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ASPECTS OF THE REGULAR SOLUTION MODEL AND ITS APPLICATION TO METALLURGICAL SLAGS

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SYNOPSIS

Published thermodynamic data on slags containing two or more of the following species: Al_2O_3, CaO, CoO, Cu_2O, FeO, Fe_2O_3, MgO, MnO, NiO, P_2O_5, PbO, SiO_2, TiO_2 and ZnO have been reviewed and analysed with respect to Lumsden's regular solution model. The analysis showed that most slag systems followed the regular solution behaviour over a broad composition range. However, in some systems or composition ranges, departure from the regular solution behaviour was observed. For systems which complied with the regular solution behaviour, the binary interaction energies between cations could be readily deduced from the published data. Comparison of the measured activities of species in slags with those calculated by the regular solution model show that the model gives a good representation of the thermodynamic properties of most slags over a broad range of composition and temperature. The capability and limitation of the model with respect to calculating some of the thermodynamic properties of slags are discussed.

KEY WORDS; Thermodynamics, activity, slag, regular solution.

1. INTRODUCTION

The growing interest in utilisation of the thermodynamic properties of slags to develop new processes has lead to some progress in the application of mathematical models for representing some of the thermodynamic properties of slags. However, a number of limiting factors have been responsible for the relatively slow progress in the development of accurate and general models as well as a deeper understanding of the thermodynamic behaviour of melts. Lack of comprehensive and accurate data on the activities of components in homogeneous slags has been one of these limiting factors. Other limiting factors include the uncertainty in the basic thermochemistry data (e.g. heat capacities, heats of formation and transformation) as well as our current theoretically based "physical" models.

Continuing work at the CSIRO's Division of Mineral & Process Engineering aims at developing an improved understanding of the behaviour of melts and development of suitable models for calculating some of the thermodynamics and structurally related properties of metallurgical melts. Recently the applicability of regular solution behaviour to a broad range of slag chemistry was examined and a Regular Solution Model (RSM) was developed for calculations of some of the thermodynamic properties of simple and metallurgical slags. Some aspects of this work will be briefly discussed here.

2. SELECTION OF THERMODYNAMIC/THERMOCHEMISTRY DATA

Assessment of the published data and development of databases on the thermodynamic properties of simple and complex oxide systems formed the basis of the present work. In this evaluation, data which showed discrepancy with a series of other similar investigations were excluded from the database. In systems where there were subtle differences between the results either due to different experimental techniques and/or choice of thermochemistry data, all the papers were included in the database. In such cases the data were subsequently converted to a uniform standard state (using a set of thermochemistry data) prior to their interpretation. Comparison and selection of the thermochemistry data were made from major compilations by: Barin *et al.*[1,2], Kubaschewski *et al.*[3], Turkdogan[4] and the CSIRO-Thermochemistry System[5]. In addition to these, the recommended data from various reviews and investigations were also used.

In cases where determination of the activities of species in the slag phase was dependent on the thermodynamic properties of other phase, e.g. alloys, then activities were recalculated using a set of thermodynamic data for alloys. For calculations of the activity coefficients and hence the activities of components in the metal phase, use was made of the major compilations by Hultgren *et al.*[6] for binary solutions or specific data on a particular system of interest were used. In a few cases, such as the unresolved differences in the activity of manganese in Pt-Mn, it was decided to use each investigator's activity data on the metal and slag phase.

Activities of minor elements in dilute solutions of alloys were calcualted using the method described by Lupis and Elliott[7-9] in conjunction with the selected interaction parameters by Sigworth and Elliott[10,-12]. The effects of minor elements on the activity coefficient of iron (solvent) were calculated using the method described by Ban-ya and Chipman[13,14] together with the relevant data by Ban-ya and co-workers[15-17]. In some of the metal solutions (e.g. Pb-O, Cu-O and Cu-Fe-O) the effects of minor elements on the activity coefficient of the solvent were assumed to be negligible.

The above mentioned work resulted in development of a comprehensive and self consistent database on the thermodynamics of slags. The database contains a major portion of the published data (several thousand equilibrium measurements) on simple and complex oxide systems. This database was used for examining the behaviour of binary, ternary and multi-component oxide systems with respect to the regular solution model. It is worth pointing out that despite the steps taken to unify the published data and reduce the differences between the experimental data obtained by different workers, some subtle differences still exist which would inevitably result in some degree of scatter.

3. REGULAR SOLUTIONS

In 1961 Lumsden[19] first demonstrated that ionic melts, such as slags, can exhibit regular solution behaviour. In such melts the molecular/ionic species such as SiO_2 or SiO_4^{4-} were regarded as "dissociated" ionic species consisting of Si^{4+} cations and O^{2-} anions. It was considered that the cations are almost randomly distributed among a three dimensional matrix of oxygen anions (O^{2-}). Lumsden also recognised that for calculation of the activities of species, conversion from a theoretical Regular Solution (RS) standard state to the conventional standard states (e.g. pure solid or liquid) was necessary.

The formulation of the energies of the system may then be expressed in terms of the binary interaction energies (α) between cations and the mole fractions of the cations (X). Ban-ya[20] showed that the general equations expressing the thermodynamic properties (heat of mixing (ΔH^{mix}_{RS}), activity coefficient (γ_i)) of multi-component regular solutions are as follows:

$$\Delta H^{mix}_{RS} = \sum_{i}^{n} \sum_{j}^{n-1} \alpha_{ij} X_i X_j \tag{1}$$

$$RT\ln(\gamma_i)\ (RS) = \sum_{j}^{n} \alpha_{ij} X_j^2 + \sum_{j}^{n}\sum_{k}^{n-1} (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k \tag{2}$$

where; $i \neq j$ or k, and $k > j$, $\alpha_{ij} = \alpha_{ji}$ and $\alpha_{ii} = \alpha_{jj} = \alpha_{kk} = 0$.

and $$RT\ln(\gamma_i)\ (\text{real solution}) = RT\ln(\gamma_i)\ (RS) + \Delta G_{conv} \tag{3}$$

where, ΔG_{conv} is the conversion factor associated with change in standard states.

4. Determination of the Regular Solution Binary Interaction Energies

Since Lumsden illustrated the usefulness of the RSM for calculating the activities of components in simple melts, a number of investigators[21-31] have examined the applicability of the RSM to various slag systems. These studies have indicated that activities of species in simple and complex slags (with up to 7 components) could be adequately expressed by the RSM over a range of composition. However, there was a need to re-examine the application of the model to metallurgical slags, since there are inconsistencies between the apparent binary interaction energies (α_{ij}) obtained by different groups of workers. These inconsistencies are largely due to the differences in the selected thermochemistry data as well as the choice of activity composition data, thus making the interaction energies not readily transferable from one system to another.

During the initial work on the evaluation of the RSM and determination of the model parameters it became apparent that not only the selection of the thermodynamic data, but also the method employed for determination of the binary interaction energies could influence the results. In particular, the use of multiple linear regression analysis as a quick and convenient method of determining the model parameters had to be ruled out. Instead the method used by Lumsden[19] that of Ban-ya and co-workers[26,29] was adopted in the present study. This technique uses a graphical method to verify the regular solution behaviour as well as optimising for the "best" values of the binary interaction energies. The other advantage of this method is its ability to indicate subtle differences between sets of data for a complex system as well as providing clues on possible source of errors in the data.

5. The Free Energy Change for Changes in Standard States

The use of conversion factors (ΔG_{conv}) for converting the calculated activity coefficients from a theoretical regular solution standard state to the conventional standard states has been practiced by some of investigators. In the present study, ΔG_{conv} were determined using the selected thermochemical data and the activity-composition data from the database, in conjunction with some of the published phase diagrams. Since the accuracy of most thermochemical data is about ± 3 kcal mol^{-1}, the accuracy of the expressions derived are likely to be of similar magnitude.

6. RESULTS AND DISCUSSION

To date most of the published data on slags containing two or more of the following species: Al_2O_3, CaO, CoO, Cu_2O, FeO, Fe_2O_3, MgO, MnO, NiO, P_2O_5, PbO, SiO_2, TiO_2 and ZnO have been analysed with respect to regular solution behaviour. It was found that most slag systems followed the regular solution behaviour and hence the interaction energies could be readily deduced from the published data. It is worth pointing out that in some systems studied, confirmation of the regular solution behaviour could not be obtained from the existing data. In such cases the values of interaction energies used in the model correspond to the best values for representing the published activity-composition data. There are a number of reasons for such an apparent behaviour: possible inhomogeneity of some of the melts and/or the limitations of the RSM are thought to be the main reason(s) in most of the cases studied. In addition to these, there are some doubts as to whether thermal and chemical equilibria were achieved in the few cases where data were from unique systems.

Comparison of the values of the binary interaction energies show a number of interesting trends, namely:

- Most interaction energies are exothermic, indicating affinity for "clustering" behaviour or compound formation to occur. This gives rise to the lowering of the activity coefficient of species in the melt.
- In general the phosphates show greater interactions with "basic" cations than silicates, aluminates or ferrites.
- There are strong correlations between the interaction energies/heats of mixing (e.g. $\alpha_{M^{z+}\sim Si^{4+}} X_{M^{z+}} X_{Si^{4+}}$) and the published heats of formation of compounds (see Figure 1).
- The difference in the binary interaction energies ($\alpha_{Fe^{3+}\sim M^{z+}}$ - $\alpha_{Fe^{2+}\sim M^{z+}}$) associated with the redox equilibrium FeO + 1/4 O_2 = $FeO_{1.5}$, shows a strong correlation with the ionic charge to size ratio. This finding will be discussed in more detail in the following section.

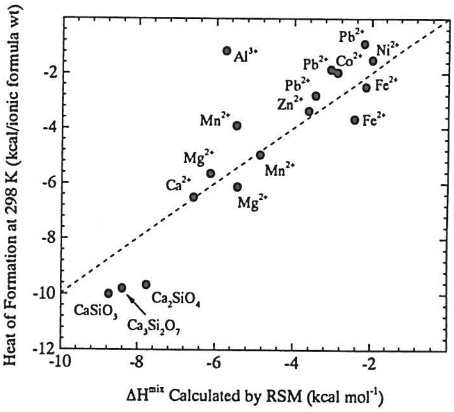

Figure 1: Correlation between heats of formation of various silicates (from oxides) with the calculated heats of mixing (ΔH^{mix}) according to the values of the regular solution binary interaction energies ($\alpha_{Si^{4+}\sim M^{z+}}$).

Figures 2-4 show some examples of the comparisons made between the calculated activities of species using the RSM with the measured values from the database. Taking into account that in some systems subtle differences exists between experimental data obtained by different investigators, then these comparisons show that the RSM gives good representation of the activities of components in most of the systems studied over a broad range of temperature and composition. However, in some composition ranges and/or systems the calculated values showed significant deviations from the measured activities. These include;

- "terminal"/saturation regions such as compositions near or on silica saturation limits,
- most multi-component systems containing phosphorus,
- systems which did not show regular solution behaviour, e.g. zinc and aluminate slags.

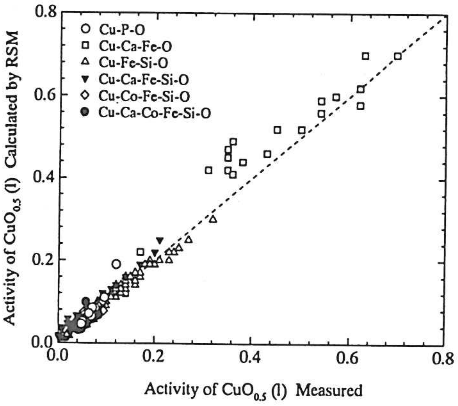

Figure 2: Comparison of measured(*) and calculated activity of $CuO_{0.5}$ (standard state pure liquid) in various systems.

* See extended version of this paper for references.

The inaccuracy of the RSM at the silica saturation regions is to be expected as a consequence of structural changes (e.g. polymerisation or "clustering") and hence departure from random distribution of cations in the melts. Similar explanation could be offered for phosphate slags, where the binary interaction energies were found to be very exothermic, hence indicating the potential for clustering behaviour. This explanation would be consistent with the findings of Sano[32], who showed that even in lime saturated CaO-SiO_2-CaF_2 melts, formation of the phosphate dimer can occur at phosphorus contents of greater than 2 wt%.

Another example of departure from regular solution behaviour at the "terminal" regions is in the FeO rich regions, where according to Lumsden[19] partial dissociation of Fe^{2+} ions could be responsible for the observed behaviour/departure.

Systems which apparently did not comply with the regular solution behaviour were investigated for possible reasons for the non-regular solution behaviour. An example is that activity data used for slags containing zinc and iron oxides are likely to be affected by inhomogenity of melts. The weakness of the RSM with respect to the amphoteric oxides, such as alumina, could also be responsible for some of the apparent departure from the regular solution behaviour.

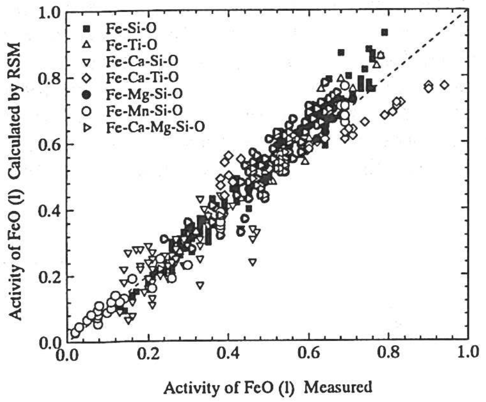

Figure 3: Comparison of measured(*) and calculated activity of FeO (standard state pure liquid) in various systems.

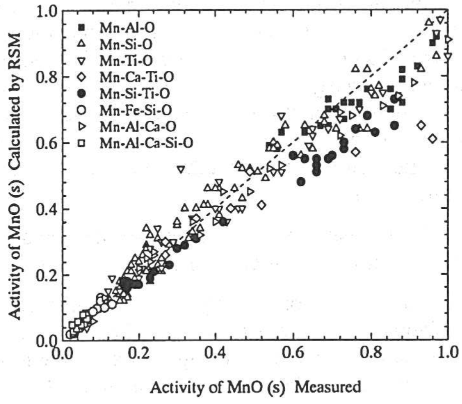

Figure 4: Comparison of measured(*) and calculated activity of MnO (standard state pure solid MnO) in various systems.

7. Binary Interaction Energies Associated with Redox Equilibria

On considering the redox reaction

$$FeO\ (RS) + 1/4\ O_2\ (g)\ =\ FeO_{1.5}\ (RS) \qquad (4)$$

$$\Delta G^\circ_4 = \ -30{,}310 + 12.67\ T\ (cal\ mol^{-1})[19] \qquad (5)$$

thus,

$$RT\ ln\ (\gamma_{FeO1.5}/\gamma_{FeO}) = \ -RTln\ (X_{FeO1.5}/X_{FeO}) \\ -\ \Delta G^\circ_4 + 0.25RTln\ p_{O2} \qquad (6)$$

For multi-component systems, expansion of the general equation for RSM,

$$RTln(\gamma_i)\ (RS) = \sum_j \alpha_{ij}\ X_j^2 + \sum_j\sum_k (\alpha_{ij}+\alpha_{ik}-\alpha_{jk})X_jX_k\ (2)$$

and combining it with Eqn. (6) gives;

$$0.25RTln\ p_{O2} = -\ \Delta G^\circ_4 + RTln(X_{FeO1.5}/X_{FeO}) \\ +\ \alpha_{FeO\sim FeO1.5}(X_{FeO}-X_{FeO1.5}) \\ +\ \sum_i\ (\alpha_{iO\sim FeO1.5} - \alpha_{iO\sim FeO})X_{iO} \quad (7)$$

It follows that for systems which comply with the redox reaction (4) and the difference in the binary interaction energies ($\alpha_{iO\sim FeO1.5} - \alpha_{iO\sim FeO}$) are known, equation (7) can be used for calculation of the equilibrium oxygen potential from the slag composition and temperature of the system, or alternatively the equilibrium Fe^{3+}/Fe^{2+} ratio from the oxygen potential, concentration of the component M^{Z+} and temperature of the system.

In Figures 5 and 6 comparisons are made of the measured and calculated values of the Fe^{3+}/Fe^{2+} ratio (according to the above equation) for a number of slag systems. Given the broad range of oxygen potential (10^{-11} to 1 atm) and the diversity of systems covered by these data, the good agreement obtained for most systems provides some confidence in using the above expression for estimating the Fe^{3+}/Fe^{2+} ratio or oxygen potential of complex slags.

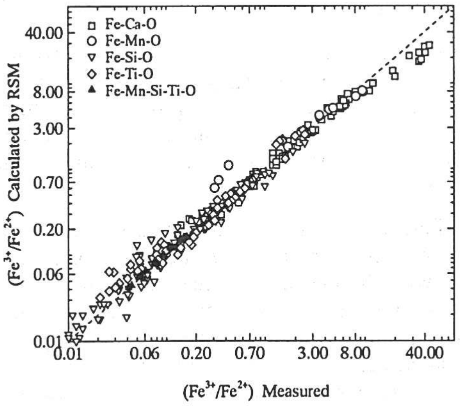

Figure 5: Comparison of measured(*) and calculated Fe^{3+}/Fe^{2+} ratio in the various systems.

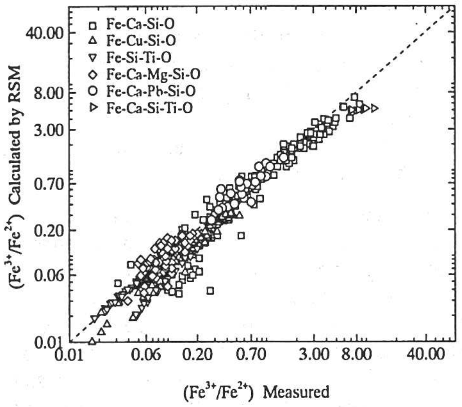

Figure 6: Comparison of measured(*) and calculated Fe^{3+}/Fe^{2+} ratio in the various systems.

An interesting finding from the present work is the correlation between the ionic charge to size ratio of cation M^{z+} and the difference in binary interaction energies ($\alpha_{MO\sim FeO1.5} - \alpha_{MO\sim FeO}$) associated with the redox reaction (4). This dependence is illustrated in Figure 7, where strongly electronegative cations ($P^{5+}$and Si^{4+}) show departure from the behaviour of the less electronegative cations which are usually octahedrally co-ordinated. The large apparent difference in the interaction energies associated with Zn^{2+} is thought to be due to the possibility of presence of zinc ferrite spinel phase in slags containing zinc and iron oxide. The correlation presented in Figure 7 indicates that in homogeneous melts, values of ($\alpha_{MO\sim FeO1.5}$ - $\alpha_{MO\sim FeO}$) also reflect a measure of relative basicity of different oxides. Furthermore, this correlation can also serve as a means of estimating the values of ($\alpha_{MO\sim FeO1.5}$ - $\alpha_{MO\sim FeO}$) for systems where there is lack of measured data.

On considering the CaO-FeO-$FeO_{1.5}$-SiO_2 system, the regular solution binary interaction energies were determined to be; $\alpha_{CaO\sim FeO}$ = -6.04 kcal mol^{-1} , $\alpha_{CaO\sim FeO1.5}$ = -20.4 kcal mol^{-1} , $\alpha_{CaO\sim SiO2}$ = -35 kcal mol^{-1} , $\alpha_{FeO\sim FeO1.5}$ = -4.46 kcal mol^{-1} , $\alpha_{FeO\sim SiO2}$ = -9.79 kcal mol^{-1} and $\alpha_{FeO1.5\sim SiO2}$ = 5.45 kcal mol^{-1} . The calculated heat of mixing according to equation (1) and these interaction energies range from about -9 kcal mol^{-1} for the calcium silicate rich end to about -1 kcal mol^{-1} for the iron oxide rich end of the quaternary system. For iron oxide containing melts, where measurements of the heat of mixing[33,34] and activity of FeO are available, the calculated values according to the regular solution model are in good agreement with measured ones. For the binary CaO-SiO_2 system the measured and calculated values of activities of CaO and SiO_2 ,and hence ΔG^{Mix}, are in good accord at compositions away from the silica saturation. Given that $\alpha_{CaO\sim SiO2}$ is about -35 kcal mol^{-1} and for such a strong interaction between cations, energetically preferred groupings can result in departure from random mixing, then the apparent good agreement between the measured and calculated ΔG^{Mix} indicates that the expressions used for ΔG_{conv} tend to compensate for the possible departure from random mixing.

On the other hand for relatively weak interactions which do not affect the co-ordinations of cations significantly, the underlying assumptions of the model remain valid and hence this model can be used for describing properties of such solutions reasonably well. Similarly for melts with moderate concentrations of strongly interactive cations, the resultant effect of such "clustering" appears not to affect the overall behaviour of the melt to a significant extent and representation of the measured properties by the regular solution model is possible.

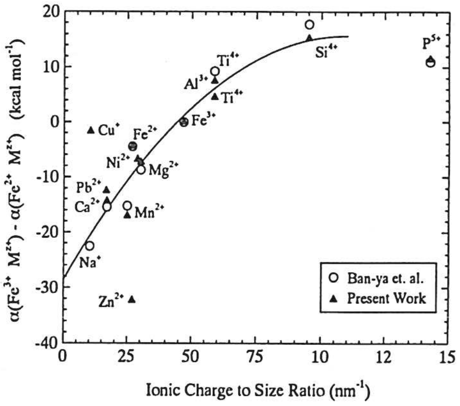

Figure 7: Correlation between ionic charge to size ratio and the difference in the binary interaction energies associated with redox equilibria (e.g. $\alpha_{Fe^{3+}\sim M^{Z+}}$ - $\alpha_{Fe^{2+}\sim M^{Z+}}$).

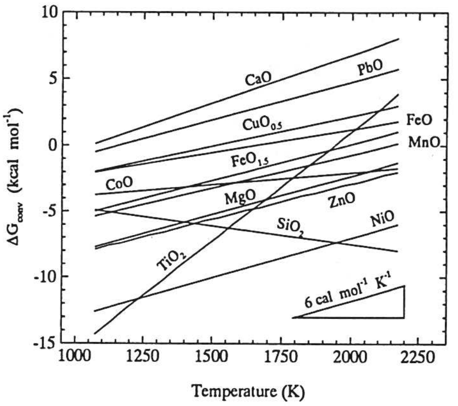

Figure 8: Variation of the $\Delta G_{conv(RS => solid)}$ with temperature for some oxides.

In Figure 8 the variation of the conversion factors associated with changing standard state from a theoretical one for random mixing of cations to pure solid oxide (ΔG_{conv}) is shown. In most cases, the temperature dependence term of the ΔG_{conv} is close to the value expected for entropy of fusion of oxides (6 cal mol^{-1} K^{-1}). However in some cases differences of up to several kcal mol^{-1} exist between the enthalpy of fusion and the apparent temperature independent term of the ΔG_{conv}. The weakness of the RSM in accounting for energetically preferred groupings in melts containing strongly electronegative cations such as Si^{4+} and Ti^{4+} is likely to be responsible for the considerable differences in the temperature dependent term of the ΔG_{conv} for SiO_2 and TiO_2.

In essence the above findings indicate that departure from regular solution behaviour (non-random mixing of cations) can occur in systems containing strongly interactive species. In such cases, in order to represent the measured thermodynamic properties of melts, use of an additional energy term is necessary. This makes the underlying assumptions of the model internally inconsistent to some extent, but allows the model to serve as a useful tool for represention and interpolation of activity data on simple and multi-component metallurgical slags.

8. CONCLUSIONS

The published data on equilibrium studies on slags containing Al_2O_3, CaO, CoO, Cu_2O, FeO, Fe_2O_3, MgO, MnO, NiO, P_2O_5, PbO, SiO_2, TiO_2 and ZnO were assessed and used for the development of an activity-composition database. The database was used to examine the thermodynamic behaviour of simple and complex slags with respect to regular solutions. It was found that most systems complied with regular solution behaviour. In such cases the binary interaction energies showed good correlation with the heats of formation of compounds and the ionic charge to size ratio. Confirmation of regular solution behaviour in some of the slag systems studied (e.g. zinc and aluminate slags) were not obtained. The interaction energies between cations were estimated for these complex melts. The findings from the present work also indicate that the determined interaction energies are transferable between slag systems.

This study has shown that the regular solution model could be used for representing/interpolating some of the thermodynamic properties of most slags with reasonable accuracy. These properties include: all component activity coefficients and hence activities, the heat of mixing and the oxygen potential of slags (provided the concentrations of the ferric and ferrous oxides are known). The major limitations of the regular solution model are: inaccuracies at some of the terminal regions (e.g. silica saturation), inability to account for the effects of amphoteric oxides (e.g. aluminates) and departure from random mixing when strongly reactive/interactive cations at high concentrations are present in the slag.

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