Liquidus Relations of SiMn Slags

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Abstract

Liquidus compositions have been determined at 1300 °C, 1350 °C and 1450 °C for quaternary CaO-Al_2O_3-SiO_2-MnO slags in the compositional range of silicomanganese slags. The standard technique of drop quenching was used and the samples were analysed by microprobe. By analysing the quenched glass in the sample, the liquidus composition at the temperature of the experimental run was ascertained. Addition of 6 and 12% MnO as substitution for the same amounts of CaO in CaO-Al_2O_3-SiO_2 slags extended the liquid area and lowered the liquidus temperatures. The effect was more pronounced with 12 % MnO addition. The results are consistent with previous literature.

Introduction

Silicomanganese (SiMn) is produced in electric submerged arc furnaces. The raw materials are, in addition to coke, mixtures of manganese ores, MnO-rich ferromanganese slag and quartzite. It is difficult to make alloys above 20-22 % Si by direct smelting of ores, slag and quartz. The amount of slag produced varies within wide limits, say from 700 to 1500 kg/ton of metal. Typical compositions of slag and metal are shown in Table I. SiMn slag is, due to its low manganese content, a throwaway product.

The physico-chemical properties of the slag are of great importance for easy tapping and for the yield of manganese and also for the silicon and carbon content of the alloy. The SiMn process is more difficult than high carbon ferromanganese (HC-FeMn) process. Under normal smelting conditions, the slag is fairly fluid and is easily tapped from the furnace. If the process is disturbed, the SiO_2 content of the slag raises and the slag becomes extremely viscous. The tapped viscous slag entraps metal that may cause considerable loss of alloy. Therefore the slag composition, its melting relations and its viscosity should be constantly checked. The equilibrium distribution of Mn and Si between slag and metal was investigated earlier and published recently by Ding and Olsen[1]. The equilibrium content of MnO in SiMn slags at 1600 °C was reported to be close to 9% MnO in silica saturated slags and about 4% MnO in typical SiMn slags with 40-45% SiO_2.

The main components of the SiMn slags are SiO_2, CaO, Al_2O_3 MgO and MnO. The multicomponent SiMn slag system can suitably be presented in ternary slag diagrams, as shown in Figure 1. Relatively little is published about smelting relations of the five component slags. Warren *et al*[2] measured the effect of MnO on the liquidus temperatures in the system CaO- MgO-Al_2O_3-SiO_2. It was observed that addition of 13%MnO to these slags lowered the liquidus temperature except for very basic slags. Urquhart[3] reviewed published information on liquidus relations for the same slag system. It was found that addition of 5-20% MnO and of SiO_2 will lower the liquidus temperatures. MgO at small additions was also claimed to reduce the liquidus temperature whereas larger additions would have the reverse effect. Addition of CaO was claimed to increase the liquidus temperatures. Eric *et al*[4] measured liquidus temperatures in CaO-MnO(5-30%)-MgO-SiO_2-Al_2O_3 slags using the hot-stage microscope. Liquidus temperatures were found to vary between 1300 °C to 1380 °C in the slags investigated, and increased with increasing basicity ratio.

For estimation of liquidus temperatures in SiMn slags, the relatively small content of MnO is often added to the MgO or to the CaO content. Then the system is simplified to the four component system SiO_2-CaO-Al_2O_3-MgO which is thoroughly described in the literature by Muan and Osborn[5] and in the Slag Atlas[6]. The intention of the present work has been to study the effect of MnO on liquidus relations and to compare the effects of MnO and MgO additions to the system CaO-Al_2O_3-SiO_2 in the compositional range of SiMn slags.

The standard technique of drop quenching have been used, and the samples were analysed by microprobe. By analysing the quenched glass in the sample, the liquidus composition at the temperature of the experimental run can be ascertained.

Experimental procedure

Master slags with different silica contents and a selection of $(CaO+MnO)/Al_2O_3$ ratios were prepared from pure oxides: SiO_2 (Pro analysis grade), CaO (Lab grade), Al_2O_3 (Pro analysis grade), and α MnO (99.5%). The slags were melted under argon in graphite crucibles, using a vertical graphite tube furnace. The slags were quenched under a high flow rate of argon and crushed in a Sieb Tecknik ring mill. The master slags were analysed by MOLAB AS using XRF. The initial compositions of the slags are given in Table II and illustrated in Figure 2. To the master slags were added 5 and 10% manganese oxide which resulted in about 6 and 12% MnO in the liquid phases. About one gram of slag was used for each experiment.

A vertical tube furnace with graphite element was used in the liquidus temperature experiments. The furnace consisted of two sections, one of plexiglass that acted as the waterbath, and the other the hot region of the furnace. The hot region was isolated from the waterbath by a VAT gate vacuum valve. This valve allowed the furnace to be heated at the same time as having water in the bottom section. Samples were placed in Mo crucibles and were loaded into the furnace from the bottom. They were suspended from a special hook on the sample release device. This device allowed the sample to be released by an anticlockwise turn, without the furnace interior being exposed to air. The entire furnace was evacuated for oxygen removal using a rotary pump and a diffusion pump, followed by the release of argon into the system to atmospheric pressure. The VAT gate was then closed and water released into the lower plexiglass section. The furnace was heated to the experimental temperature of 1300 °C, 1350 °C or 1450 °C. The samples were held in the hot zone for 1.5 hours and then quenched by opening the VAT gate and rotating the sample release device, allowing the sample to drop into the water bath beneath the furnace. An illustration of the apparatus is presented in Figure 3.

Argon gas of 99.99% purity with oxygen levels <10 ppm was used in the experiments. Furthermore, the graphite environment in the furnace was expected to secure sufficiently low oxygen potential. No analyses were carried out to determine the Mn^{2+}/Mn^{3+} ratio of the slags.

The errors introduced in these experiments came from the temperature measurements and the microprobe analysis. The thermocouple was calibrated using an Isotec Saturn furnace, a reference thermocouple and a Solarton voltmeter 7061. The thermocouple was calibrated using standards whose accuracy was traceable to national and international standards. An error of ±2.2 °C at 1300 °C was determined.

The quenched slag samples were sectioned to allow examination in a JEOL superprobe. Slags that were held below the liquidus temperature, contained both a glass and a crystalline phase. Both phases were analysed. 3 repeat analyses by the microprobe of each sample were carried out to obtain an average value. The glass phase represents the liquidus composition at the temperature of the experimental run. The composition of the solid phase tells in which phase field the slags are located.

Experimental results and discussion

At experimental temperatures the slag consists of various amounts of two phases, the liquid phase and the solid gehlenite or anorthite. The microprobe analyses of the glass phase, representing the liquids, are shown in Table III. 5% and 10% MnO were added to the initial slags. Most of added MnO is recovered in the liquid phase, where the average content is close to 6% and to 12% for low and high additions respectively. The MnO contents of the liquids are somewhat higher for experiments at the lowest temperature due to the larger amount of the low-MnO solid phase.

Liquidus lines for the slags containing on average about 6% and 12% MnO are shown in the Figures 4 and 5 respectively. Only one of the slags, S3.1, contained solid phase at 1450 °C. Therefore, the majority of the experimental runs were completed at 1300 °C and 1350 °C. The liquidus composition lines were constructed from the data points for individual liquidus compositions. Due to scatter in the data, there is little separation between the 1300°C and the 1350°C lines. The 1450°C liquidus curve was estimated from observed trends in the lower liquidus data and the individual data point at 1450°C.

Two separate phase fields were ascertained, gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) and anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$). Analyses of the solid phases were carried out and typical analyses are shown in Table IV. The gehlenite phase contained on average about 1.6 % MnO and the anorthite phase about 0.3 % MnO. However, as these analyses were influenced by incorporation of surrounding glass, it is uncertain how much of this MnO that stems from the glass phase.

The Figures 6(a) and 6(b) show liquidus compositions for slags with 6 % and 12 % MnO compared with MnO-free slags at 1300 °C and 1350 °C respectively. The MnO addition extends the liquid area, and the liquidus temperatures are from 50 °C to 100 °C lower than in corresponding MnO-free slags. Comparison with the CaO-Al_2O_3-SiO_2 phase diagram[5] shows that the phase fields are similar to the system without MnO.

The effects of 6% MnO and of 5% MgO addition to CaO-Al_2O_3-SiO_2 slags are compared at 1300 °C in Figure 7(a) and at 1350 °C in Figure 7(b). The MgO data were taken from the Slag

Atlas[6]. It should be noticed that MnO and MgO are added as substitution for the same amounts of CaO. Then the left corner of the slag diagrams, Figure 4 to 9, will represent the sum of the basic oxides CaO, MnO and MgO. That makes it easy to compare the relative effect of these oxides. Slags containing MnO extends the liquid area towards slags with less silica, whereas the MgO containing slag has a larger liquid field in the direction of higher silica and lower alumina contents.

Slags with 12 % MnO are compared in a schematic outline with slags containing 10% MgO in Figure 8. The effect of 12% MnO is described above, whereas the replacement of 10% CaO with MgO has the effect of decreasing the liquid area and to increase the liquidus temperature somewhat.

Warren *et al*[2] presented individual data points for slags containing 13% MnO over a range of temperatures and compositions. An estimated liquidus line at 1300 °C, based on their data, has been drawn in Figure 9 for comparison with present results for the slags with approx. 12% MnO. The agreement is good for slags with about 20% Al_2O_3 and not so good for slags with around 10% Al_2O_3.

Conclusion

Silicomanganese slags will normally contain between 6 and 12% MnO. The well-established CaO-Al_2O_3-SiO_2-MgO liquidus diagrams may be used to estimate liquidus temperatures of such slags. A substitution of 6 and 12% CaO in CaO-Al_2O_3-SiO_2 slags with MnO leads to an extension of the liquid area and a lowering of the liquidus temperatures. Replacement of 5 to 10% CaO in CaO-Al_2O_3-SiO_2 slags with the same amounts of MgO has the opposite effect, which is to increase the liquidus temperature somewhat.

Typical silicomanganese slags with around 40% SiO_2, 10 to 20% Al_2O_3, and 6% MnO are expected to have liquidus temperatures close to 1300 °C whereas higher MnO contents will give liquidus temperatures below 1300 °C.

Acknowledgements

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Table I. Typical compositions of silicomanganese alloy and silicomanganese slag (mass%).

Silicomanganese alloy				Silicomanganese slag				
Mn	Fe	Si	C	CaO	Al_2O_3	SiO_2	MgO	MnO
65-70	10-15	17-20	1.5-2.0	20-35	10-25	38-42	2-12	5-8

Table II: Initial slag compositions used in experimental runs (mass%).

Sample	CaO	Al_2O_3	SiO_2	MnO	Total	CaO/Al_2O_3
S1.1	31.5	32.9	29.0	5.1	98.5	0.96
S1.2	29.7	31.8	32.1	5.0	98.6	0.93
S1.3	28.9	30.5	34.4	4.8	98.6	0.95
S2.1	36.8	25.6	30.4	5.4	98.2	1.44
S2.2	34.0	23.1	30.5	5.0	92.6	1.47
S2.3	33.8	24.2	36.1	5.0	99.1	1.40
S3.1	41.8	20.0	30.8	5.4	98.0	2.09
S3.2	40.2	19.4	33.9	5.3	98.8	2.07
S3.3	38.5	18.2	36.0	5.0	97.7	2.12
S4.1	29.3	28.8	29.5	9.0	96.6	1.02
S4.2	28.2	27.9	31.6	9.1	96.8	1.01
S4.3	29.5	20.6	36.5	9.9	96.5	1.43
S5.1	34.5	24.0	29.8	8.9	97.2	1.44
S5.2	34.0	23.7	30.6	9.1	97.4	1.43
S5.3	33.2	22.8	32.1	9.0	97.1	1.46
S6.1	40.3	18.0	29.3	8.9	96.5	2.24
S6.2	39.4	17.6	30.6	8.9	96.5	2.24
S6.3	38.0	17.1	32.3	8.9	96.3	2.22

Table III: Liquidus compositions of slags at 1450, 1350 and 1300 °C determined by analysis of glass in the slags by JOEL microprobe (mass%).

Sample	Temperature (°C)	CaO	Al_2O_3	SiO_2	MgO	MnO	Total	CaO/Al_2O_3
S1.1	1300	31.69	23.16	37.33	0.56	7.31	100.06	1.37
S1.2	1300	40.55	13.65	41.50	0.50	4.71	100.91	2.97
S2.1	1300	37.61	14.05	40.43	0.51	7.55	100.14	2.68
S2.2	1300	37.82	15.83	39.91	0.52	6.74	100.82	2.39
S2.3	1300	32.67	25.00	36.85	0.50	5.02	100.04	1.31
S3.1	1300	30.62	23.38	37.81	0.50	6.14	98.45	1.31
S3.2	1300	42.25	11.43	41.11	0.46	5.34	100.59	3.70
S3.3	1300	30.59	23.10	39.46	0.57	5.99	99.70	1.32
S1.1	1350	30.52	25.95	35.43	0.58	6.63	99.11	1.18
S1.2	1350	29.61	26.64	34.94	0.51	5.74	97.44	1.11
S1.3	1350	29.27	27.54	37.21	0.50	4.83	99.36	1.06
S2.1	1350	38.30	14.56	38.66	0.60	7.64	99.75	2.63
S2.2	1350	36.73	17.16	38.08	0.55	6.03	98.55	2.14
S2.3	1350	34.72	21.71	39.41	0.51	4.46	100.80	1.60
S3.1	1350	43.74	9.98	36.26	0.58	7.48	98.04	4.38
S3.2	1350	41.41	12.60	39.54	0.55	5.09	99.20	3.29
S3.3	1350	39.72	14.80	40.46	0.54	4.71	100.23	2.68
S3.1	1450	44.43	14.48	35.84	0.67	5.54	100.96	3.07
S4.1	1300	41.26	8.67	36.38	0.72	13.94	100.97	4.76
S4.2	1300	27.95	24.63	35.03	0.48	10.55	98.63	1.13
S4.3	1300	33.78	14.25	36.37	0.59	14.61	99.61	2.37
S5.1	1300	31.08	19.36	37.01	0.56	12.27	100.27	1.61
S5.2	1300	39.53	11.13	38.09	0.63	10.39	99.77	3.55
S5.3	1300	33.00	16.30	37.05	0.61	12.52	99.48	2.02
S6.1	1300	27.65	24.51	34.85	0.52	11.55	99.08	1.13
S6.2	1300	42.27	7.22	37.40	0.34	11.85	99.08	5.85
S6.3	1300	33.19	15.42	36.22	0.59	14.37	99.80	2.15
S4.1	1350	33.49	18.22	35.12	0.66	12.82	100.31	2.61
S4.2	1350	39.64	14.01	37.08	0.70	9.85	101.28	4.02
S4.3	1350	40.64	11.69	35.10	0.70	10.54	98.66	3.86
S5.1	1350	29.03	26.91	33.36	0.54	10.63	100.46	2.73
S5.2	1350	42.06	9.86	36.04	0.59	12.14	100.69	3.47
S5.3	1350	27.15	26.50	33.96	0.55	10.83	98.98	2.51
S6.1	1350	33.68	18.41	35.14	0.64	12.65	100.51	2.66
S6.2	1350	30.57	20.44	36.07	0.49	10.26	97.83	2.98
S6.3	1350	29.15	26.66	34.46	0.47	9.60	100.33	3.04

Table IV: JEOL microprobe analyses of the solid phases - gehlenite and anorthite (mass%).

Sample	Temperature (°C)	%CaO	%Al_2O_3	%SiO_2	%MgO	%MnO	Total
Gehlenite:	**$2CaO{\cdot}Al_2O_3{\cdot}SiO_2$**	**40,9**	**37,2**	**21,9**			
Gehl. 3.1	1450	40,11	34,87	22,90	0,15	0,60	98,64
Gehl. 4.1	1350	40,54	33,01	23,58	0,43	2,06	99,61
Gehl. 4.2	1350	40,12	32,85	23,45	0,37	1,85	98,63
Gehl. 4.3	1350	40,86	33,26	22,46	0,37	1,07	98,01
Gehl. 5.1	1350	40,64	35,93	21,85	0,12	1,41	99,95
Gehl. 5.2	1350	41,46	33,02	23,94	0,59	1,63	100,63
Gehl. 5.3	1350	39,13	33,32	23,81	0,26	2,33	98,84
Gehl. 6.1	1350	40,96	32,68	23,98	0,44	2,49	100,54
Gehl. 4.2	1350	41,10	34,42	23,06	0,38	1,42	100,37
Gehl. 6.3	1350	40,42	35,55	22,36	0,10	1,49	99,91
Gehl. Aver	1350	40,58	33,78	23,17	0,34	1,75	99,61
Gehl. 1.1	1300	40,46	33,48	24,60	0,29	1,49	100,32
Gehl. 1.2	1300	40,91	32,81	23,98	0,52	1,30	99,52
Gehl. 1.3	1300	40,73	31,54	25,62	0,56	1,62	100,06
Gehl. 2.1	1300	39,99	29,06	26,08	0,71	2,57	98,40
Gehl. 2.2	1300	41,40	32,60	23,90	0,49	1,46	99,85
Gehl. 3.2	1300	40,52	28,84	25,83	0,76	2,05	98,01
Gehl. Aver	1300	40,67	31,39	25,00	0,55	1,75	99,36
Anorthite:	**$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$**	**20,1**	**36,7**	**43,2**			
Anor. 2.3	1300	20,26	35,09	44,88	0,04	0,26	100,53
Anor. 3.3	1300	20,52	34,64	44,07	0,03	0,46	99,72
Anor. 1.3	1350	19,72	34,89	44,65	0,01	0,17	99,43
Anor. Aver	1300/1350	20,17	34,87	44,53	0,03	0,30	99,89

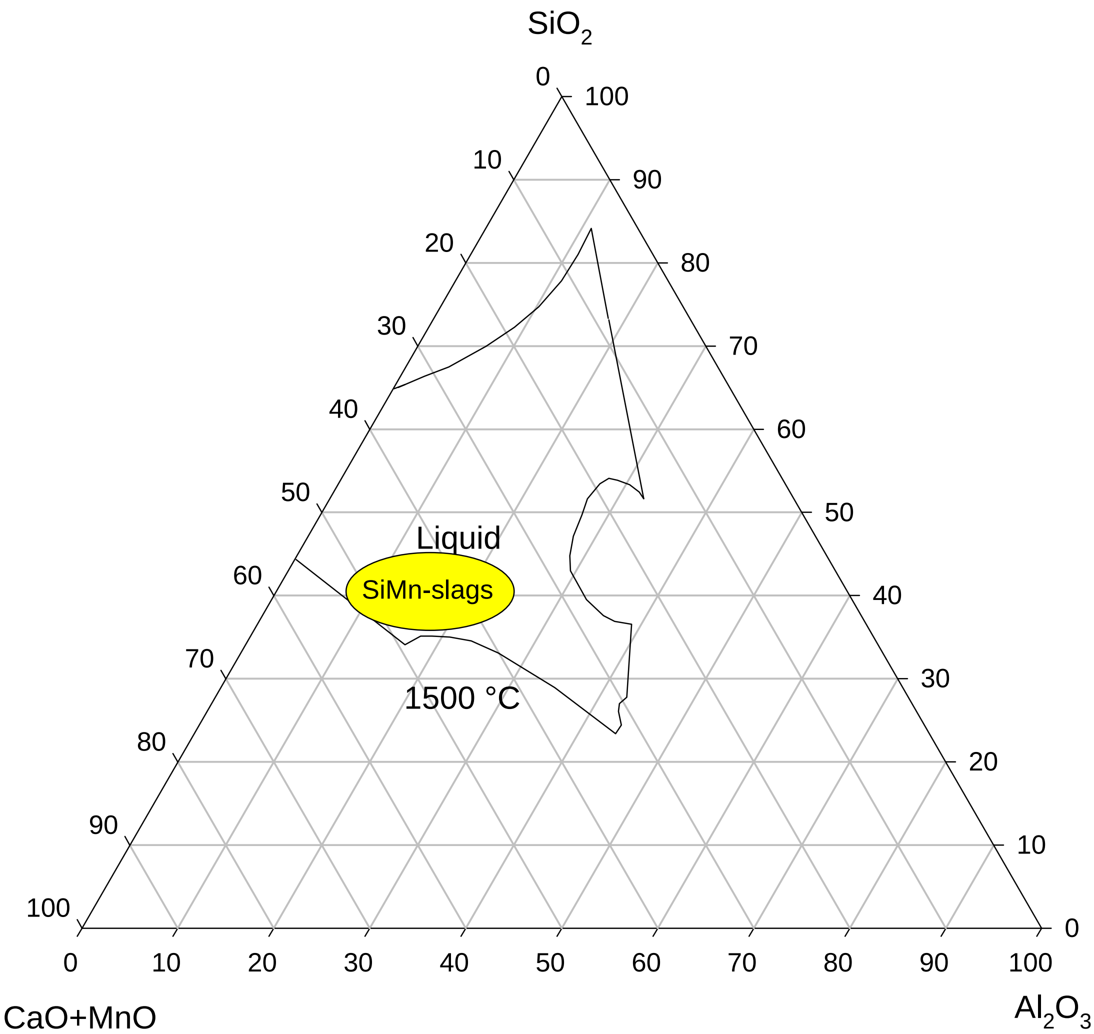


Figure 1. Ternary diagram indicating the liquid region at 1500 °C for slags in the system (CaO+MnO)-Al_2O_3-SiO_2. The composition area of silicomanganese slags is also indicated.

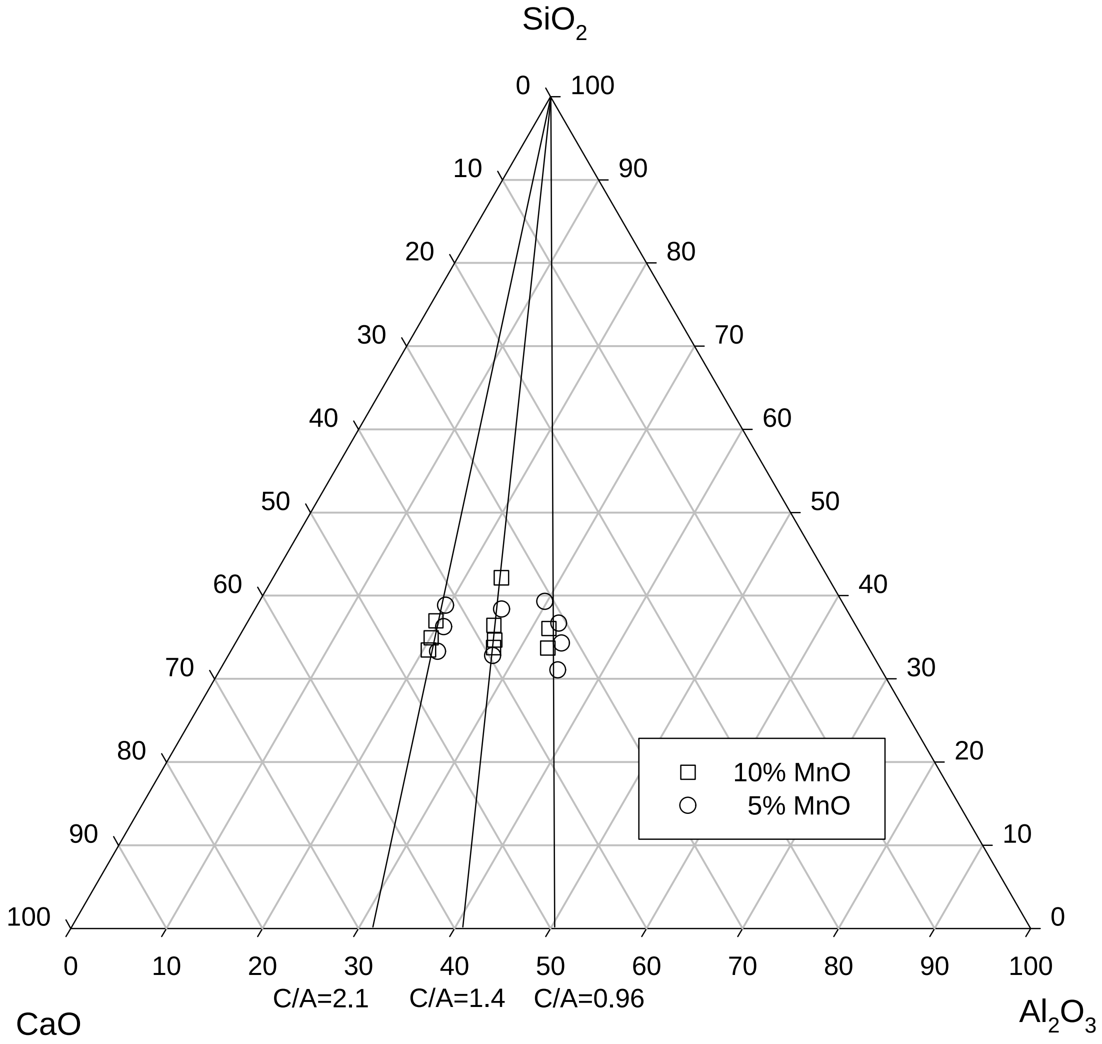


Figure 2. Initial slag compositions used in the determination of liquidus compositions. 5 and 10% MnO were added to these initial slags.

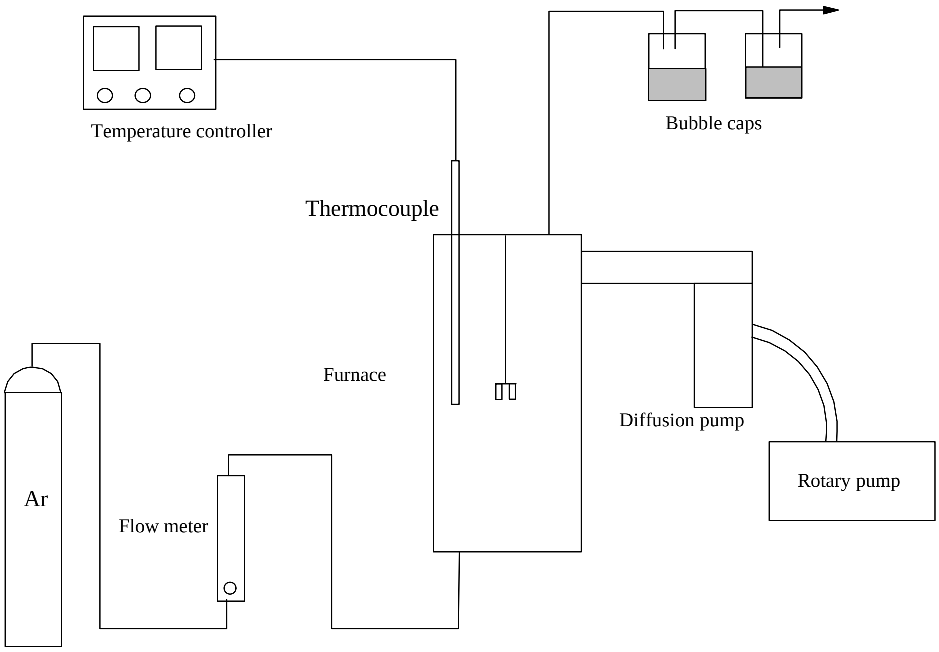


Figure 3(a). Flowsheet of experimental apparatus used in liquidus composition experiments.

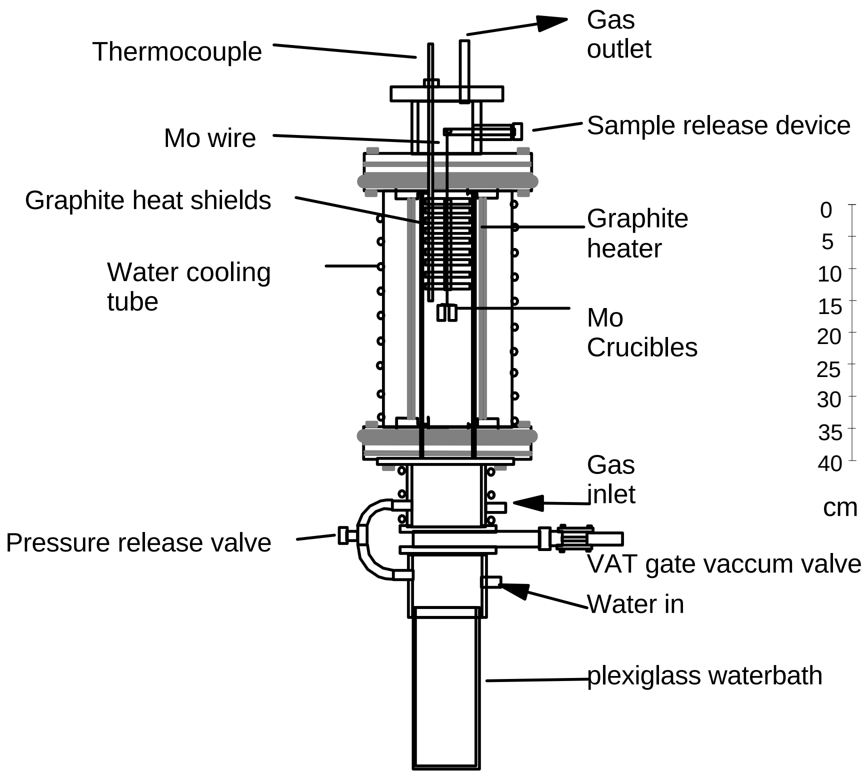


Figure 3(b). Experimental apparatus for liquidus composition experiments.

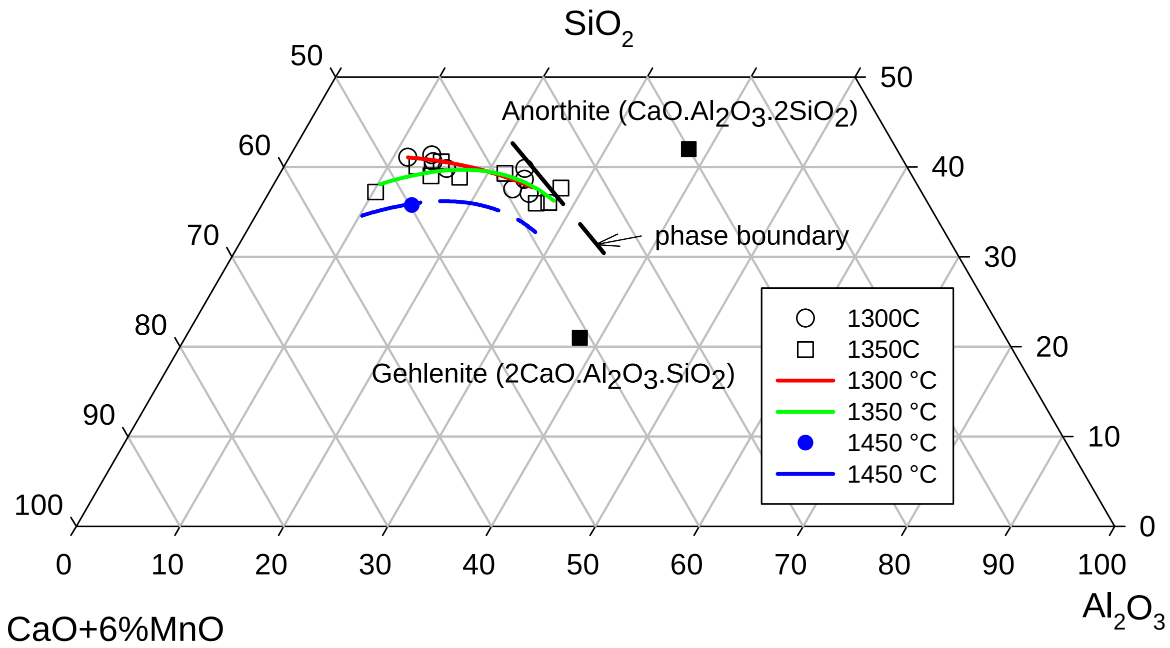


Figure 4. Phase diagram (CaO+6%MnO)-SiO_2-Al_2O_3 showing liquid compositions of slags in the present study. Liquidus lines at 1300 °C, 1350 °C and 1450 °C have been estimated from the individual data points.

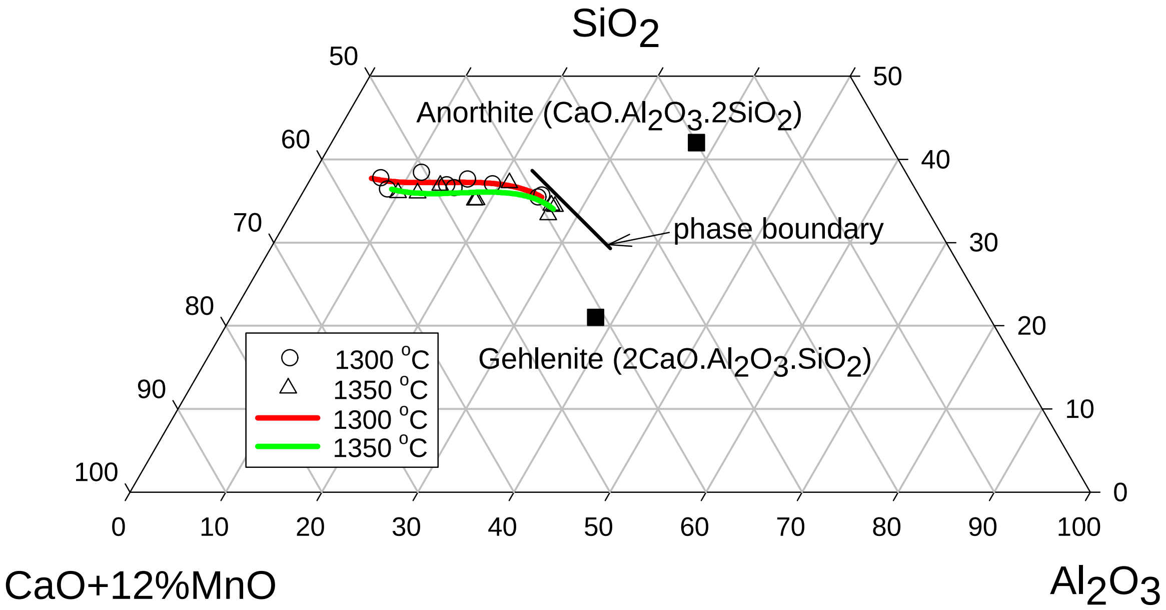
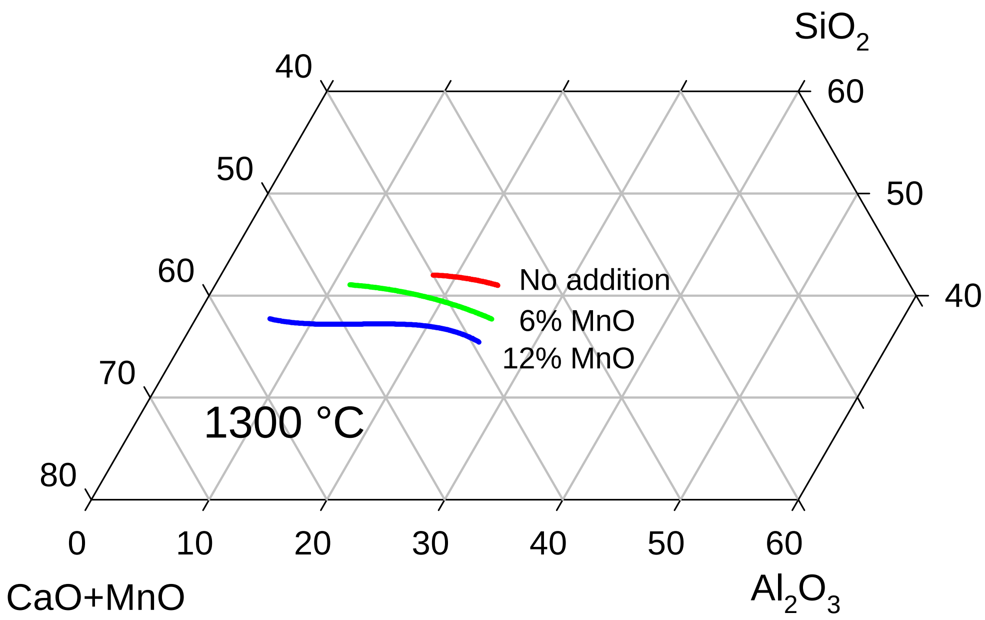
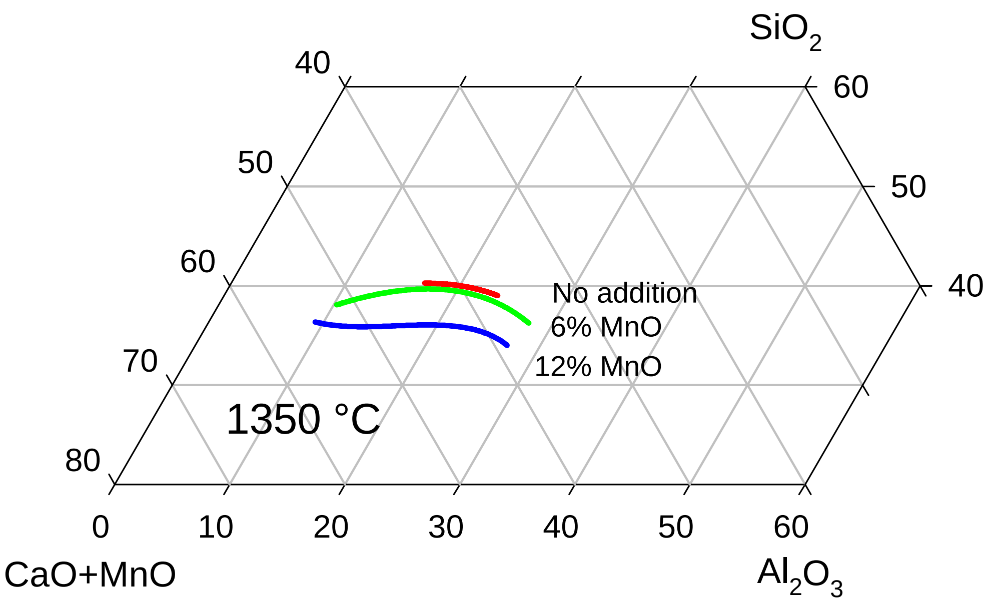


Figure 5. Phase diagram (CaO+12%MnO)-SiO_2-Al_2O_3 showing liquid compositions of slags in the present study. Liquidus lines at 1300 °C and 1350 °C have been estimated from the individual data points.

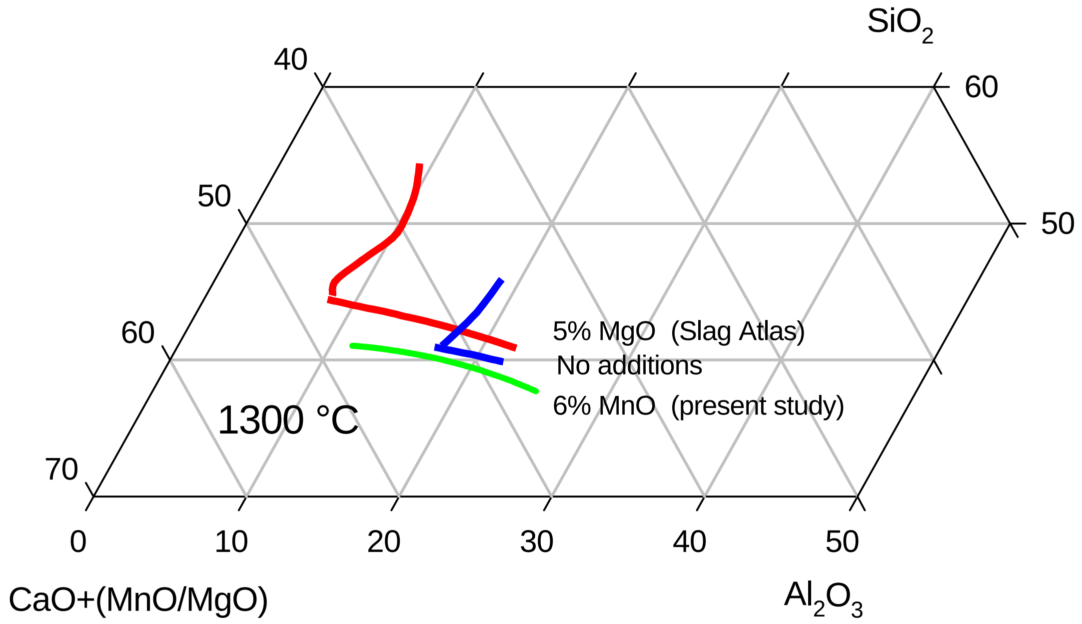


(a)

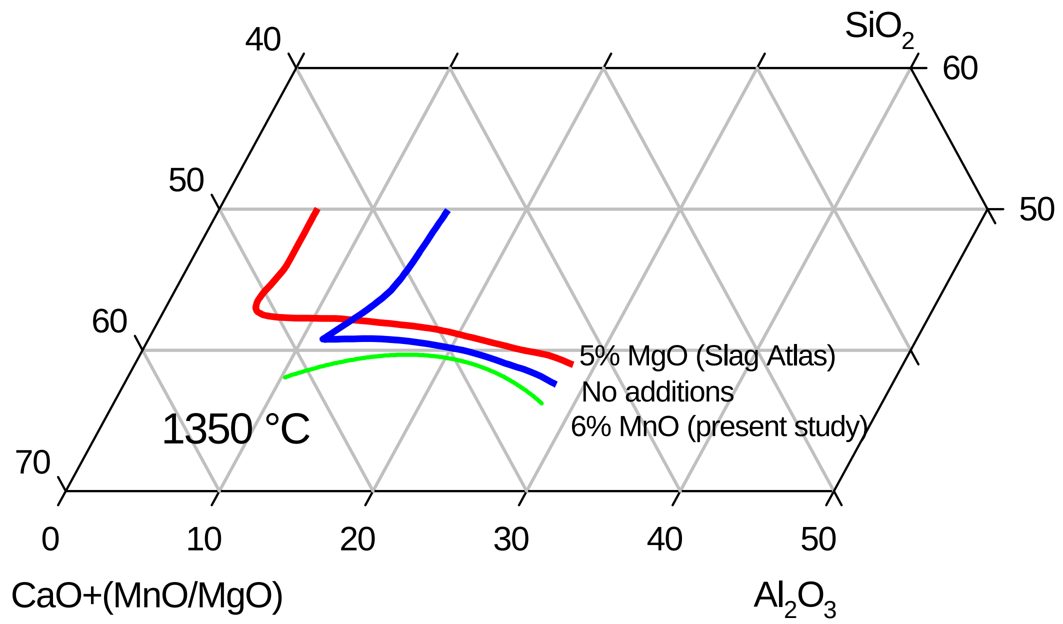


(b)

Figure 6. Effect on liquidus compositions of adding 6% and 12% MnO to CaO-Al_2O_3-SiO_2 slags at 1300 °C (a) and 1350 °C (b).



(a)



(b)

Figure 7. Effect on liquidus compositions of adding 6% MnO and of adding 5% MgO to CaO-Al_2O_3-SiO_2 slags at 1300 °C (fig. a) and at 1350 °C (fig. b).

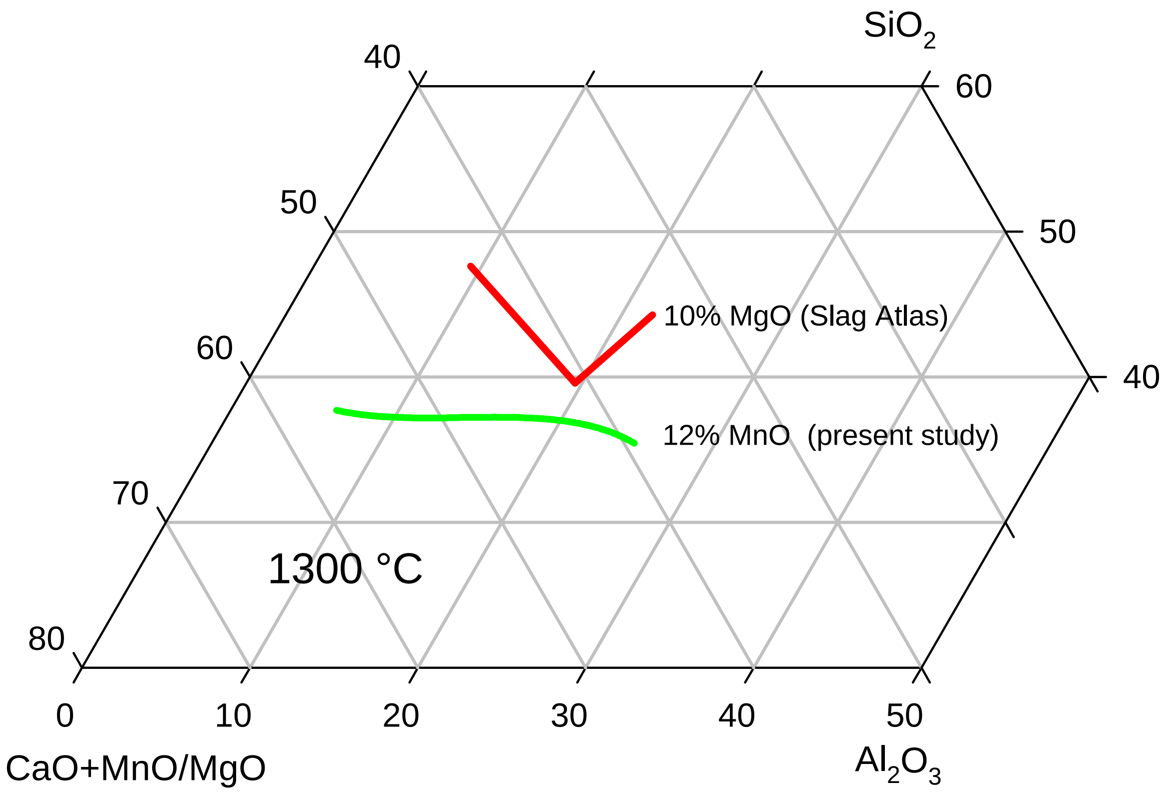


Figure 8. Effect on liquidus compositions of adding 12% MnO and of adding 10% MgO to $CaO\text{-}Al_2O_3\text{-}SiO_2$ slags at 1300 °C.

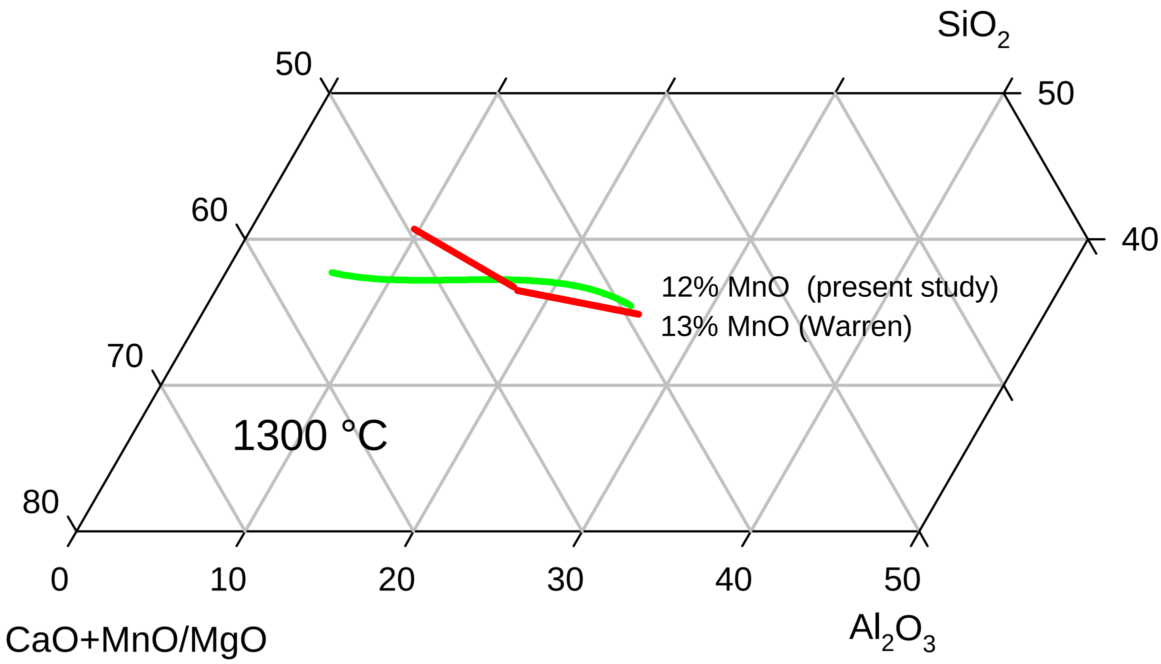


Figure 9. Estimated liquidusline at 1300 °C for MnO-CaO-Al_2O_3-SiO_2 slags containing 13% MnO, based on data from Warren *et al*[2], compared with present results with slags containing about 12% MnO.