MODELLING CR CONTAINING SLAGS FOR PGM SMELTING

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ABSTRACT

Thermodynamic and some of the transport properties of multi-component slags containing CrO-Cr_2O_3-FeO-Fe_2O_3-CaO-MgO-NiO-Cu_2O-Al_2O_3-SiO_2 *were modelled using published and in-house data on sub-systems of interest to the South African PGM concentrate smelting. The thermodynamic properties of the slag phase were described by the cell model. The solid phases, such as spinel, olivine and pyroxene were modelling by using the regular type model. The viscosity and electrical conductivity of homogenous melts or melts containing solid particles were calculated by the CSIRO models. The models have been validated against new experimental data on synthetic and industrial slags. The inclusion of Cr in the database of the Multi-Phase Equilibrium (MPE) package has allowed its application to study behaviour of phases in electric smelting of sulphide concentrates containing low level of chromium and Platinum Group Metals (PGM).*

The models with the optimised parameters could be used to simulate the equilibrium between slags and copper-nickel matte and various solid phases. The effects of Cr on the phase equilibrium, slag viscosity and electrical conductivity have been analysed. Knowledge obtained has led to the development of a quantitative guide to avoid process difficulties by control of temperature, oxygen partial pressure and slag chemistry over practical ranges.

INTRODUCTION

One of the challenges facing the South Africa PGM (Platinum Group Metals) producers is the depletion of the low cost Merensky reserves and the increasing exploitation of the UG2 reefs which contains high levels of chrome and poses difficulties during various stages of processing [2]. High chrome concentrates favours formation of spinel crystals, which tend to settle between the matte and slag layer or deposit on the refractory base during smelting and hence likely to cause operational problems. The influence of the slag properties during the smelting process has been discussed by Nell [9]. This includes the control of slag viscosity, liquidus temperature, Cr containing phases and limiting solubility of Cu, Ni and Co. The major difference between the two types of concentrates is the higher levels of MgO and Cr_2O_3 in the UG2 concentrate which can impact on the slag properties and hence the furnace operation. A good understanding of the behaviour of such slags as functions of temperature, oxygen partial pressure and slag composition is critical for smooth smelting operations.

In 2001 the present authors were presented with the opportunity of working with some of the South African PGM producers, investigating the problems with high chrome deposit and searching for solutions in treating such materials. Since 2001, the CSIRO Multi-Phase Equilibrium (MPE) package [15, 16] has been extended to include Cr containing species and phases for simulation of the smelting of the UG2 concentrates. The approach taken was to utilise both the experimental and the modelling capabilities to understand the major factors that influence the behaviour of chromium in the smelting and converting processes. Measurements have been carried out on samples from the plants to characterise properties such as phase relations in slag/matte/metal/gas, viscosity [11] and electrical conductivity of the slags [5]. The MPE package was validated using the data obtained from supplied South African melter slag samples and used in simulation of the smelting process. This paper presents the modelling results and examples of application of the MPE package to the UG2 smelting.

MODEL DEVELOPMENTS

The MPE package has been extended to include thermodynamic descriptions of Cr containing species in various phases through assessment of published data and application of such data in development of databases for solution models. The effects of Cr_2O_3 in slags on the viscosity and electrical conductivity of the slag was modelled using the in-house data.

The MPE package composes thermodynamic data of species and phases and models for solution phases. It also includes models for viscosity and electrical conductivity of the slag phase. A detailed description of the development of the thermodynamic model and viscosity models in the MPE package has been reported elsewhere [15, 16]. Only a brief introduction relating to the current work is given in the following.

Thermodynamic Models

Slag Model

The cell model proposed by Kapoor and Frohberg [7] and later extended by Gaye and Welfringer [3] was used. The components of the model for the current application included SiO_2, Al_2O_3, Cr_2O_3, Fe_2O_3, FeO, CaO, MgO, CrO, NiO, CoO, Cu_2O and S.

Solid Solution Models

Solid solutions may be approximated by the regular type behaviour of stoichiometric (line) compounds by using the Redlich-Kister equation [10]. the oxide solid solution phases used are shown below and some of them were extended for the inclusion of Cr species

- Halite: (Ca,Fe,Mg,Ni,Co)O, equivalent of wustite, periclase, etc.
- Spinel: (Fe,Mg,Ni,Co,Cr)$(Al,Fe,Cr)_2O_4$, equivalent of magnetite, etc.
- Corundum: $(Al,Fe,Cr)_2O_3$
- Olivine: $(Fe,Mg,Ni,Co,Cr)_2SiO_4$
- Pyroxene: $(Fe,Mg,Cr)SiO_3$.

Alloy Models

An alloy model using the Redlich-Kister equation for the Ni-Fe-Cu alloy is also available.

Matte Model

The quasi-chemical model by Kongoli and co-workers [8] was adapted and extended in this work and implemented in the MPE package. The model covers the matte of Fe-Cu-Ni-Co-Cr-S-O.

Viscosity Model

Compared with other common packages available, the MPE package offers a unique capability of predicting the viscosity of slags, in addition to the phase equilibria information for systems of interest. The viscosity model is structure-related and it predicts viscosity in higher order systems using only binary parameters. The model has been validated using published data in the higher order (ternary to six component) slag systems (silicate and calcium ferrite type), containing 13 oxide components [13, 14, 15,16].

Viscosity of solid-containing slags with up to 0.33 mass fractions of solid phases can also be estimated in the MPE package by using a modified Einstein-Roscoe equation [12, 15].

Electrical Conductivity Model

The details of the model are to be discussed in a separate publication and a general description of the model is as follows. The total electrical conductivity σ_T is the sum of the ionic conductivity σ_i and the electronic conductivity σ_e:

$$\sigma_T = \sigma_i + \sigma_e \tag{1}$$

The ionic conductivity σ_i is a function of temperature and slag composition. The electronic conductivity σ_e depends on the ratio of Fe^{3+} /Fe^{2+} in the melter type slags which is a function of oxygen partial pressure (P_{O2}) as well.

The model has further been extended to include the effects of i) chromium content of the slags and ii) solid phases such as chromite spinel, olivine and pyroxene on electrical conductivity [6]. For the solid containing melts the electrical conductivity is described by the mixing model proposed by Glover and co-workers [4]. It uses a simple modified Archie's law, for two conducting phases of invariable volume fractions.

RESULTS AND DISCUSSION

Model Validations using the Supplied South Africa Melter Slag Samples

The compositions of the supplied South African melter slag samples used in the model calculations are shown in Table 1. The original sample assay was normalised to one hundred percent in total. For convenience Fe_2O_3 content was set to 1 wt% considering the reducing conditions in melter. The modelling results have been compared with the measured liquidus and phase equilibrium data, viscosity [11] and electrical conductivity.

Table 1: The compositions used in the model calculations for the South African melter slags

Sample ID	Composition wt% (Total 100%)						
	SiO_2	FeO	MgO	CaO	Al_2O_3	Cr_2O_3	Fe_2O_3
S1	50.5	13.4	19.5	7.5	7	1.1	1
S2	57.5	9.4	20.7	3.1	7.2	1.1	1
S3	44.6	28.5	15	6.6	3.3	1	1
S4	46.5	13	22	10	5	2.5	1
S5	47.3	23.3	17.5	5.3	4.4	1.2	1
S6	48.8	12	24.4	5	5.3	3.5	1

Liquidus Temperature and Phase Equilibration

The calculated liquidus temperatures and the phase changes as a function of temperature for the South African melter slags have been obtained and compared with the measured data [11]. The results are presented in Table 2, which shows the temperature and the primary and second solid phases. The experimental schedule gives temperature intervals of generally 25-30°C, and up to 50°C in some occasions with the secondary solid phase. The maximum experimental temperature was 1630°C in this series of experiments. It can be seen that the model reproduces the experimental findings well in terms of the relative stability of the solid phase, i.e., spinel being the primary solid phase and olivine or pyroxene, depending on the SiO_2 level, being the secondary solid phases in these slags. The model prediction of the liquidus temperatures are in good agreement with measured values except for sample S3.

Table 2: Comparison between calculated and measured temperatures for appearance of solid phases from the equilibration tests of the supplied South African melter slags. ('-' indicates that the phase was not found in the slag samples).

Sample	Temperature (°C) at which solid phases appear					
	Spinel		Olivine		Pyroxene	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
S1	1600-1630	1552	1400-1425	1389	-	1249
S2	1570-1600	1546	-	-	1400-1425	1386
S3	1570-1600	1455	1300-1350	1408	-	-
S4	>1630	1719	1425-1450	1462	-	-
S5	1570-1600	1503	1300-1350	1416	-	-
S6	>1630	1760	1460-1475	1473	-	1324

The stability of spinel crystals was directly related to the chrome content of the slag and this is reflected by the measured liquidus temperature for the melter slags increasing from about 1570°C (S3) to in excess of 1630°C (S4 and S6) as the Cr_2O_3 was increased from about 1 to 3.5 wt%. The model reproduced such trend and predicted 1760°C for S6 which has the highest Cr_2O_3 of 3.5 wt% and 1719°C for S4 which has the second highest Cr_2O_3 of 2.5 wt%. The model also predicted a liquidus temperature of 1455°C for S3, the lowest among all the samples. The stability of spinel also depends on MgO content. S3 has the lowest MgO (15%) among the samples of similar Cr_2O_3 contents (1 to 1.2 wt% in S1, S2, S3 and S5), therefore the relatively low liquidus temperature. In these equilibrium experiments platinum foil was used as container materials for the slag samples and it was likely that some of the iron from the slag was lost to the foil during the equilibration period. Thus the other probable cause of observed differences between the measure and calculated liquidus temperatures is due to changing slag chemistry through loss of iron in the experiments.

The temperature range in which the second solid phase appeared was much narrower than that of the spinel. The experimental data showed within 200°C while the model predicted within 100°C. The model predicted temperatures at which the second solid phase appeared were in very close agreement with the measurements (within ±50°C). The model was also able to reproduce the effects of MgO/SiO_2 ratio or MgO content on the stability of the olivine phase, i.e., the stability of olivine increased as MgO/SiO_2 ratio or MgO content of the slag increased. The experiments showed that pyroxene was the second solid phase for S2 and the model was able to reproduce the finding. It is noted that S2 has the highest SiO_2 content where pyroxene becomes more stable compared with olivine.

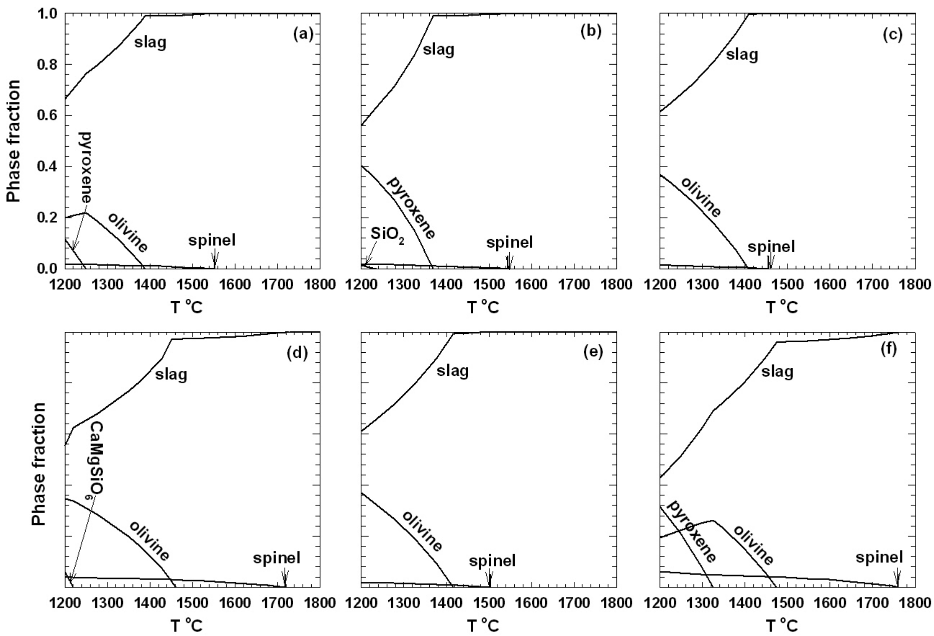

Figure 1: Calculated phase distributions as a function of temperature for the South African melter slags ((a) for S1, (b) for S2, (c) for S3, (d) for S4, (e) for S5 and (e) for S6)

The model was also used for prediction of the quantity of phases and their compositions during the cooling of the slag sample, to provide additional information which are difficult to obtain through experiments. Figure 1 showed the calculated phase distributions as a function of temperature for the supplied South African melter slags. The model calculations showed that the Cr_2O_3 content not only affected the stability of the spinel but also the amount of the spinel phase. This is consistent with the findings on the viscosity behaviour of the melter slags [11]. The model also predicted that the third solid phase of pyroxene was stable for S1 and S6, and SiO_2 for S2 above 1200°C.

Viscosity

Figure 2a shows a comparison between the calculated and the measured [11] viscosity as a function of temperature for the supplied South African melter slags. It can be seen that viscosity increases with decreasing temperature and increasing silica content. It is also noted that sudden increase in viscosity becomes apparent when the slag reached the temperature at which the second solid phase started to form. While the pronounced effect of suspended solid phases on the viscosity of slags is well established, the actual concentration, shape and size of such particles are expected to show different effects on the viscosity of the slurry. It was shown in Figure 1a-f that the amount of the second solid phase increased much more sharply than the spinel with decreasing temperature. Thus it is likely the increasing amount of the solid particles in slags is the primary cause of the sharp increase in viscosity, however one should also consider their shape and possibly size. Close agreement between the model and the measurement is evident, from Figure 2a, even for slags containing a reasonable amount of solids.

Electrical Conductivity

Figure 2b shows comparison between the calculated electrical conductivity and the measured values as a function of temperature for the supplied melter slags. The electrical conductivity of these slags increased with increasing temperature and decreasing silica content. It is interesting to note that the electrical conductivity has opposite behaviour comparing with viscosity as to the dependence on SiO_2 in particular. The sample with the lowest silica content, S3, is at the top in Figure 2b (conductivity) and the bottom of Figure 2a (viscosity). Sample S2 with the highest silica content appeared at the bottom in Figure 2b and top in Figure 2a.

The calculated values are in close agreement with those measured though the calculated values are in general slightly lower than the measured data. There is noticeable difference for S5, due to large uncertainties for this set of data. Nevertheless the model is able to reproduce the correct trend in terms of the effects of, temperature, the amount of solid particles and slag chemistry, in particular, silica content on the electrical conductivity of the melter slags.

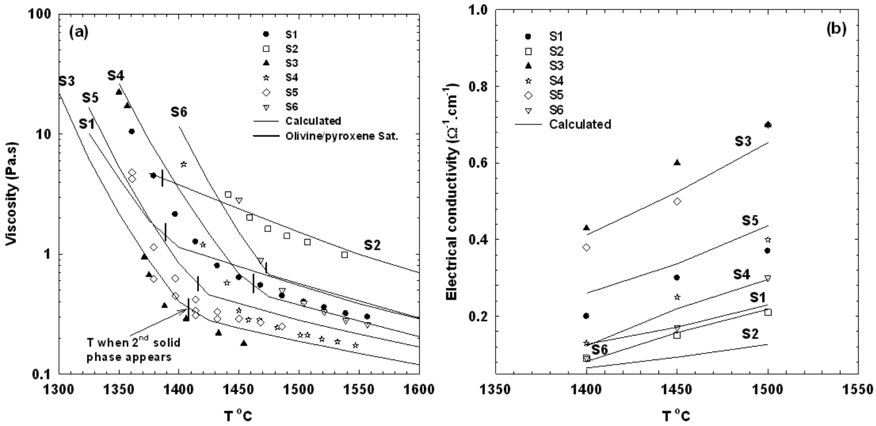

Figure 2: Comparison between the calculated and the measured (a) viscosity [11] and (b) electrical conductivity as a function of temperature for the supplied South African melter slags

APPLICATION OF THE MPE PACKAGE

The optimised and validated models in MPE have been used to simulate the various aspects of the UG2 smelting process. In the following section, some examples illustrating the dependence of chromium solubility in the slag on the slag composition, temperature and oxygen potential are presented and discussed.

Solubility of Cr in Melter Slags

For smooth operation, it is desirable to contain Cr in the liquid phase to avoid the formation of spinel, which causes operational difficulties, by controlling temperature and oxygen potential. Bartie has carried out some measurements [1] on synthetic slags to investigate the effect of temperature and oxygen potential on the solubility of Cr in the melter type slags with varying starting Cr_2O_3 content. His results and those predicted by the MPE model are shown in Figures 3a and b. These results confirmed the expectation that the solubility of Cr in the melter slags increases with increasing temperature and decreasing oxygen potential. The MPE calculated Cr solubility values for the same slags (with compositions shown in Table 3) were found in excellent agreement with the experimental data (Figure 3a and b). This indicates that the MPE package can be used to predict the solubility of Cr in the melter slags over a fairly broad range of temperature and oxygen partial pressure of interest to the operations.

Table 3: Slag composition used in model calculations of Cr solubility in synthetic melter slags

Sample ID	Composition wt%					
	MgO	Cr_2O_3	FeO_x	SiO_2	CaO	Al_2O_3
SCR1	19	1.5	21.5	48.3	4.8	4.9
SCR2	19.8	3.7	22	44.8	4.8	4.9
SCR3	18.2	6.4	20.3	45.2	4.9	5
SCR4	14.3	7.1	18	50.5	5	5.1

Temperature and Oxygen Potential

Examples showing the correlation between the solubility of Cr and the level of Cr addition to melter type slags are presented in Figure 4a for slags under a fixed oxygen partial pressure of 10^{-10} atm and three temperatures (1400, 1500 and 1600°C). Similarly, in Figure 4b the variation in the Cr solubility in the slag with Cr addition at three oxygen partial pressures (10^{-8}, 10^{-10} and 10^{-12} atm) and at 1500°C are shown.

It can be seen that temperature has a pronounced effect on the solubility of Cr in the slag phase. At 1600°C the slag remains homogeneous with Cr loading in slag reaching 7.5 wt%. At temperatures of 1500 and 1400°C, solubilities of Cr in the slag phase are approaching 4 wt% and 1.3 wt% respectively (increasing slightly with Cr loading up to 7.5 wt%). In other words at a given temperature, Cr loading below this limit should result in all the Cr dissolved in slags for the relevant temperature without the formation of the spinel phase.

The effect of oxygen partial pressure is shown in Figure 4b. Under a reducing atmosphere of $P_{O2}=10^{-12}$ atm, the slag remains fully molten even when Cr content reached as high as 7.5 wt%. However, as oxygen partial pressure increases, the spinel phase starts to precipitate out at 4 wt% for $P_{O2}=10^{-10}$ atm and 1.7 wt% Cr for $P_{O2}=10^{-8}$ atm. Further addition of Cr to the melts will cause the amount of spinel to increase and slag to decrease. It is worth noting that the solubility limits are insensitive to further Cr addition beyond the initial saturation point.

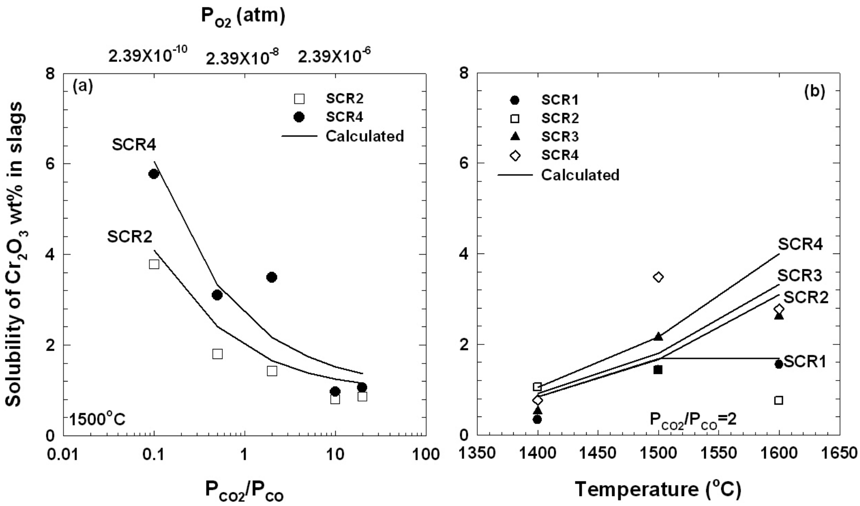

Figure 3: Comparison between the experimental data [1] and the MPE calculations on solubility of Cr as functions of (a) oxygen partial pressure, at 1500°C and (b) temperature, at $P_{CO2}/P_{CO}=2$ in melter type slags

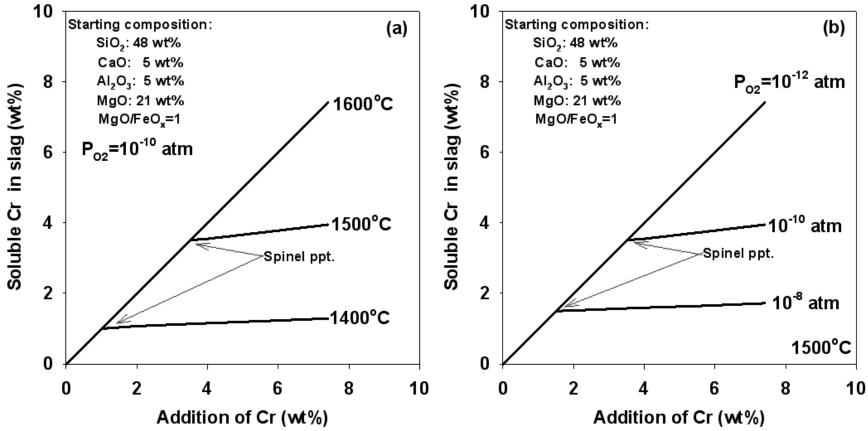

Figure 4: (a) Model predictions of the effect of temperature on solubility of Cr in the slag phase $P_{O2}=10^{-10}$ atm, and (b) the effect of oxygen partial pressure on the solubility of Cr in the slag phase at 1500°C

Slag Chemistry

In Figure 5a and 5b the effect of MgO/FeO ratio in the melter type slags on Cr solubility in the slag phase was examined for melts containing initially 3 and 5 wt% of Cr and three levels of silica. The oxygen partial pressure is fixed to $P_{O2}=10^{-10}$ atm and temperature 1500°C. The key factor is again the slag compositions at which the spinel phase starts to form. It is shown that in general high silica content and low MgO/FeO ratio favour high Cr solubility. These results also show that the drop in Cr solubility with the MgO/FeO ratio is more significant in slag plus spinel region than in region of slag plus both spinel and olivine. Nevertheless, comparing with results in Figure 5a and b, the effect of slag chemistry is not as significant as the effects of temperature and oxygen partial pressure within the ranges covered in this study.

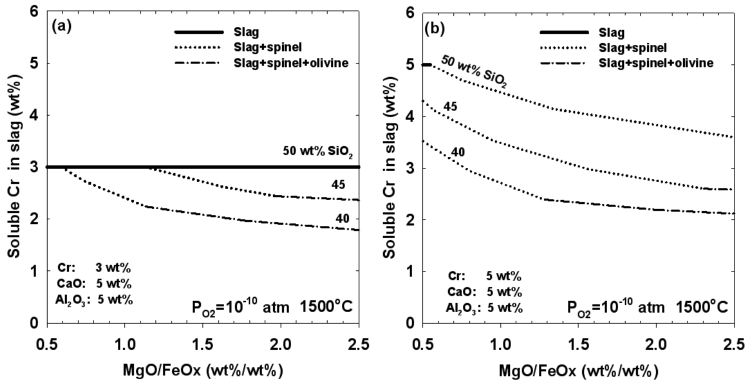

Figure 5: Effects of silica content on solubility of Cr in the slag phase as functions of MgO/FeO ratio of the melter type slags with initial (a) 3wt% Cr and (b) 5wt % Cr at $P_{O2}=10^{-10}$ atm at 1500°C

CONCLUSIONS

The capability of CSIRO MPE package has been extended to Cr containing slags and solid solution phases, for simulations of smelting of the Cu-Ni-Fe sulphide concentrates containing chromite and other oxide mineral phases.

The models have been validated over the operational range of temperature, oxygen potential and slag chemistry for phase equilibria, slag viscosity and electrical conductivity. The validation results have shown that the models are able to reproduce the experimental findings on the phase equilibria, viscosity and electrical conductivity of multi-component melter slags.

Predictions by the model illustrate the important effects of temperature, oxygen partial pressure as well as slag chemistry on the stability of solid phases and slag viscosity and electrical conductivity. Model simulations with respect to mapping operating windows for UG2 smelting were presented. The package could be readily used for development of optimum practices for treatment of Cr containing concentrates as well as interactions between melts and refractories in various other smelting processes.

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