TIN SOLUBILITY IN CAO-BEARING SLAGS

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Abstract
A series of laboratory experiments were undertaken to study the tin (Sn) solubility in lime (CaO) bearing slags. The equilibrium Sn solubility at 1873K was investigated using a gas-slag-metal equilibrium technique. Sn solubilities from the high CaO slags are discussed as a function of slag composition and oxygen potential.

INTRODUCTION

The interaction of tin (Sn) with a polymeric melt is of interest in many industries. Thermodynamic studies have typically focused either on high oxygen potentials where Sn dissolves oxidatively[1-6], or to a lesser degree on low oxygen potentials where Sn dissolves reductively.[7,9,10] In the production of glass the diffusion profile and polyvalent behavior of Sn has been studied. The Sn content of soda-lime-silica float glass has been shown to be influenced by temperature and oxygen potential,[1] the Sn being present as Sn^0, Sn^{2+}, and Sn^{4+}.[2] The dissolution of Sn in fayalitic slags as used in copper smelting was studied by Nagamori and Mackey.[3] For dilute solutions it was shown that Sn dissolves as Sn^{2+} and that the solubility of Sn was found to increase with increasing oxygen potential. Grimsey and Dawson investigated the activity of tin oxide in iron silicate type slags as used in Sn smelting.[4] They determined that at 1573K for the silica saturated slags Sn dissolves in slag as Sn^{2+} according to

$$(\%Sn) = 2.51x10^{-6} a_{Sn} p_{O_2}^{\frac{1}{2}} \tag{1}$$

where () represents the slag solution, a_{Sn} is the activity coefficient of Sn in the metal, and p_{O_2} is the oxygen partial pressure. They also suggest that the equilibrium distribution coefficient (*k*) for Sn rich Sn-Fe alloys, up to the miscibility gap, can be predicted by

$$\log k = 1.82 \, x_{Sn} + 1.59 - 1894/T \tag{2}$$

where

$$k = [\%Sn/\%Fe] \, . \, (\%Fe/\%Sn) \tag{3}$$

and where [] is the metal solution, x_{Sn} is the mole fraction of Sn in the metal, and T is the temperature in Kelvin. In regards to the speciation of the Sn, Grimsey and Dawson showed that the Sn was present in the slag as Sn^{2+}.

The effect of the CaO/SiO_2 ratio on the distribution of Sn between metal and slag in Sn smelting was investigated by Rankin.[5] It was found for slags containing up to 31.8% CaO that at 1473K

$$\gamma_{SnO}/\gamma_{FeO} = 2.502(\%CaO/\%SiO_2) + 1.142 \tag{4}$$

where the distribution coefficient (*k*) could be described by

$$\log k = 3.249 - 1894/T - 1.820 \, x_{Fe} + \log \gamma_{SnO}/\gamma_{FeO} \tag{5}$$

where γ is the activity coefficient of component *i* in the slag. The equilibrium between Sn and slag for Sn smelting was also studied by Takeda et al.[6] The effects of oxygen potential, slag composition and temperature on Sn solubility were investigated for FeO_x-CaO-SiO_2 slags containing up to 39% CaO. Sn solubility was found to increase with increasing oxygen potential and decreasing temperature. While increasing the CaO/SiO_2 ratio in the slag reduced the Sn solubility. It was also determined that Sn dissolved in the slag as Sn^{2+}.

The interaction of Sn and calcium-calcium halide slags has also been studied.[7-9] Isawa et al performed equilibrium experiments at 1773K for CaO-CaF_2 slags and Sn.[7] It was found that for oxygen potentials less than 6.8×10^{-18}atm Sn solubility increased with decreasing oxygen potential. The Sn dissolving in the calcium based slag according to:

$$Sn + 2CaO = Ca_2Sn + O_2 \tag{6}$$
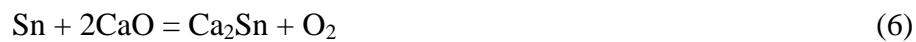
However, to date few studies have focused on the interaction of Sn with the high CaO bearing slags commonly employed in ferrous metallurgy. To gain an understanding of the dissolution behavior of Sn in CaO-Al_2O_3-SiO_2 type slags a series of laboratory experiments

were undertaken. In particular the effects of slag composition and oxygen potential on the Sn solubility were studied.

EXPERIMENTAL

Gas-slag-metal equilibrium experiments were performed in a vertical tube furnace under controlled atmospheres as shown in Fig.1. Equilibrium experiments were performed in graphite crucibles. The crucibles had an inner diameter of 12mm, a depth of 20mm, and contained 1g of Sn and 3g of slag. Master slags were prepared by pre-melting reagent grade fluxes in graphite crucibles using an induction furnace. The Sn was of analytical grade with a purity of 99.94%. Mixtures of high purity Ar and CO gas were used to control the oxygen potential of the system. In total a series of 5 high CaO bearing slags were investigated. The target compositions of the slags are shown in Table 1.

Reaction crucibles were supported via an alumina tube from beneath. The furnace was maintained at the reaction temperature whilst the sample was kept in the lower cool zone during a 2 hour flushing period. Following the flushing time the sample was raised quickly into the uniform hot zone of the furnace. After an elapsed reaction time (0.1 to 10hours) the reaction crucible was quickly lowered into a water/gas cooled chamber to facilitate rapid cooling. An online gas chromatography unit was used to monitor to gas compositions throughout the equilibrium experiments.

After cooling the slag and metal were removed from the graphite crucible. Briefly milling the material separated the slag and metal phase. Separated slag, crushed and sized to – 250Mesh, was then analysed for Sn, Ca, Al and Si using ICP (Inductively Coupled Plasma).

RESULTS

It was assumed that experimental control was sufficient that during the kinetic and equilibrium experiments there was no side reactions and that the reaction area was defined by the internal diameter of the crucible. It was also assumed that no concentration gradients existed in the slag phase. For the kinetic experiments zero time was determined to be achieved relatively fast. Crushed master slag, contained in the graphite crucibles, inserted into the hot zone melted in less than 60s.

Slag-metal equilibrium was not attained in a manner consistent with the reported dissolution behavior of Sn at low oxygen potentials. It was found that the Sn content of the slags rapidly rose before decreasing again, as shown in Fig. 2. For the slag systems studied it appeared that at low oxygen potentials, the area of most interest in this study, equilibrium was only attained for reaction times in excess of 4 hours. The observed behavior is postulated to be due to a greater than expected oxygen content of the metal during the initial stages of the experiments. In addition low gas flow rates through the furnace may not have flushed the oxygen rich atmosphere surrounding the packed material within the crucible. Under these conditions it could be expected that the Sn would dissolve oxidatively in the slag before being reduced by the graphite and attaining final equilibrium with the system. The exact cause of the behavior is still under investigation, however, this would appear to be the most likely explanation with a similar experimental influence being observed in another study within our laboratory,[11] and also reported by Rankin.[5] Because of the potential change in dissolution behavior from oxidative to reductive, and concerns over the volatilisation of SnO, it was not possible to conduct kinetic experiments and further work was only performed on those samples which had been produced in the 10 hour runs.

The Sn content of the slags equilibrated at 1873K for 10 hours were not only greater than expected (0.02 to 0.99wt%), but also lacked any clear dependence on the system oxygen potential, as shown in Fig. 3. Closer examination of the quenched slags showed that many of

the samples contained metallic Sn. The Sn being present as metallic spherules or veins throughout the slag as illustrated in Fig. 4. The formation of these Sn veins suggest that dissolved Sn may precipitate on cooling, which also suggests that Sn^0 is at least one of the dissolved species. This would be independent of oxygen potential and would lead to a distortion of the results at low oxygen potentials. It was intended that the using a sample preparation procedure including crushing and sieving would have been adequate to remove any metallic Sn. However, it is likely that some metallic Sn reported to the –250Mesh fraction, and hence the Sn contents of the slags would be artificially high. Only data from those slags that were clear and glassy, and obviously free of metallic Sn are discussed further in this work.

DISCUSSION

The dissolution behavior of a minor element, such as Sn, can be investigated by examining the dependency of the distribution ratio on the oxygen potential such as outlined by Nagamori and Mackey.[3] For the experimental procedure employed in this study the Sn content in slag is used in place of the distribution ratio since the metallic phase contains only Sn.

Oxygen potentials were controlled using CO and Ar gas mixtures, where the p_{O_2} value can be calculated by

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} = CO_{(g)} \tag{7}$$

$$\Delta G^0 = -114{,}400 - 85.8T \text{ (J/mol)[12]} \tag{8}$$

Equilibrium experiments were performed using CO/ (CO + Ar) ratios of between 0.01 and 1. At 1873K this is equivalent to oxygen potentials of between 4.52×10^{-20} to 4.52×10^{-16}.

The Sn content of the slags are shown along with the data of Isawa et al[7] in Fig. 5. From this figure it would appear that Sn dissolution in the slag system studied occurs along similar mechanisms to that identified previously.[7]

The variation in Sn content at fixed oxygen potentials can be ascribed to the different slag compositions used. Isawa et al utilised a single slag composition that had a fixed CaO activity of 0.62, while this study utilised a range of compositions. The slag compositions determined after equilibration are indicated on the $CaO-Al_2O_3-SiO_2$ phase diagram[12] shown in Fig. 6. Although studying higher oxygen potentials Takeda et al also found that Sn solubility is highly dependant on slag composition as shown in Fig. 7.[6]

The CaO activity of the slags (a_{CaO}) used in the study were calculated according to

$$\log a_{CaO} = 12.5\Lambda - 10 \text{[13]} \tag{9}$$

where Λ is the optical basicity of the slag. Data to calculate Λ were those recommended by Mills.[14] The relationship between the Sn content of the slag and the CaO activity at low oxygen potentials is shown in Fig. 8. In general, under low oxygen potential conditions as lime activity increases the Sn content of the slag increases.

This data shows a significant scatter about the trend line taken from the data of Isawa et al.[7] It could be argued that the scatter appears no greater than other similar studies. However, the CaO activity in itself is not the control factor as shown in equation (10). The significant factor is the Ca activity, which at the lower oxygen potentials employed in this study will be in equilibrium with CaC_2.

$$2Ca_{(l)} + Sn_{(l)} = Ca_2Sn_{(s)} \tag{10}$$
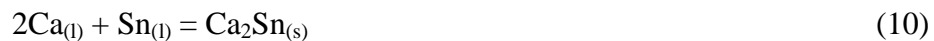
$$\Delta G^0 = -353{,}970 \ (\pm 1670) + 79.28 \ (\pm 1.26)T \text{ (J/mol)[17]} \tag{11}$$

The calcium activity operating under the conditions of this investigation can be calculated from

$$Ca_{(l)} + \tfrac{1}{2}O_{2(g)} = CaO_{(s)} \tag{12}$$

$$\Delta G^0 = -628{,}000 + 118T \text{ (J/mol)[15]} \tag{13}$$

at the higher oxygen potentials where reaction (12) is controlling, and by

$$Ca_{(l)} + 2C_{(s)} = CaC_{2(s)} \tag{14}$$

$$\Delta G^0 = 60{,}250 + 26.28T \text{ (J/mol)[12]} \tag{15}$$

at the lower oxygen potentials when reaction (14) is controlling.

Fig. 9. shows the relationship between the calcium activity and the Sn content of the slags where the activity has been calculated so that CaC_2 controls the calcium activity. The results from the study are compared against earlier experimental data of Kohler and Engell[10] and the theoretical estimations of Wakasugi and Sano[16]. When considered in this way the results of the present study are remarkable close with both previous studies.[7,10,16]

If it is assumed that at low oxygen potentials Sn exists in slag as solely Ca_2Sn, then the activity coefficient of Ca_2Sn (γ_{Ca_2Sn}) can be determined. Where the activity of Ca_2Sn can be calculated using equations (10) and (11).

There is little thermodynamic data on the intermetallic compound Ca_2Sn. One of the few studies is that by Min and Sano who calculated that γ_{Ca_2Sn} was 150.[17] The activity coefficient determined in this study is about one order of magnitude greater than that of Min and Sano.[17] This can be explained by the slightly higher free energy of formation employed by Wakasugi and Sano[16], which was used in this study, compared with that used by Min and Sano in calculating the activity coefficient of Ca_2Sn.

The dissolution behavior of Sn in calcium bearing slags at higher oxygen potentials is shown in Fig. 10. Although there is some difference in the slag systems it would appear reasonable to claim that Sn dissolves oxidatively as SnO rather than as SnO_2. For the range of oxygen potentials studied it is reasonable to say that Sn dissolves according to

$$Sn_{(l)} + \tfrac{1}{2}O_2 = SnO_{(l)} \tag{16}$$

CONCLUSIONS

A series of laboratory experiments were undertaken to study the Sn solubility in CaO-Al_2O_3-SiO_2 slags at 1873K. Sn contents in the slag were determined to be between 0.02 and 0.99wt% for the range of slags investigated. It was identified that the oxygen potential of the system and the slag chemistry influenced the Sn content. It was shown that at oxygen potentials of lower than 3×10^{-18}atm Sn dissolves reductively, and oxygen potentials higher than 1×10^{-17}atm Sn dissolves oxidatively. Higher Sn contents were found with decreasing oxygen potentials when the Sn dissolved reductively, and increasing oxygen potentials when Sn dissolved oxidatively which is consistent with previously determined behavior. The influence of the calcium activity on the Ca_2Sn content of the slag shows remarkable agreement with previous workers. Differences in the activity coefficient of Ca_2Sn between this study and that previously reported can be explained by differences in the data used for the free energy of formation of CaO.

ACKNOWLEDGEMENTS

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1. Water cooled aluminum cap
2. Outlet gas to G.C. unit
3. Al_2O_3 furnace tube
4. $LaCrO_3$ elements
5. Graphite crucible
6. CaO bearing slag
7. Sn
8. Al_2O_3 rod
9. Water cooled aluminum cap
10. Ar-CO gas inlet
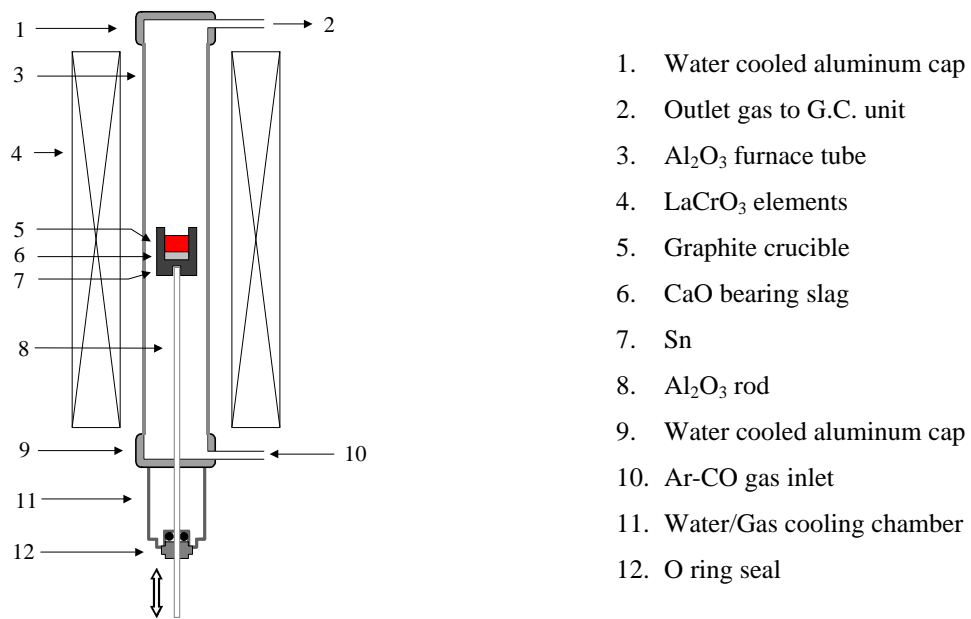11. Water/Gas cooling chamber
12. O ring seal

Figure 1: Schematic diagram of experimental equipment for gas-slag-metal equilibrium tests.
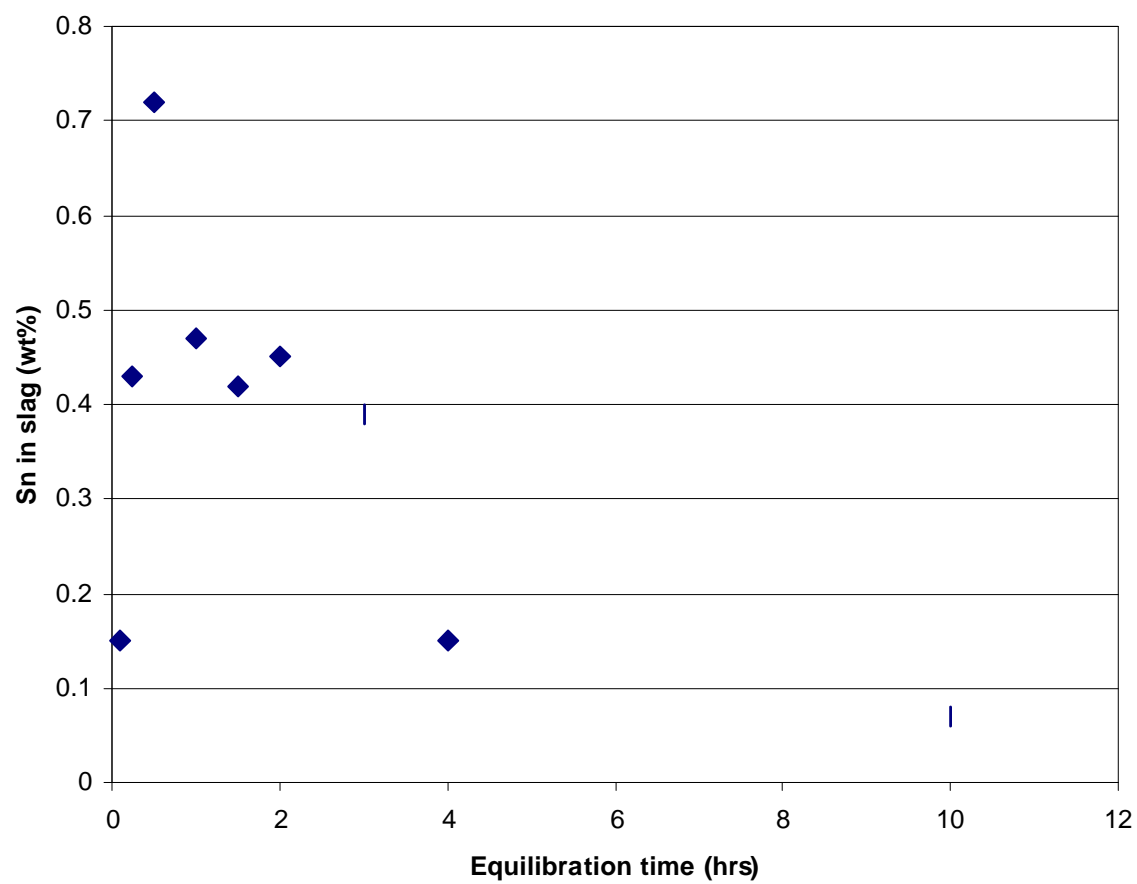
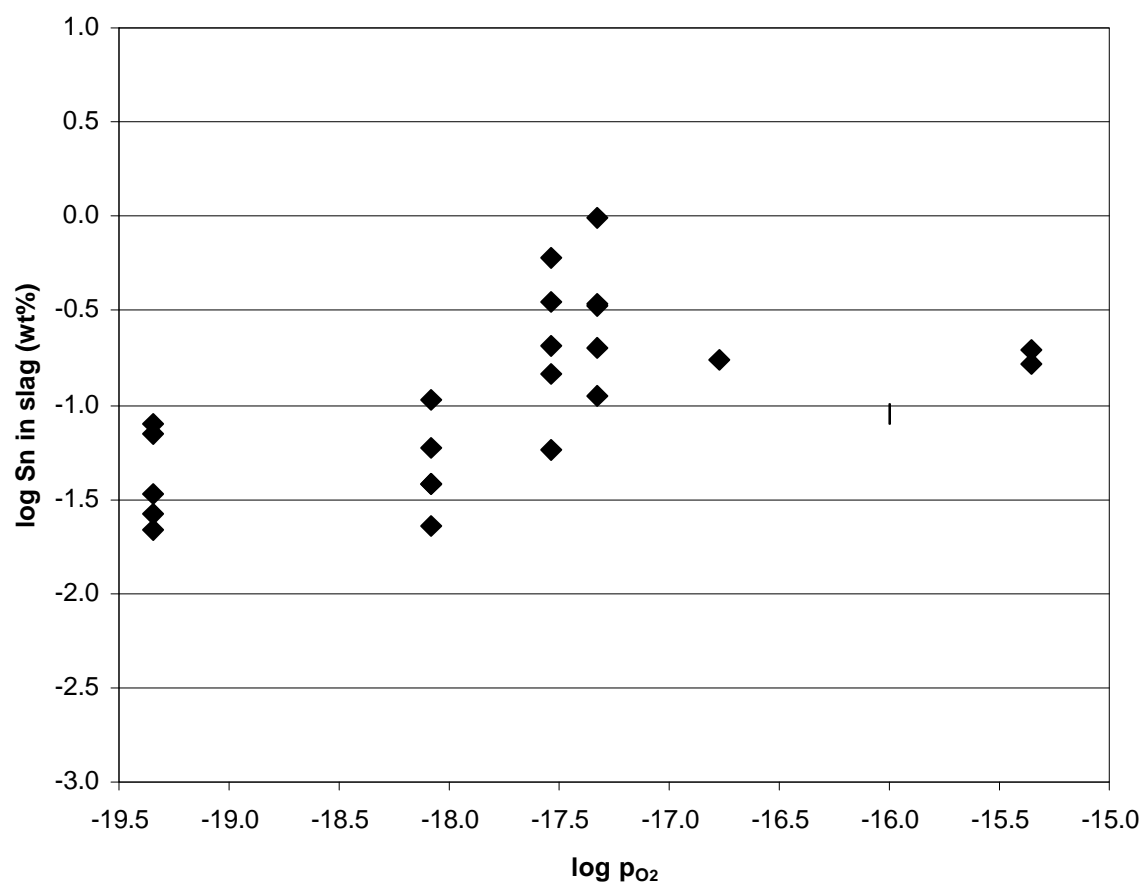Figure 2: Typical variation in Sn content of CaO bearing slags at 1873K.

Figure 3: Sn content in CaO bearing slags at varying oxygen potentials. 10hr equilibration at 1873K.
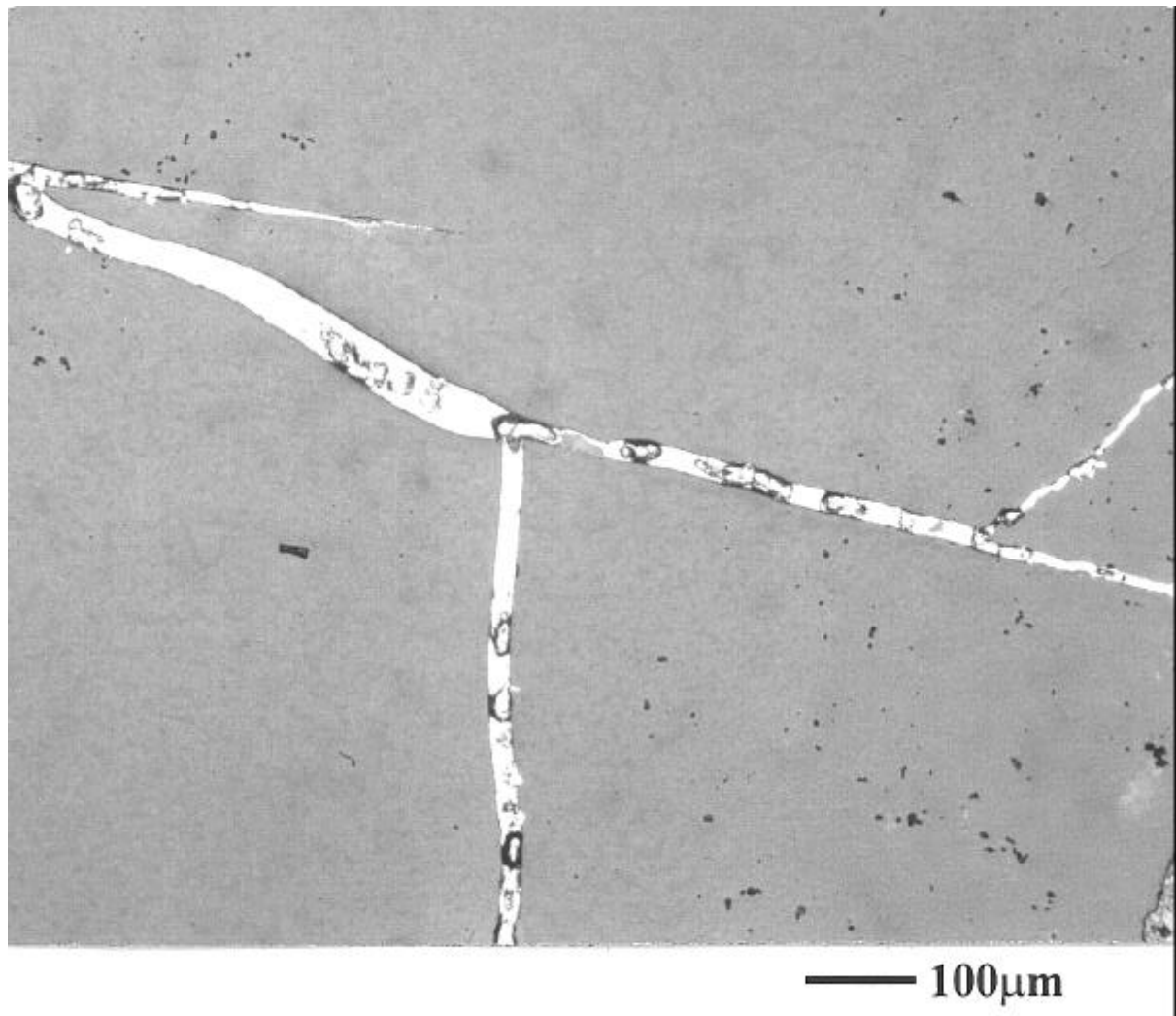
Figure 4: Sn veins in quenched slag sample.
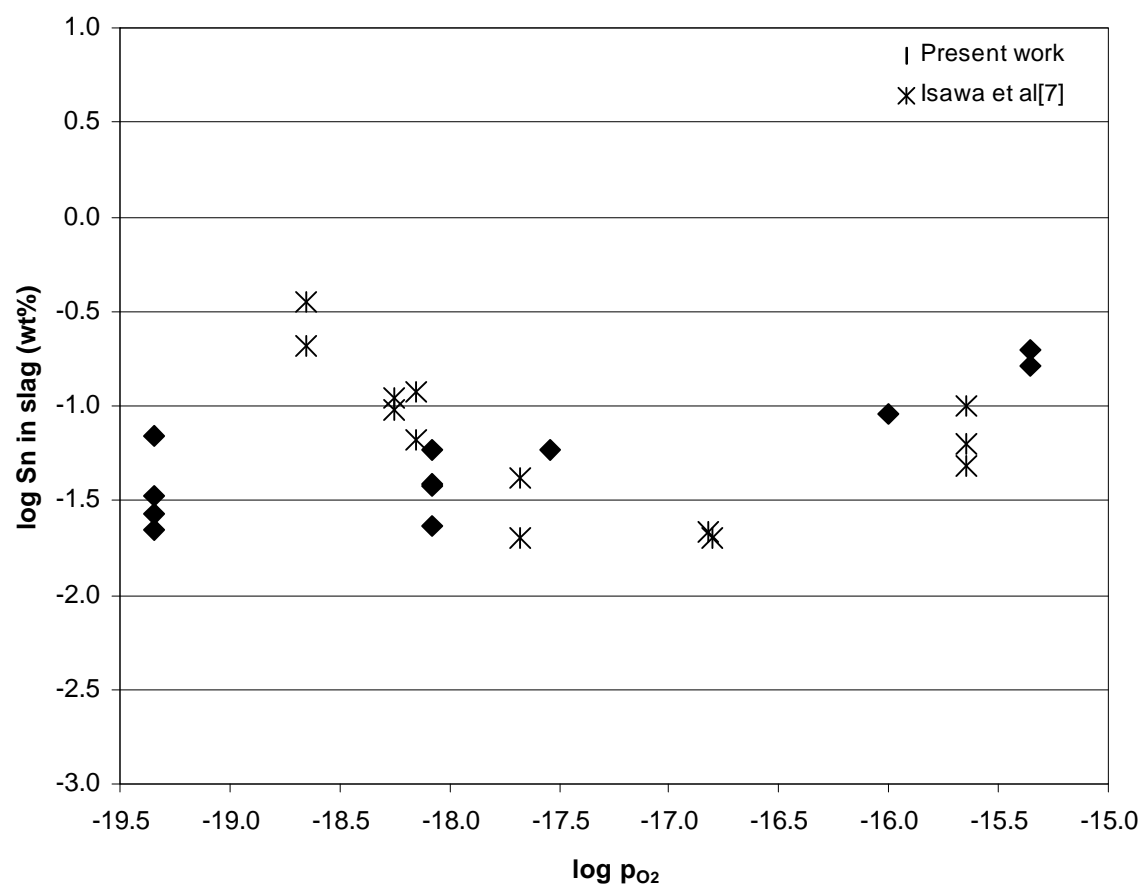
Figure 5: Sn content in calcium based slags at varying oxygen potentials.
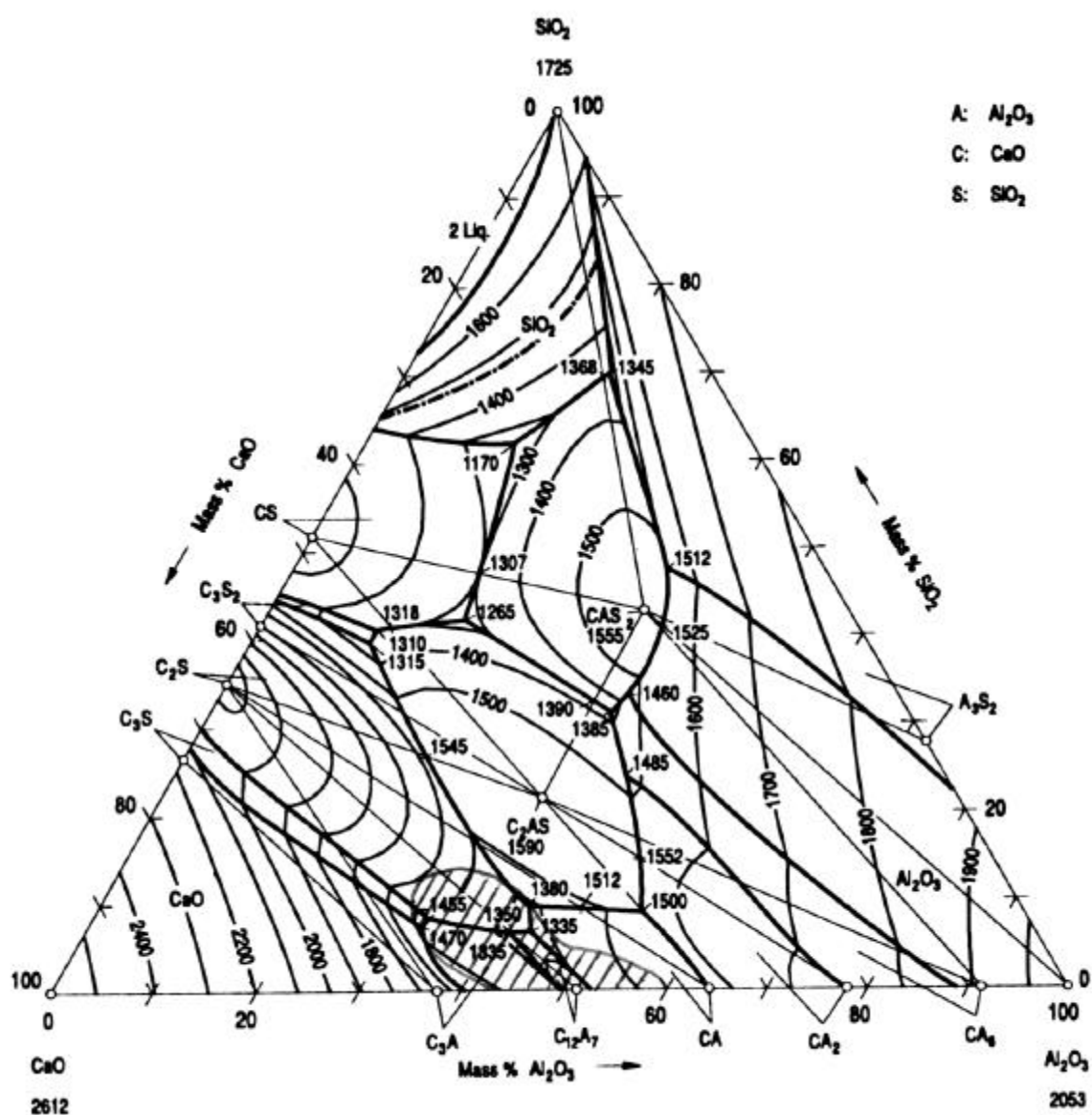
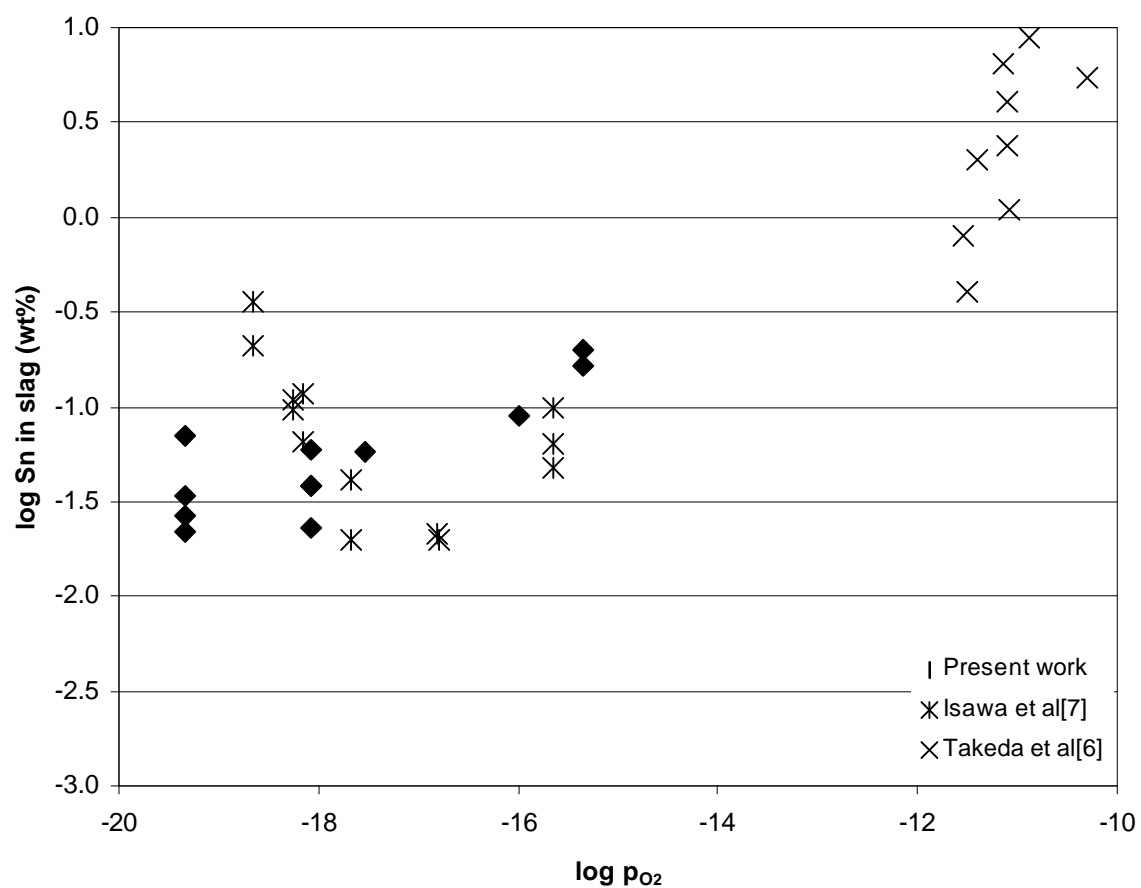Figure 6. Composition of CaO-SiO$_2$-Al$_2$O$_3$ slags used in study, shown as hatched area.

Figure 7: Variation in Sn content in calcium based slags due to varying slag compositions and oxygen potential.
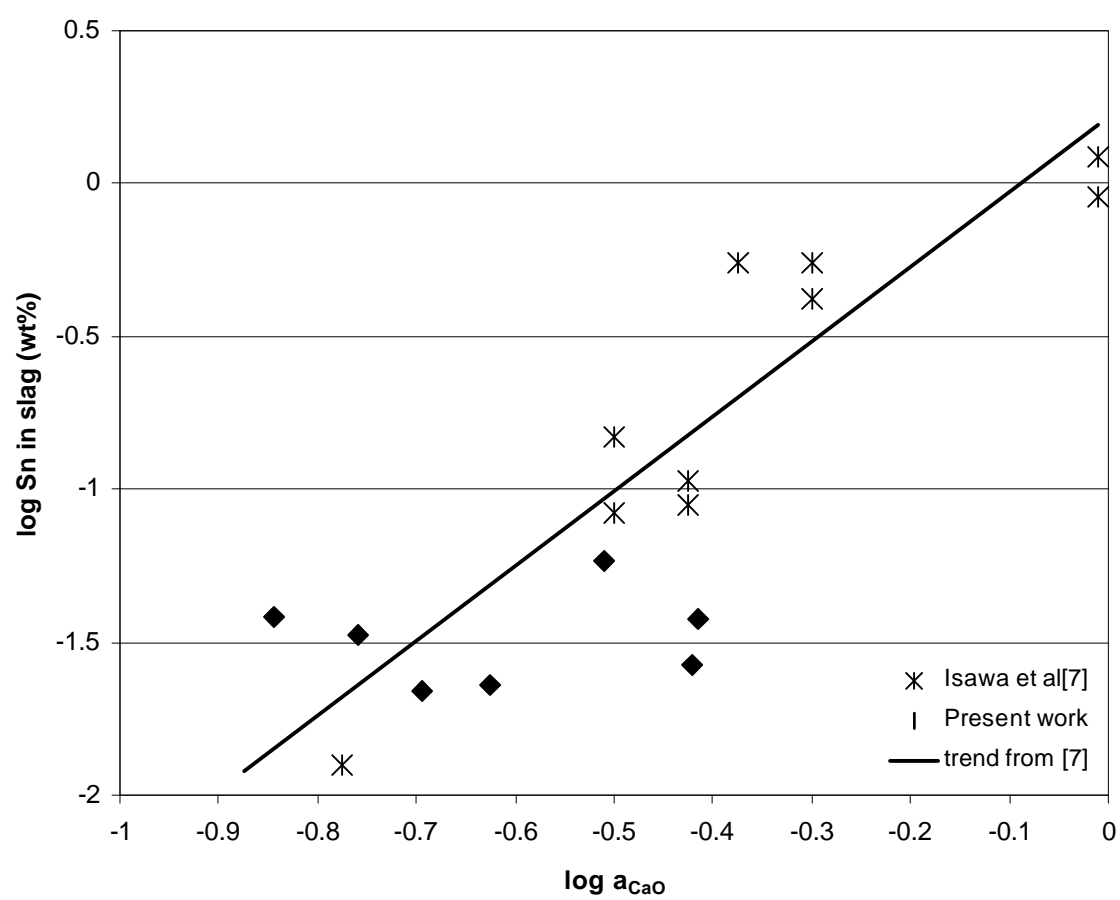
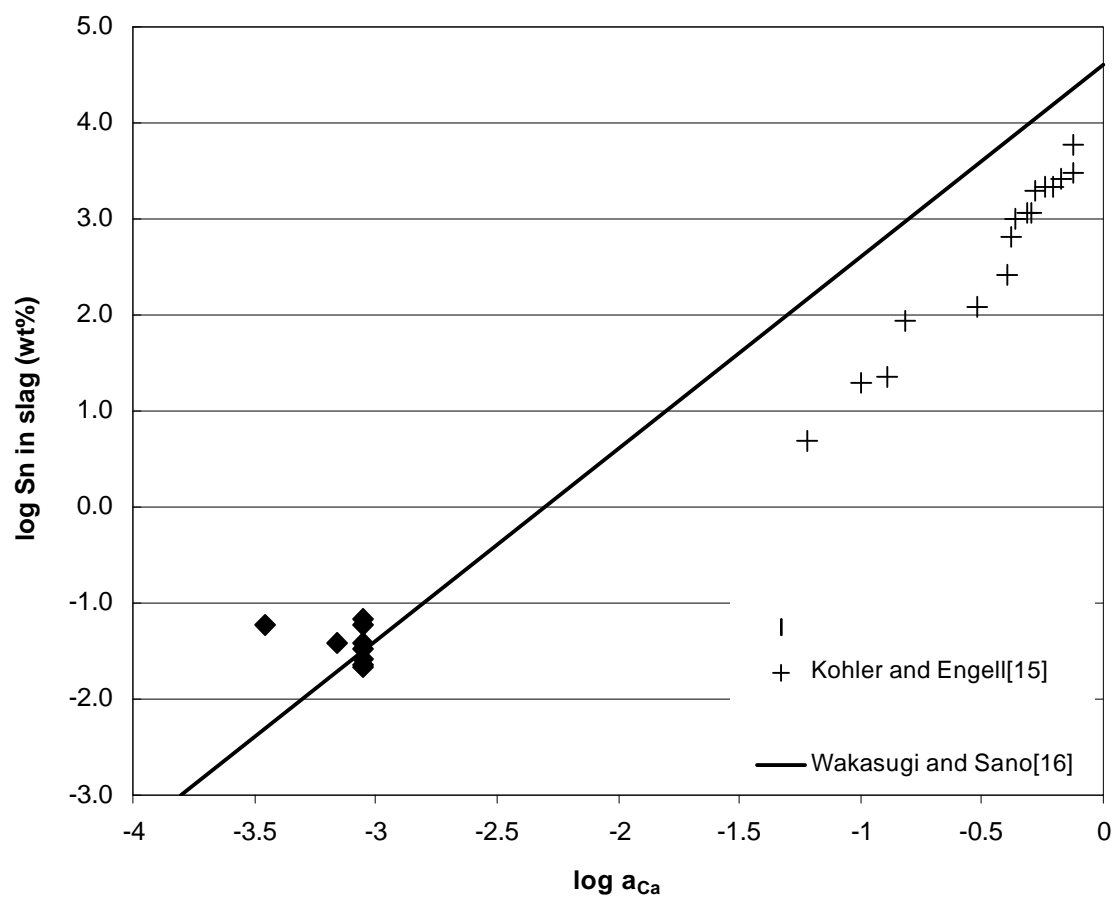Figure 8: Influence of slag composition on Sn content in slag.

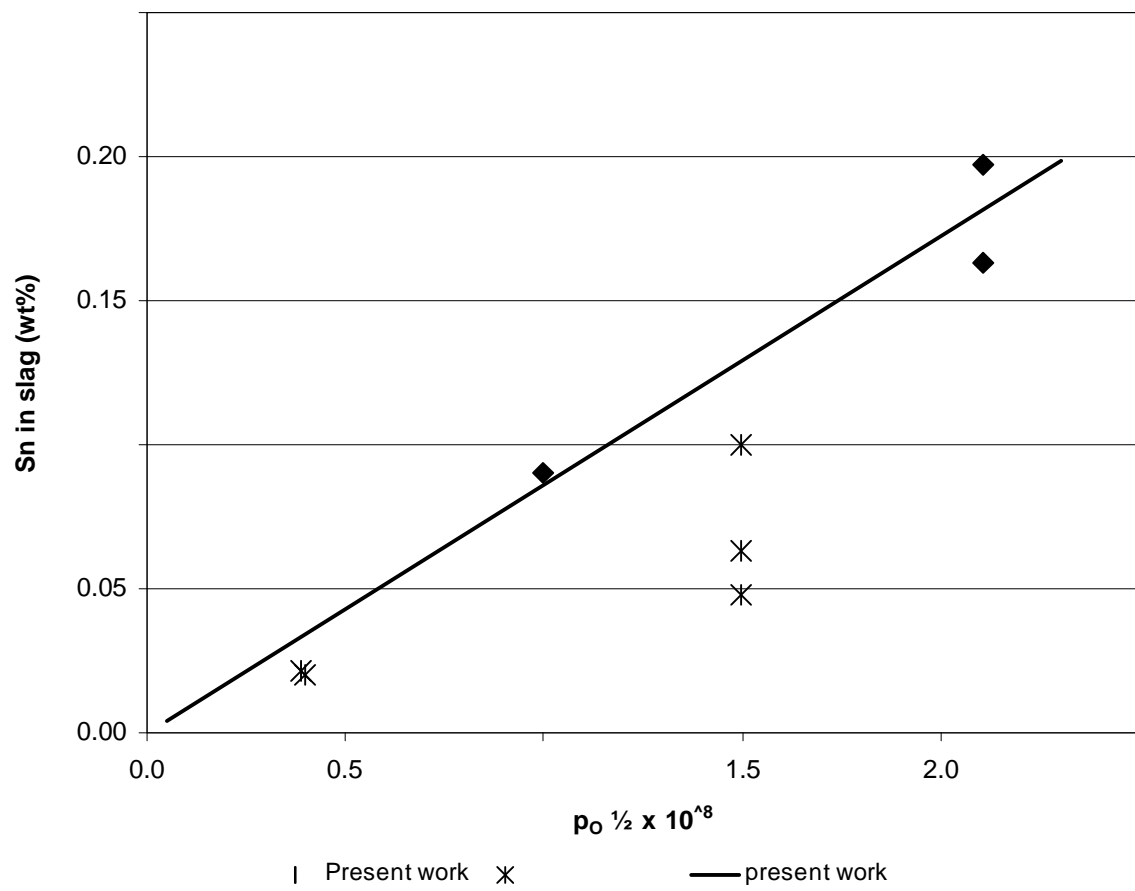Figure 9: Influence of Ca activity on the Sn content of Ca based slags.

Figure 10: Influence of oxygen potential on Sn content of Ca bearing slags.

Table 1 Slag compositions studied.

Component\Slag	Slag A	Slag B	Slag C	Slag D	Slag E
CaO (wt%)	52	57.3	51	57	59
Al_2O_3 (wt%)	44	37.2	46	34	41
SiO2 (wt%)	4	5.5	3	9	0