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Distribution of Impurity Elements in Slag-Silicon Equilibria for Oxidative Refining of Metallurgical Silicon for Solar Cell Applications

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Abstract

The possibility of refining metallurgical grade silicon to a high-purity product for solar cell applications by the slagging of impurity elements was investigated. Distribution coefficients were determined for B, Ca, Mg, Fe, K and P between magnesia or alumina saturated Al_2O_3 -CaO-MgO-SiO₂ and Al_2O_3 -BaO-SiO₂ slags and silicon at 1500 °C. The partitioning of the impurity elements between the molten silicon and slag was examined in terms of the basicity and oxygen potential of the slag, with particular focus on the behaviour of boron and phosphorus. The experimental results showed that both of these aspects of slag chemistry have a significant influence on the distribution coefficient of B and P. Increasing the oxygen potential by additions of silica was found to increase the distribution coefficients for both B and P. Increasing the basicity of the slag was not always effective in achieving high removal of these elements from the silicon as excess amounts of basic oxides lower the activity of silica and consequently the oxygen potential. The extent of this effect is such that increasing basicity can lead to a decrease in the distribution coefficient. Increasing lime in the slag increased distribution coefficients for B and P, but this counterbalancing effect was such that distributions were lowest in the barium-containing slags, despite barium oxide being the most basic of the fluxes used in this study. The highest removal efficiencies achieved were of the order of 80% and 90% for B and P respectively. It was demonstrated that for the removal of B and P from metallurgical-grade silicon to solar-grade levels, a slag mass about 5 times the mass of silicon would be required.

Keywords: metallurgical silicon; impurity distribution; slag treatment; solar-grade silicon

1. Introduction

Several studies on energy generation and the environmental impact of solar-based power have shown that photovoltaic (PV) electricity is amongst the most environmentally benign sources of energy. A study [1] on the environmental impact of solar silicon presents very attractive figures for greenhouse gas emissions and energy payback time; 30 g/kWh and 1.2 years, respectively. Another study [2] on CO₂ emission of various electricity generation options estimates that solar electricity generates as low as 0.013 kg CO₂-e/kWh, about 80 times lower than that of coal-based electricity. However, today's cost of solar electricity being around \$0.3 /kWh, is about four times larger than the dominant nuclear and coal-based electricity [3]. This is partly because of the high cost and limited availability of silicon used in the manufacture of the PV cells. High-purity scrap silicon from the semiconductor industry (99.9999999% Si) has

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mainly been used as the starting material for producing solar-grade silicon (SoG-Si) (99.9999% Si), which is ultimately used to fabricate a crystalline silicon PV cell.

The quest for developing a low-cost method of producing SoG-Si has been moving forward in the last decade to overcome the economic hurdle against widespread generation of PV electricity. Metallurgical-grade silicon (MG-Si) is a cheaper alternative to electronic scrap that can be produced on the large scale, but is of considerably lower purity (98-99% Si). Furthermore, it contains impurity elements that must be removed to low levels for the PV cell to operate at optimum efficiency. As such, MG-Si must still be refined by a cost-effective means for it to remain a possible starting material for the production of SoG-Si. Many techniques for refining MG-Si exist and must often be used in conjunction with one another to achieve the requisite purity for solar applications. Of all the impurities present in MG-Si, boron and phosphorus are often the most difficult to remove. This is because they are unresponsive to directional solidification, which is usually the final step in silicon refining. This is a major concern as these elements are typically doped to precise levels in photovoltaic silicon. It is the behaviour of these elements that will be the focus of this study.

Some impurity elements are easier to remove because of their low segregation coefficient between solid and liquid silicon. Studies have shown that using techniques such as the zone refining plasma-arc method [4], the impurities with a low segregation coefficient can be collected in a liquid portion of a sample then discarded. However, boron and phosphorus have relatively high segregation coefficients so are not readily removed by this method. One possible method of decreasing the segregation coefficient of these elements is to first alloy the silicon with a “getter” metal such as copper or iron [5], then solidify the liquid alloy to grow pure dendrites of Si. The getter metal, having a higher affinity for such impurities than silicon, increases absorption of these elements in the liquid phase; hence, a more pure Si crystal can form during solidification. However, the technique is not capable of achieving SoG-Si specifications in one stage, meaning further refining will still be required. Vacuum refining has been shown to be able to remove phosphorus, but long times and high power requirements make this technique unsuitable [6].

Another metallurgical refining technique for MG-Si involves melting it in the presence of a flux to produce a slag phase which can take up the impurity elements. For non-metallic impurities such as boron and phosphorus that will have acidic oxides, basic melts such as those based on alkali and alkali-earth oxides are expected to be the most appropriate to facilitate their extraction to a slag phase. Impurity elements are stabilised as an oxide in the slag with the inclusion of a suitable flux or gas to create oxidising conditions. Tanahashi *et al.*, [7] proposed the treatment of Si with CaO based fluxes as one part of a more complex overall refining procedure. Other previous studies have focused on the use of highly basic fluxes containing CaO and CaF₂ [8,9] but also make use of SiO₂ to give the slag suitable oxidising potential. While this will reduce the basicity of the slag, saturating the slag with SiO₂ may also prevent unacceptably high losses of silicon to the slag. Weiss and Schwerdtfeger [10] examined the behaviour of many elements in CaO-SiO₂ based ternary systems and showed that the removal of some metallic elements is also feasible by this method. However, it is reported [11] that the addition of excess CaO can increase the concentration of Ca in silicon, which, through ternary interactions, can in turn draw phosphorus back from the slag into the metal phase. Furthermore, boron, in group IIIA on the periodic table, is considered less acidic in nature and may not behave in exactly the same manner as phosphorus, in group VA. It is apparent, therefore, that the slag composition must be subject to fine control to optimise removal of both of these elements.

Equilibrium studies between silicon and oxide phases have also been carried out to determine thermodynamic quantities for impurities in silicon. A review of the available thermodynamic data pertaining to impurities that are typically required to be removed from Si for PV applications was conducted by Morita and Miki [12].

Despite the expected complexity associated with optimising slag chemistry, comprehensive data on the behaviour of impurities in terms of fundamental variables such as temperature and slag composition are quite limited. In this work, the flux-refining of MG-Si is examined in detail using Al_2O_3 -CaO-MgO-SiO₂ and Al_2O_3 -BaO-SiO₂ slags. The slag composition was selectively varied with the intent of determining the effect of slag basicity and oxygen potential on the extraction of impurities from the silicon metal phase.

2. Experimental

2.1 Materials

To facilitate the analysis of impurities, a silicon master alloy was synthesized by doping one kilogram of milled metallurgical silicon with 3 g each of 95-97% B (Sigma-Aldrich) and >97% red P powders (Riedel-de Haem). This mixture was melted in two portions, approximately 500 g each, in magnesia crucibles under an argon atmosphere inside a muffle furnace at 1485 °C for 2.75 hours. Analysis of these master alloys is given in Table I.

Fluxes used in the preparation of the slags were first dried at 105 °C for one hour then weighed and mixed thoroughly in the desired ratio for each particular experiment. Where basicity (B) was to be varied in the Al_2O_3 -CaO-MgO-SiO₂ system, slags were prepared in the range $0.21 < B < 1.4$. Where basicity was held constant, slags were prepared with $B = 1.08$. The effect of slag basicity was to be further investigated by varying the BaO:SiO₂ ratio of the Al_2O_3 -BaO-SiO₂ slag. Here, slags were prepared in the range $0.33 < B < 0.82$. For the purposes of this study, (B) refers to the ratio, by weight, of $(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$, or, $(\text{BaO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$. The composition ranges in all cases were designed to give a single molten slag phase at 1500 °C.

2.2 Methods

Before melting, flux mixtures were pressed into a pellet. Typically, 5.5 g of doped Si and 7.5 g of fluxes were used in each experiment. The slag and alloy were brought into equilibrium in a magnesia or alumina crucible in an inert atmosphere inside a vertical tube furnace. The crucible was suspended inside the furnace by means of an alumina rod and pin that were attached to the top end cap. A schematic diagram of the furnace setup is shown in Fig. 1. The crucible was held in the cold zone of the furnace while it was flushed with argon for 30 minutes. After flushing, the crucible was slowly lowered to the hot zone before the temperature was increased to 1500 °C. The temperature of the hot zone was measured using a B-type (Pt-6% Rh/Pt-30% Rh) thermocouple, held in place by the bottom end-cap at the level of the base of the crucible. Argon was passed through the furnace at a rate of approximately 300 mL/min for the duration of the experiment.

At the end of each experiment, the crucible assembly was removed from the top of the furnace and quenched in a water bath. Quenching typically took several seconds. After being left to dry, the slag and metal phases were physically separated from the crucible, then ground to a powder for digestion and analysis.

A series of slag-metal experiments was first carried out to determine the reaction time needed for the system to reach equilibrium. A slag of composition 30% Al_2O_3 -40% CaO -10% MgO -20% SiO_2 (by weight) was equilibrated with Si alloy at 1500 °C at six reaction times up to 6 hours. Analysis of the Si at the completion of each run showed that the concentration of phosphorus and boron became steady after 2 hours. Similarly, the SiO_2 content of the slag, which can possibly increase due to the oxidation of Si, did not show appreciable systematic variation after this time. This is shown in Fig. 2. On the basis of this, a reaction time of 2 hours was used in subsequent experiments.

2.3 Analysis

Silicon alloys were digested in a mixture of concentrated nitric and hydrofluoric acids (trace-element grade, Celadon) in PTFE beakers at about 80 °C and the resulting solutions analysed by ICP-OES. Slags were fused with sodium hydroxide (99.99%, Sigma-Aldrich) in an Inconel 601¹ crucible at around 450 °C then dissolved in diluted nitric acid prior to ICP analysis for boron and iron. The slags were analysed by XRF for all other elements reported.

3. Results

From the analytical results, distribution coefficients and removal efficiencies were calculated. The distribution coefficient is the simple ratio of concentration of impurity M (in wt%) in the slag phase (M) to that in the metal phase [M].

$$L_M = (M)/[M] \quad (1)$$

Because of the possibility of oxidized silicon entering the slag (as in Fig. 2 above) and the saturation of the slag by the crucible material over the course of the experiments, the distribution data are presented and discussed below in terms of the final slag composition as determined by chemical analysis. Published phase diagrams of the Al_2O_3 - CaO - MgO - SiO_2 system [13] show that the mullite phase is stabilized at high silica contents, but in the present work it is expected that the alumina content is always low enough such that this phase does not form. The target and final slag compositions are given in Table II.

3.1 Varying $\text{CaO}:\text{SiO}_2$

The effect of slag basicity on the removal of impurities from silicon was investigated by varying the $\text{CaO}:\text{SiO}_2$ ratio of the Al_2O_3 - CaO - MgO - SiO_2 slag with Al_2O_3 and MgO fixed at 35 and 3 wt% respectively. All experiments were conducted in alumina crucibles. Values of L_M for the varying $\text{CaO}:\text{SiO}_2$ system are shown in Fig. 3. For boron, the changing dependence on basicity is clearly highlighted by the local maximum observed at a $\text{CaO}:\text{SiO}_2$ ratio of about 0.6. The actual values of L_B are greater than unity for all but one composition, indicating boron partitions preferentially to the slag phase. However the maximum reached is only about 1.6, indicating that this preference is only slight. For phosphorus, the distribution coefficient increases steadily over the entire range of basicity studied. This indicates that the influences on

¹ Inconel is a registered trademark of Special Metals Corporation, New Hartford, New York, USA.

phosphorus are different to those responsible for removal of boron. The actual values of L_P are all less than unity, indicating a preference to remain in the metal phase.

Values for iron and potassium are subject to significant scatter, most likely due to their low concentrations in the starting alloy. Generally, values of L_{Fe} are of the order of 0.1, indicating that Fe is retained in the metal, although do become just greater than unity in the most basic slags. For potassium, values are mostly in the range $1 < L_K < 2$, indicating a slight preference for the slag phase.

3.2 Varying $SiO_2:Al_2O_3$

The effect of the oxygen potential (p_{O_2}) of the slag on the removal of impurities from silicon was investigated at constant (B) by varying the $SiO_2:Al_2O_3$ ratio of the Al_2O_3 -CaO-MgO- SiO_2 slag with CaO and MgO fixed at 42 and 10 wt% respectively. All experiments were conducted in magnesia crucibles. Distribution coefficients for impurity elements in these experiments are shown in Fig. 4. In this case, the distribution coefficient of boron shows a slight increasing trend with increasing $SiO_2:Al_2O_3$ ratio. Values all lie in the range $1 < L_B < 2$ so again, boron only slightly favours the slag phase. The distribution coefficient of phosphorus shows a change in dependence with a continued increase in p_{O_2} , in that above an $SiO_2:Al_2O_3$ ratio of 2, L_P shows a sharp increase. This is despite the slag being expected to become less basic over this interval, as the quantitative measure of basicity, the optical basicity (Λ), is higher for Al_2O_3 than for SiO_2 [13]. The highest L_B and L_P in the present study were recorded in the slag with the highest $SiO_2:Al_2O_3$ ratio, which suggests that the p_{O_2} , and not basicity, may be the major influencing factor on the removal of these impurities. Distribution coefficients for iron and phosphorus were very similar to those measured in the varying CaO: SiO_2 system and are again subject to scatter. This suggests that these metallic impurities are not particularly responsive to changes in slag chemistry.

3.3 Varying $BaO:SiO_2$

The effect of slag basicity on the removal of impurities from silicon was further investigated by varying the $BaO:SiO_2$ ratio of the Al_2O_3 -BaO-- SiO_2 slag with Al_2O_3 fixed at 20 wt%. All experiments were conducted in alumina crucibles. Distribution coefficients for impurity elements in these experiments are shown in Fig. 5. Values for boron follow a similar trend as for the varying CaO: SiO_2 slags in that they increase with increasing basicity, but in this case are all less than unity. The distribution coefficient of phosphorus, on the other hand, was seen to be independent of basicity in this system. This is a somewhat unexpected result, as barium is expected to be the most basic flux used in this study, so should be more efficient at taking up acidic impurity elements. Distribution coefficients of Ca and Mg are interesting in that they appear to follow opposite trends, despite being chemically very similar. Values for Mg decrease with increasing $BaO:SiO_2$, while those for Ca increase over the same range. Values for both are always greater than unity, with those for Mg about an order of magnitude higher than for Ca. Values for K very closely follow the same trend as Ca. Distribution coefficients for iron are at similar levels as found previously and again do not follow any particular trend against basicity.

4. Discussion

The reaction for boron entering the slag by oxidation with silica as the oxidising agent can be represented by the ionic reaction

Similarly, phosphorus enters the slag by the reaction

In each case, oxygen ions are provided by basic oxides such as lime

and the oxygen partial pressure is that resulting from the equilibrium between Si and SiO₂

To estimate the p_{O_2} , the activities of Si (a_{Si}) and SiO₂ (a_{SiO_2}) were first estimated using the FactSage² thermodynamic package for the Al₂O₃-CaO-MgO-SiO₂ slags and the correlation of Meraikib [14] for the barium-containing slags (for a_{SiO_2} only). A value for the equilibrium constant (K) of Eq. (5) above of 3.95×10^{-18} [15] was also used. It should be noted, however, that the p_{O_2} may change slowly in response to the compositional changes of the slag, such that full chemical equilibrium may not be attained in the reaction time of 2 hours. In the varying SiO₂:Al₂O₃ system, the p_{O_2} was lower, in the range 4×10^{-20} to 9×10^{-20} atm. Based on previous studies in a similar system [16], phosphorus is expected to exist in the slag as the phosphide (P³⁻) under these conditions. Under these conditions, phosphorus is expected to exist solely as a reduced phosphide species. However, the observed increase in L_P and L_B with varying SiO₂:Al₂O₃ ratio in this system corresponds with increasing p_{O_2} . This suggests that these elements exist in the slag as an oxidized species under the conditions employed in the present work. For the varying CaO:SiO₂ and varying BaO:SiO₂ systems, the p_{O_2} was always in the range 1×10^{-19} to 4×10^{-18} atm. In this range, phosphorus was found to exist as both the phosphide and phosphate (PO₄³⁻) in a previous study [16]. But as these conditions are more oxidizing than those in the varying SiO₂:Al₂O₃ system, it is expected that boron and phosphorus exist solely as oxidized species in these systems. This was supported by further calculations using FactSage that showed the phosphate as the stable form of phosphorus in the slag in all experiments.

Thus, the removal and hence distribution of these elements will be a function of both slag basicity and a_{SiO_2} . However, since slag network modifiers such as CaO and MgO have a strong affinity for silica, an excess amount of these fluxes will give a highly basic slag at the expense of

² FactSage is a registered trademark of GTT Technologies, Herzogenrath, Germany.

lowering a_{SiO_2} . Increasing the basicity too far may then have the effect of impeding the removal of these elements as the p_{O_2} is in turn reduced.

This can account for the observed trend in L_B values in the varying CaO:SiO₂ system. Boron, having a relatively weakly acidic oxide, is likely to only have weak affinity for a basic slag. Therefore, it is apparent that there is a point where the p_{O_2} takes over from basicity as the dominant influence on boron removal. Since basicity no longer has a significant effect on the weakly acidic BO_3^{3-} beyond this point, the continuing decrease in a_{SiO_2} will bring about the observed decrease in L_B . Such a trend has also been observed in CaO-CaF₂-SiO₂ slags at 1500 °C [17], and in Al₂O₃-CaO-SiO₂ slag at 1600 °C [18]. The actual maximum value of $L_B = 1.6$ in the varying CaO:SiO₂ system of this study is slightly higher than the 1.1 recorded for the Al₂O₃-CaO-SiO₂ slag by Fujiwara *et al.* [18]. This may be due to the presence of MgO in the slag in the present work, which is a reasonably strong basic oxide, so is expected to contribute significantly to the removal of boron. The L_B of 1.6 is also very close to the value of 1.7 recorded in the CaO-CaF₂-SiO₂ slags by Suzuki *et al.* [17], indicating that CaF₂ as a flux can also contribute to slag basicity and removal of impurities. In both of these magnesia-free systems, the maximum L_B was recorded at a CaO:SiO₂ ratio of about 1.9, which corresponds to the calcium orthosilicate (2CaO.SiO₂) composition. For the Al₂O₃-CaO-MgO-SiO₂ slag in the present work, the maximum L_B was measured at a CaO:SiO₂ ratio of about 0.7. Lynch [11] states that the orthosilicate composition will exist at lower ratios when MgO is present in the slag, which may account for this discrepancy.

Phosphorus, having a stronger acidic oxide than boron, should be more susceptible to changes in the slag basicity. As the values of L_P increase over the entire range of CaO:SiO₂ ratios studied, it is apparent that basicity always has a stronger influence than p_{O_2} on the removal behaviour of phosphorus in this case. However, the overall influence is sufficiently weak that values of L_P are always less than unity, indicating a preference for the metal phase. An increase in L_P through a local maximum value was observed with increasing lime content of slag for the Al₂O₃-CaO-SiO₂ system at 1600 °C [19], but was not observed in the present work.

While basicity in terms of (B) was constant in the varying SiO₂:Al₂O₃ system, the increase in the SiO₂:Al₂O₃ ratio of the slag leads to an increase in a_{SiO_2} and therefore p_{O_2} . The increasing trend observed in L_B and L_P over the same interval confirms that the p_{O_2} does have a strong influence on the removal of these elements when basicity is constant. However, the effect of p_{O_2} on phosphorus is much stronger compared to that for boron, as is evident from the sharp increase in the L_P data. Also, the effect of basicity on phosphorus must still be sufficiently strong such that L_P does not decrease where highly basic slags reduce the p_{O_2} , as was apparent in the varying CaO:SiO₂ system.

Distribution coefficients for boron and phosphorus in the varying BaO:SiO₂ system follow a similar trend to those observed in the varying CaO:SiO₂ system. However, the values measured are lower, and always favour the metal phase. Also, L_P appears to be independent of the slag basicity. This is an unexpected result, as BaO was the most basic flux used and was expected to have a stronger influence on partitioning than lime or magnesia. The reason that L_M for these slags behave as observed is that BaO has a much higher molecular weight than CaO or MgO, such that at the concentrations in these slags, the number of moles present in the slag is comparatively lower. As a result, the overall basicity of the slags in terms of Λ in this system

were lower than the others studied in this work. Values for the varying BaO:SiO₂ system are in the range $0.55 < \Lambda < 0.61$ compared to $0.58 < \Lambda < 0.66$ for the varying CaO:SiO₂ system. Furthermore, due to the action of BaO as a strong base, the decreasing a_{SiO_2} effect will be greater, resulting in slags with lower oxygen potential. Thus, L_M will be smaller in both regions of influence.

5. Impurity Removal efficiency

The percent removal of boron and phosphorus from silicon was calculated from the difference between the initial and final mass of the impurity in the metal phase as a ratio to the initial mass in the Si alloy as determined from the chemical analyses and was reported elsewhere [20]. Removal efficiencies (R) and L_M are related through the expression shown as Eq. (6), assuming negligible impurity (M) content of the starting slag

$$L_M = \left(\frac{R}{1-R} \right) \frac{m_{\text{Si}}}{m_{\text{slag}}} \quad (6)$$

where m_{Si} and m_{slag} are the mass of silicon and slag respectively and. When $R/(1-R)$ is then plotted against $L_M(m_{\text{slag}}/m_{\text{Si}})$ as shown in Fig. 6, a straight line with a slope of 1 should be obtained. Thus, one parameter can be used to predict the other.

Rearranging Eq. (6) to the form of Eq. (7) shows how the absolute removal is determined by the distribution coefficient (which is characteristic of the particular slag) and the ratio of masses of silicon and slag.

$$R = \frac{L_M}{L_M + \frac{m_{\text{Si}}}{m_{\text{slag}}}} \quad (7)$$

Thus it is apparent that an excess of slag will give higher removals, but as in any pyrometallurgical process, it is not desirable to handle large slag volumes from a cost and practicality standpoint. For a typical MG-Si containing 15 ppm B and 30 ppm P, the amount of slag required for it to be refined to SoG-Si purity can be estimated. For final levels of 1.5 ppm B and 1 ppm P, R need to be 90% and 97% respectively. For treatment with the slag that resulted in the highest L_M ,³ this translates to a slag mass roughly 5.5 times that of silicon for treatment of boron and 3.3 times that of silicon for treatment of phosphorus. Obviously where both these elements are present, the larger slag amount will be needed to remove both to SoG-Si levels. The amount of slag required can be lowered by operating where L_M will be higher, but it follows that the composition of the slag must only be adjusted such that the melting point is not so high as to have an excessively large energy requirement to keep a large volume of slag molten. This may be achieved by adding small amounts of other fluxes such as CaF₂ to the melt.

6. Summary and Conclusions

³ 9% Al₂O₃-24% CaO-33% MgO-34% SiO₂; $L_B = 1.8$, $L_P = 8.8$

The distribution of impurity elements present in MG-Si between slag and silicon metal phases was examined using $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-BaO-SiO}_2$ slags at 1500 °C with particular focus on boron and phosphorus. Where the basicity of the barium-free slag was increased by increasing the CaO:SiO_2 ratio, distribution coefficients for phosphorus increased slightly, while those for boron increased through a local maximum. This indicated that the oxygen potential of the slag, which is dependent on the activity of the slag components, also has a strong influence on impurity partitioning. This was confirmed through increasing the p_{O_2} of the slag by varying the $\text{SiO}_2\text{:Al}_2\text{O}_3$ ratio at constant basicity, which leads to an increase in distribution coefficient for both boron and phosphorus. The low values and weak dependence of the distribution coefficients in the barium-containing slags is attributed to the relatively low optical basicity and p_{O_2} for the compositions studied. It is suggested that a slag with strongly basic and oxidising characteristics would be most useful for extracting boron and phosphorus from silicon. However, it may be difficult to remove both of these elements to the required levels for SoG-Si effectively with a single slagging step due to the different magnitude of the distribution coefficients and different responses to changing slag chemistry. A multi-step programme of refining is therefore likely to be necessary to achieve the required level of silicon purity.

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Table 1. Chemical analysis of silicon master alloys used in equilibration experiments. All values are in wt pct.

Alloy	Al	Ca	Mg	B	P	K	Fe
1	0.208	0.012	0.238	0.190	0.038	0.012	0.395
2	0.095	0.055	0.114	0.261	0.063	0.009	0.270

Table 2. Composition of slags before and after equilibrium experiments.

Test ID	Target (wt%)					Final (wt%)				
	Al ₂ O ₃	BaO	CaO	MgO	SiO ₂	Al ₂ O ₃	BaO	CaO	MgO	SiO ₂
Alumina crucibles										
CS031	35	-	14.5	3	47.5	40.8	-	12.1	3.81	44.5
CS044	35	-	19	3	43	41.1	-	14.5	4.16	42.1
CS061	35	-	23.5	3	38.5	39.8	-	16.5	3.20	41.6
CS082	35	-	28	3	34	39.1	-	17.6	3.39	41.3
CS107	35	-	32	3	30	38.1	-	18.6	2.91	41.6
CS288	35	-	46	3	16	51.5	-	22.7	2.11	24.4
CS377	35	-	49	3	13	53.3	-	24.8	2.09	20.4
CS520	35	-	52	3	10	52.7	-	27.7	2.86	18.0
CS786	35	-	55	3	7	52.9	-	28.8	2.67	16.6
BS045	20	25	-	-	55	25.6	22.6	-	-	51.7
BS060	20	30	-	-	50	27.8	25.7	-	-	46.5
BS077	20	35	-	-	45	28.0	31.8	-	-	40.1
BS100	20	40	-	-	40	32.0	33.3	-	-	34.6
BS128	20	45	-	-	35	30.7	38.7	-	-	30.6
Magnesia crucibles										
SA007	45	-	42	10	3	27.3	-	30.3	19.8	17.4
SA020	40	-	42	10	8	23.5	-	26.0	25.9	23.3
SA037	35	-	42	10	13	21.4	-	29.7	20.7	24.7
SA060	30	-	42	10	18	16.8	-	27.8	25.2	27.2
SA092	25	-	42	10	23	14.2	-	27.4	27.5	28.8
SA140	20	-	42	10	28	10.5	-	25.7	30.7	31.4
SA220	15	-	42	10	33	8.87	-	24.6	32.9	33.8

Figure 1. Schematic diagram of the furnace setup

Figure 2. Normalised slag composition. Major oxides comprise ~99.7% of total assay

Figure 3. Distribution coefficients for impurities between slag and Si in varying CaO:SiO₂ (35%Al₂O₃-CaO-3%MgO-SiO₂) slags

Figure 4. Distribution coefficients for impurities between slag and Si in varying $\text{SiO}_2:\text{Al}_2\text{O}_3$ (Al_2O_3 -42%CaO-10%MgO- SiO_2) slags

Figure 5. Distribution coefficients for impurities between slag and Si in varying $\text{BaO}:\text{SiO}_2$ (20%- Al_2O_3 -BaO- SiO_2) slags