1000 or 1500 grams of synthetic slag which, when melted, would reach a level of around 40 mm from the crucible bottom. The temperature was then heated at a rate of 40 °C/min until the desired temperature of 1400 °C, 1500 °C or 1600 °C was reached. Once the temperature stabilized, 50-150 grams of either 5 mm or 25 mm quartz particles were dropped into the molten slag, as shown in Figure 5. Behaviour of the quartz during dissolution was recorded using a DJI Osmo video camera for experiments at 1500 °C and 1600 °C. The crucible was held at the designated temperature for either 0 minute or 30 minutes, after which it was removed from the furnace for rapid cooling. The cooled crucible was then vertically cut into two halves. Samples were taken from the lower part of the crucible and their compositions determined by chemical analysis by XRF at a commercial laboratory, Nemko Norlab. Samples from the upper part of the crucible with partly dissolved quartz were drilled out and investigated using a back-scattered electron probe micro-analyser (EPMA), type JEOL JXA-8500, The investigations included qualitative elemental mapping as well as quantitative phase composition analysis from various positions. Composition of the various slags were calculated from composition of the solidified phases determined by EPMA, and their relative amounts determined by Adobe Photoshop CC.

Liquidus temperatures and equilibrium solid phase below this, was calculated by FactSage 8.3 with the Equilib module using the FToxid and FactPS databases.

In total, 24 dissolution experiments were conducted, with the experimental parameters detailed in Table 4 in the results section.

RESULTS

The main effects of the investigated parameters can be seen in Table 4 where conditions for the different experiments are provided and the experiments where undissolved quartz particles were found, by EPMA, in the slag after the experiment are marked with grey.

No clear effect of quartz particle size could be observed in these experiments Slag composition had, as expected, a major influence on quartz dissolution: in Slag 2 with high SiO_2 content, quartz was only completely dissolved only when it had been held for 30 minutes at 1600 °C, while in Slag 1 with lower SiO_2 content quartz was completely dissolved after 0 minutes at 1600 °C and 30 minutes at 1500 °C. The temperatures will also affect the dissolution, and quartz was not dissolved in any of the slags after 30 minutes at 1400 °C, while all quartz was dissolved in both slags after 30 minutes at 1600 °C. Similarly, the holding time was of importance and in Slag 1 quartz had not dissolved after 0 minutes at 1500 °C but was completely dissolved after 30 minutes at this temperature. The same was observed at 1600 °C in Slag 2.

TABLE 4 – Overview over conditions in the conducted experiments with experiments with undissolved quartz particles marked in grey.

	Slag 1	**Slag 2**	**Quartz size**		**Temperature**			**Holding time**		**Amount, gram**	
Exp	**26 % SiO_2**	**48 % SiO_2**	**5mm**	**25 mm**	**1400 °C**	**1500 °C**	**1600 °C**	**0 min**	**30 min**	**Slag**	**Quartz**
1	x		x				x	x		1500	100
2	x		x				x		x	1500	100
3	x			x			x	x		1000	153
4	x			x			x		x	1000	156
5	x		x			x		x		1000	50
6	x		x			x			x	1000	50
7	x			x		x		x		1000	107
8	x			x		x			x	1000	104
9	x		x		x			x		1000	50
10	x		x		x				x	1000	50
11	x			x	x			x		1000	104
12	x			x	x				x	1000	102
13		x	x				x	x		1000	100
14		x	x				x		x	1000	100
15		x		x			x	x		1000	100
16		x		x			x		x	1000	100
17		x	x			x		x		1000	50
18		x	x			x			x	1000	50
19		x		x		x		x		1000	102
20		x		x		x			x	1000	113
21		x	x		x			x		1000	50
22		x	x		x				x	1000	50
23		x		x	x			x		1000	104
24		x		x	x				x	1000	108

Introduction of the quartz to the slag bath lowered the temperature of the slag by around 50 °C for a short time. Together with the assumption of uniform temperature in the slag bath, this introduced uncertainties in the experimental temperature. This is not expected to have a major influence on the qualitative effects described above.

Videos from dropping of quartz into the slag revealed, as illustrated in Figure 6, that the large 25 mm quartz particles formed cracks and disintegrated to smaller pieces in the initial stages of the dissolution when quartz met and reacted with the slag bath. Occurrence of slag filled cracks in the partly dissolved 25 mm particles, as seen in Figure 7, was confirmed by EPMA investigations of particles from experiments stopped immediately after the quartz was introduced. In Figure 6 quartz seem to have been completely dissolved in the last pictures, after 2 minutes. This is not the case: the quartz has just disintegrated and been immersed in the slag to a degree where it cannot be observed. Slag 2 contained undissolved quartz particles after 30 minutes at 1500 °C.

Cracking and disintegration of quartz particles that meet the warm slag can explain why particle size will not affect the observed dissolution of quartz after 0 minutes and 30 minutes.

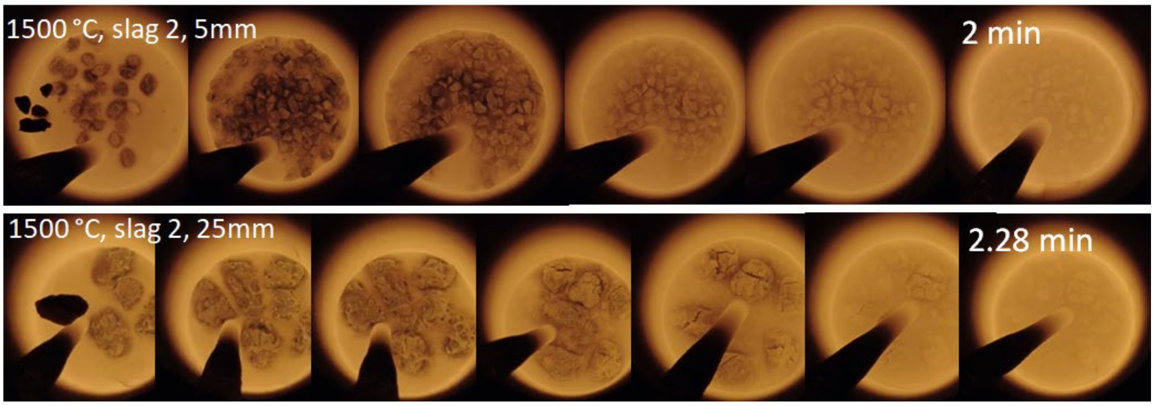


FIG 6 – Details from dissolution of 5 mm and 25 mm quartz particles into slag 2 at 1500 °C, Pictures taken from videos from the first 2 minutes of dissolution.

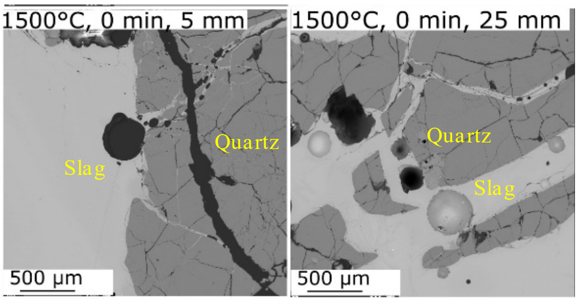


FIG 7 – Quartz, 5 mm and 25 mm particles, partly dissolved in slag 2 with 48 % SiO_2 after 0 minutes.

Detailed studies of the first minutes of dissolution indicates, as seen in Figure 8, that the larger, 25 mm particles in spite of the cracking kept their shape longer and needed longer time than the smaller particles to be immersed in the slag. These observations are only indicative. More quantitative data regarding reactions the first 2 minutes will require a clearly defined zero point and high accuracy for the temperature measurements at the top of the slag. This phenomenon and its effect were thus not further investigated in the current work.

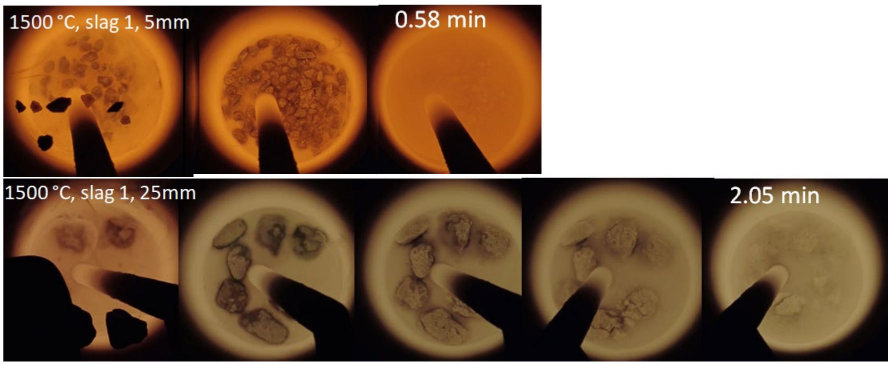


FIG 8 – Difference between 5 mm and 25 mm quartz during first 2 min of dissolution in Slag 1 at 1500 °C. Pictures taken from videos.

Slag 2, simulating the slag in the coke bed, has a higher SiO_2 content (48 % SiO_2) than Slag 1 with (26 % SiO_2) simulating slag at the top of the coke bed, formed from the charge mixture without any MnO reduction. Both slags are, at all the experimental temperatures, at or above their liquidus temperature and SiO_2 will not be the first phase formed in any of the two slags.

TABLE 7 – Liquidus temperature and first solid phase formed during solidification of the two investigated slags. Calculated by FactSage 8.3 with the Equilib module using the FToxid and FactPS databases.

	MnO [wt%]	**SiO_2 [wt%]**	**Liquidus [°C]**	**First solid phase**
Slag 1	54.05	26.58	1401	MnO
Slag 2	15.12	48.71	1255	$(Mn,Ca)SiO_3$

Quartz, SiO_2 particles, dissolved easiest in the slag with the lowest SiO_2 content and was completely dissolved at lower temperatures and after shorter time in Slag 1 than in Slag 2. Quartz was, for example, dissolved at 1500 °C after 30 minutes in Slag 1, but not after 30 minutes in Slag 2. At 0 minutes, quartz was not dissolved in Slag 1 at 1500 °C, and completely dissolved at 1600 °C in Slag 1, but not dissolved in Slag 2 at 1600 °C. This difference is also indicated when the first minutes of dissolution of quartz at 1500 °C in Slag 1 and Slag 2 are compared in Figure 9. Quartz particles were completely immersed in Slag 1 after around 1 minute while around 2 minutes were needed for the quartz to be immersed in Slag 2.

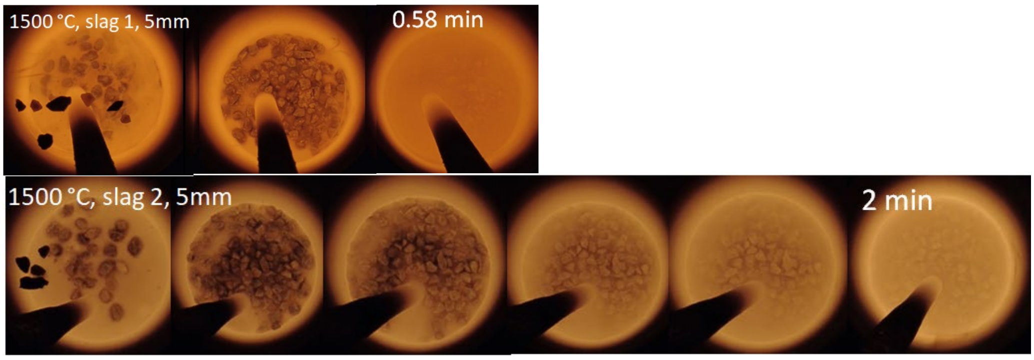


FIG 9 – Comparison of first minutes of dissolution of quartz in Slag 1 and Slag 2 at 1500 °C. Pictures taken from videos.

The difference between dissolution in the two slags were investigated more in detail by studying partly dissolved quartz particles and the slag surrounding them with backscatter pictures and analysis by EPMA. This showed a major difference between the dissolution in the two slags as illustrated in Figure 10.

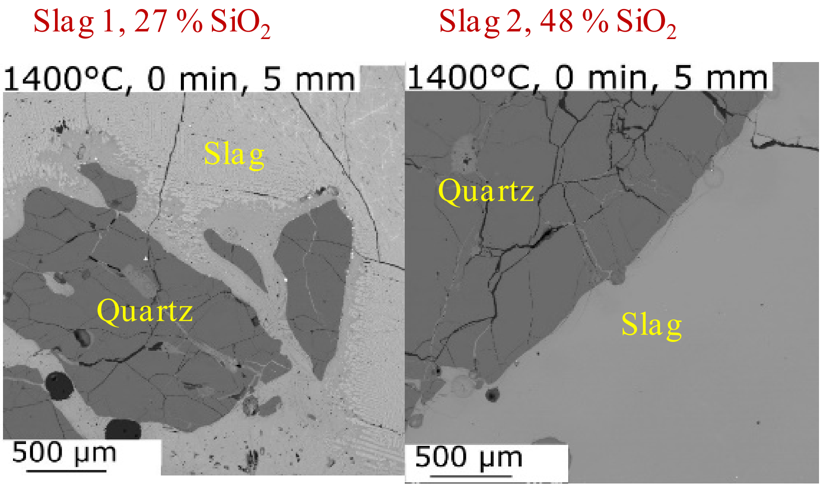
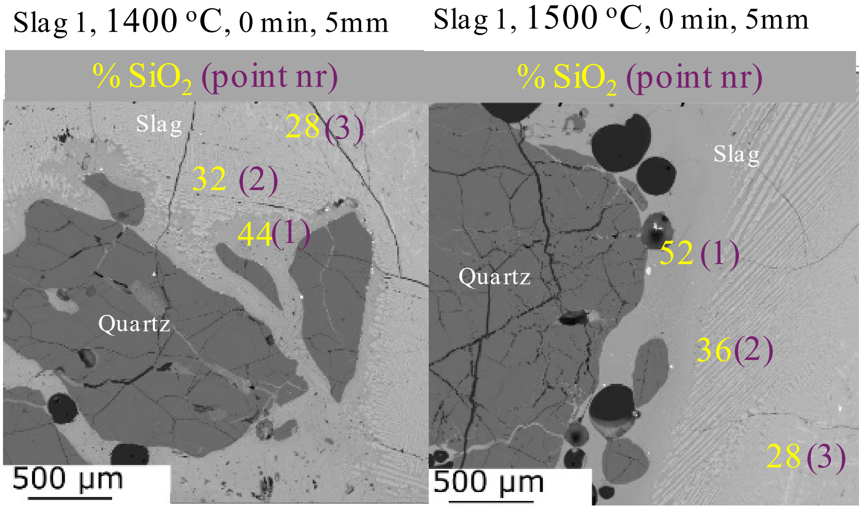


FIG 10 – Quartz, partly dissolved in Slag 1 left and slag 2 to right. 5 mm particles after 0 minutes at 1400 °C.

Slag surrounding quartz particles dissolved in Slag 2, with highest SiO_2 content, was homogenous and had approximately the same composition as the original slag. This was seen in all cases with undissolved quartz in Slag 2 for all temperatures, holding times and particle sizes. There were no indications of concentration gradients of elements due to slow mass transfer in the slag phase. This could indicate that dissolution mechanism of quartz in Slag 2, is controlled by the chemical reaction at the quartz/slag interface.

In contrast quartz partly dissolved in Slag 1 was, as shown in Figure 11, surrounded with layers of slag with different compositions. % SiO_2 was highest in slag closest to the quartz particles and decreased outwards. Around 500-1000 µm away from the quartz particle, the slag had the same composition as the original slag. Solid MnO, the first solid phase to form in Slag 1, was not found in any of the slags. The slag must then have been above liquidus also at 1400 °C. Composition of the slag layers varied with temperature and at 1500 °C the layers closest to the quartz had higher SiO_2 content than corresponding layers at 1400 °C. At 1600 °C all quartz was dissolved. Similar layering was seen for dissolution of 25 mm quartz particles.


Slag 1, 1400 °C, 0 min, 5mm

Slag 1, 1500 °C, 0 min, 5mm

FIG 11 – Layers of slag surrounding quartz partly dissolved in Slag 1 at 1400 °C to left and at 1500 °C to the right, % SiO_2 and point nr for the different slag layers are marked. Backscatter images with analysis from EPMA.

Content of the other elements in the slag vary with distance from the quartz particles and is given in Table 6 for the points marked in Figure 11.

TABLE 6 – Content of selected elements in slag around 5 mm quartz partly dissolved in Slag 1 after 0 minutes at 1400 °C and 1500 °C, given for points marked in Figure 11. Liquidus and first solid phase calculated by FactSage 8.3 with the Equilib module using the FToxid and FactPS databases.

	SiO_2		MnO		CaO		Al_2O_3		K_2O		Liquidus °C		First solid phase	
T °C	**1400**	**1500**	**1400**	**1500**	**1400**	**1500**	**1400**	**1500**	**1400**	**1500**	**1400**	**1500**	**1400**	**1500**
(1)	44	52	36	33	14	10	6	5	0.20	0.23	1355	1310	$(Mn,Ca)SiO_3$	SiO_2
(2)	32	36	41	48	15	13	12*	5	0.18	0.23	1112	1234	Olivine	Olivine
(3)	28	28	53	53	16	16	5	5	0.01	0.01	1355	1338	MnO	MnO

* This Al_2O_3 value is assumed to be an outlier

All the slags were, during the experiments, above their liquidus temperature and thus completely molten. K_2O content is not included in these calculations but is expected to reduce the liquidus temperature. In the experiments at 1400 °C, liquidus temperature for the slag in contact with quartz was less than 50 °C below the experimental temperature. This is within the range of temperature reduction that can be caused by quartz introduction in the slag bath. A solid phase could have been present in this slag, but no indications of this were observed. Since the equilibrium solid phase just below liquidus for this slag is $(Mn,Ca)SiO_3$, and not SiO_2, existence of the solid phase would not have stopped the dissolution of SiO_2. K_2O had accumulated around the quartz was with 0,20-0,23% higher here than in the quartz where it is 0.14% and in the bulk slag where it is 0,01 %. Quartz was the source of K_2O while there was no K_2O in the synthetic slag. The accumulation of K_2O around the quartz particles can be a factor affecting the dissolution. Since K_2O in the original quartz occur mainly in cracks and along grain boundaries, its concentration is not expected to have a major impact on the dissolution of the SiO_2 grains. K_2O content affects the slag properties such as viscosities and diffusivities and may through this affect both the dissolution of SiO_2 at the grain boundaries and the mass transfer in the slag.

Formation of slag in or intrusion of slag along grain boundaries or into cracks was observed in many of the experiments as illustrated in Figure 12. In the case shown here, there was a thin zone with slag around the quartz particle, with small SiO_2 grains partly connected to the quartz. This phenomenon can provide more information about the mechanism for quartz dissolution but was not systematically studied in the current investigation and will not be further discussed.

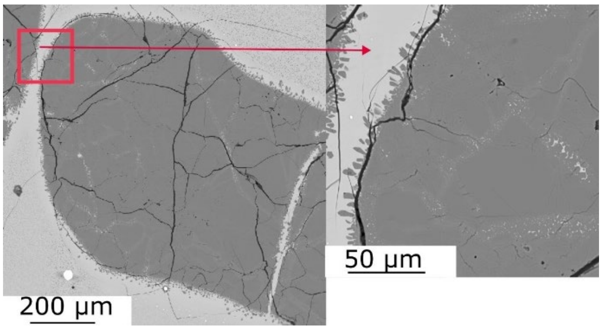


FIG 12 – Details of dissolution of 25 mm quartz particles in Slag 1 after 30 minutes at 1400 °C.

DISCUSSION

The main objective of the current investigations was to study the effect of quartz particle size on the dissolution in slags relevant for SiMn-production, e.g. slag at top of coke bed (Slag 1) and slag in coke bed (Slag 2). Slag composition was based on a case with Comilog ore as Mn source.

Particle size of quartz, 5 mm versus 25 mm, seems to have very little effect on the time or the temperature needed for quartz to dissolve in any of the slags. The larger quartz particles disintegrated to smaller particles when meeting the slag, cancelling out the original size difference. The quartz particles were immersed in the slag during the first 1 to 2 minutes, and larger particles seemed to need longer time, around 1 minute more than the smaller particles to be completely immersed. Disintegration of the particles and intrusion of slag into the cracks are assumed to have taken place during this period. In industrial SiMn-production, quartz is heated together with the other materials, and will have the same temperature as the slag it is dissolved in. The quartz will then not experience the same thermal shock as in these experiments. In industrial SiMn production it could thus be possible that the particles keep their original size down to the coke bed and size effects could be seen. Investigations for Si and FeSi production on cracking and fines formation from quartz during continuous heating for 1 hour by the TSI method, show that quartz will disintegrate during heating, but the extent varies considerably with quartz source (Ringdalen, 2015). Based on this some disintegration of quartz that will cancel out effect of original size differences is expected.

Time and temperature needed for dissolution of quartz in slag depend on slag composition. Quartz was completely dissolved in Slag 1, simulating slag at the top of the quartz bed, after 30 minutes at 1500 °C, while it was not dissolved under the same conditions in Slag 2 simulating the slag in the coke bed. A main difference between the two slags is the lower SiO_2 content in the slag at the top of the coke bed where quartz dissolved at lowest temperatures.

When quartz dissolved in Slag 1, simulating the slag at the top of the coke bed, layers with different slag composition were formed around the quartz particles. SiO_2 and K_2O contents were highest close to the quartz-slag interface. The slags were above liquidus, not saturated with SiO_2. But the high SiO_2 content in slag, in immediate contact with quartz, will give a lower driving force for the dissolution. Both mass transfer and quartz-slag reaction at the interface can thus be of importance. A higher SiO_2 content in the boundary layer at 1500 °C versus 1400 °C indicates that rate of the chemical reaction increases more with temperature than the mass transfer in the slag. The boundary slag layer also had a higher K_2O content than the slag further away from the quartz particles indicating slow mass transfer of this compound from its source, quartz. In studies with continuous heating of similar charge mixtures, slag was formed at lower temperatures than the liquidus temperature for the charge mixture (Tangstad et al, 2021; Larssen, 2017; Kim, 2018). In these cases, longer heating times were used. A major difference is that in these cases the slag was formed from ores that contained minor elements that are expected to affect slag properties and wetting between solid phases and slag, with K_2O being one of those. The studies of continuous heating of a charge mixture are more a simulation of the conditions in an industrial production, while the current studies give more detailed information about the dissolution of quartz and effect of parameters related to this.

When quartz was dissolved in a slag simulating the conditions in the coke bed, higher temperatures or longer time were needed for complete dissolution compared with the slag with lower SiO_2 content at the top of the coke bed. The difference was seen both in the cooled down samples and in the videos of the first minutes of dissolution. Slag close to the interface of quartz partly dissolved in Slag 2 had the same composition as the bulk slag. Based on the characterisation methods used in these investigations, it was not observed any. layers of slag with higher concentration of SiO_2 close the quartz particles. Dissolution of quartz in the coke bed is thus assumed not to be governed by mass transfer in the slag. Reaction between quartz and slag is believed to determine rate of dissolution. The high SiO_2 content in this slag compared with Slag 1 will give a lower driving force for dissolution that can be a main reason for this. Other investigations have, in contrast, found mass transfer in the slag to be rate determining (Maroufi et al, 2014). The investigation this was based on used a slag with a slightly lower SiO_2 content than in the present work. The raw materials were an industrial SiMn slag and fused silica, in contrast to the synthetic slag and industrial SiO_2 sources used in the current investigations. In the current investigations K_2O, which is 0.14 % in the quartz, was dissolved into a slag without K_2O, while in the other case pure SiO_2 was dissolved in a slag with 2.7 % K_2O (Maroufi et al, 2014). Behaviour of K_2O or other minor elements may affect the dissolution and is a potential reason for the observed differences. Such phenomena were not investigated in the current work.

CONCLUSIONS

Dissolution of 5 mm and 25 mm quartz particles at 1400 °C, 1500 °C and 1600 °C in two different slags have been investigated, one simulating conditions at the top of the coke bed and one simulating conditions in the coke bed during SiMn production. With the investigation methods used here, it was not observed any effect of particle size on time or temperature needed for complete dissolution. The coarser particles disintegrated to smaller particles when they met the slag. Dissolution of quartz in slag at the top of the coke bed required shorter time and lower temperature to be completed than dissolution of slag in the coke bed. When quartz dissolves in slag at the top of the coke bed it is surrounded by layers with different slag composition with decreasing SiO_2 content outwards from quartz. When quartz dissolves in the coke bed, it was surrounded by bulk slag without any layering. In both cases, all slags were above liquidus. Mass transfer seems to play a role in dissolution of quartz at the top of the coke bed but was in the current case not of importance for dissolution of quartz in the coke bed. This can be changed by minor elements that occur in industrial slags.

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