



Fundamentals of freeze lining behaviour in ilmenite smelting

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Synopsis

Changes in reductant and energy inputs which are required to adjust the slag composition in an ilmenite smelter to a higher or lower FeO content are calculated. The calculated changes are based on the assumption that solidification equilibrium with the freeze lining constrains the slag composition to follow a eutectic groove in the $\text{TiO}_2\text{-FeO-TiO}_{1.5}$ phase diagram. Calculated equilibrium conditions along the eutectic groove are presented, and form the basis of the calculations. The inputs of energy and carbon need to deviate strongly from the steady-state values to adjust the slag composition. The inputs required at any given time depend on the desired rate of change of the slag composition, and the current slag composition. The steady-state relationship of a change in energy input of 5 kWh corresponding to a 1 kg change in carbon input also holds for the changed inputs during transient changes in FeO content.

Keywords: Ilmenite smelting, freeze lining, solidification, eutectic

Background

The high-titania slag which is produced during ilmenite smelting is corrosive to all known refractories, and hence ilmenite smelters operate with a freeze lining of solidified slag. While it is essential to maintain the freeze lining, it is also important not to allow the temperature of the slag to drop below its liquidus temperature. As reviewed recently¹, these slags are characterized by very small liquidus-solidus gaps (of perhaps 20°C), and hence a small temperature decrease causes a large increase in the fraction of solids, with increased apparent viscosity. Such partial solidification is presumably responsible for incidents of uncontrolled foaming, which affect such smelters from time to time.

The balance between maintaining the freeze lining and avoidance of partial solidification is struck by careful attention to the mass and energy balance of the smelter. As reported earlier², this means that the steady-state inputs of energy and reductant (relative to the ilmenite input) must match one another.

These two inputs cannot be changed independently without negatively affecting furnace stability.

Inputs of energy, reductant and ilmenite need to be closely matched because the composition of the slag follows a set compositional path, which is close to the M_3O_5 stoichiometry³. Recent work has indicated that a plausible reason for this compositional invariance is the solidification behaviour of these slags⁴. As Figure 1 illustrates, a minimum melting point (eutectic) is found in this system, at compositions towards the TiO_2 -richside of the M_3O_5 composition. This minimum melting point is labelled 'A' in Figure 1 (The composition and temperature where this minimum melting point is found depend on the FeO content of the slag. The set of minimum melting points form a 'eutectic groove' which is shown as line 'D-E' in Figure 2.)

The hypothesis is that the presumed solidification equilibrium (with the freeze lining) constrains the slag composition to be along the eutectic groove, with the freeze lining taking up any variation from eutectic compositions. This predicts that the slag composition should be close to M_3O_5 , but should also contain some rutile after solidification. Examination of slag compositions with a wide range of FeO contents confirmed this general principle⁴, although it does appear that the calculated phase equilibria somewhat over-predict the rutile content of solidified slags. (This means that point 'A' and the others along the eutectic groove in fact lie somewhat closer to stoichiometric M_3O_5 than as predicted in Figures 1 and 2.)

In this paper, one of the implications of the presumed eutectic solidification equilibrium between molten slag and freeze lining is explored, namely the required changes in reductant and energy input if a change in slag

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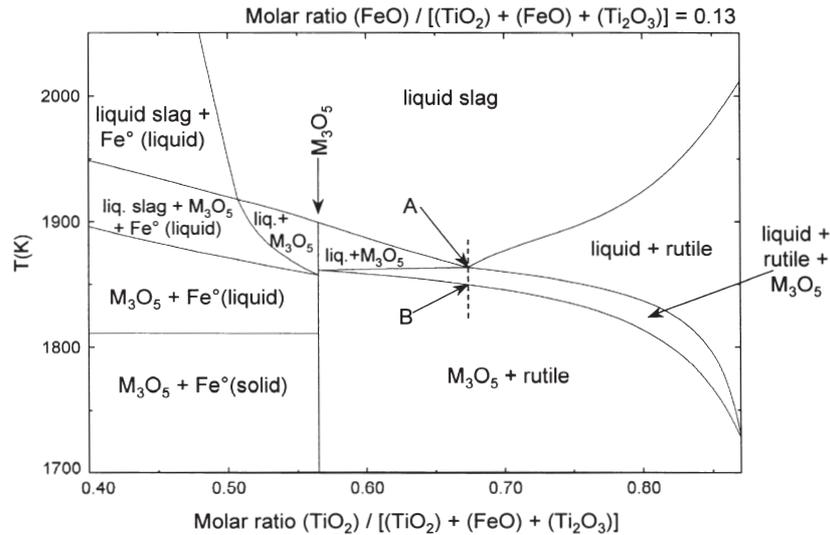


Figure 1—Calculated partial section through the FeO-TiO₂-Ti₂O₃ phase diagram, at an FeO mole fraction of 0.13 (corresponding to a high-titanium smelter slag). The stoichiometric M₃O₅ composition is labelled, as are the point in the eutectic groove ('A') and the lower-temperature limit of three-phase solidification ('B') for this FeO content

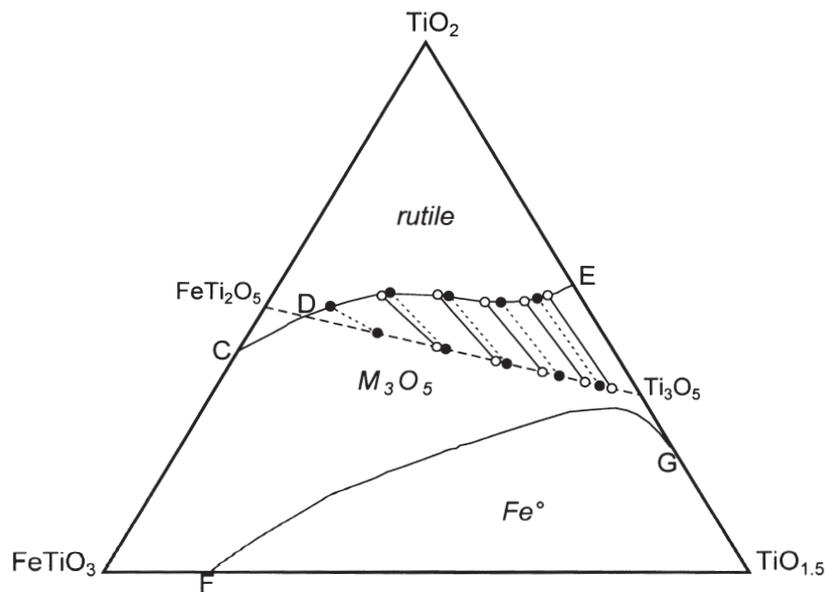


Figure 2—Calculated primary phase fields (these phases are labelled in italics), and tie-lines for combinations of liquid slag (compositions along line 'D-E') and solid M₃O₅ (compositions along the FeTi₂O₅-Ti₃O₅ join), for the conditions at the upper-temperature limit of three-phase equilibrium (tie-lines with solid lines and open circles), and the lower-temperature limit of three-phase equilibrium (tie-lines with broken lines and filled circles)

composition is desired. This is part of a larger project, which aims to understand freeze lining dynamics generally, including heat conduction. Here, predicted solidification equilibria along the eutectic groove are summarized first, and then the required inputs to move to a new slag composition (FeO content) are presented.

Solidification equilibria

The equilibrium results presented in this section were calculated using the FACT-Sage program, utilizing a quasi-chemical model for the slag, and a sublattice model for the M₃O₅ phase; details of these models are given elsewhere⁵. In the calculations presented here, rutile was taken to be stoichiometric TiO₂ for simplicity. The small amount of

solubility of Ti₂O₃ in rutile⁶ was not found to affect the positions of the phase boundaries to a large extent in the present work.

Figure 2 shows the boundary ('C-D-E') between the primary phase fields of rutile (upper part of diagram) and M₃O₅ (middle part). Compositions rich in Ti₂O₃—to the lower right of the diagram, below line 'F-G'—form metallic iron before slag solidification. The labels in italics in Figure 2 indicate the primary phases. Based on the hypothesis of eutectic solidification equilibrium with the freeze lining, slags are predicted to lie along the eutectic groove (line 'D-E'), at the boundary between the rutile and M₃O₅ primary phase fields (compositions along 'C-D' show peritectic solidification, and are not part of this discussion). During solidification,

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these slags are in equilibrium with rutile, and with M_3O_5 . The tie-lines in Figure 2 indicate the equilibrium combinations of slag and M_3O_5 , for both the upper-temperature limit of three-phase solidification (corresponding to point 'A' in Figure 1; solid lines and open circles in Figure 2), and the lower-temperature limit (corresponding to point 'B' in Figure 1; broken lines and filled circles in Figure 2). These equilibrium relationships are summarized in another form in Figure 3, which shows the change in compositions of solid and liquid along the eutectic groove, as well as the liquidus temperature. The relationships in Figure 3 were fitted to simple polynomials, which are summarized in Table I.

Slag FeO change: required inputs to maintain solidification equilibrium

Mass and energy balance

The equilibrium relationships along the eutectic groove can be used to predict the appropriate way in which inputs must be manipulated to keep the slag in equilibrium with the freeze lining. The example considered here is a change in slag composition. Three requirements must be met to maintain the slag-lining equilibrium if the slag composition is changed: First, the slag composition must follow the eutectic groove (line 'D-E' in Figure 2); second, the slag temperature must remain at the (changing) liquidus temperature (Figure 3); third, the composition of the surface

of the freeze lining must change to correspond to the tie-lines in Figure 2 (for example, if the slag becomes richer in FeO, the surface of the freeze lining must also become more FeO-rich). The last of these requirements is probably the easiest to meet, since manipulating the inputs such that the slag temperature would remain close to the liquidus temperature should cause a thin layer of additional solid lining. Hence, while renewal and change of the solid lining will be studied in future work, it is not considered here, except in qualitative terms when some of the results are discussed.

Meeting the first two requirements requires maintaining the mass and energy balance of the process within appropriate limits. For the energy balance calculations, the enthalpy of the slag was calculated from the correlation as given in Table II; this is based on the enthalpies of the pure species and the quasichemical model⁶. It was assumed that stoichiometric ilmenite ($FeO \cdot TiO_3$) and pure carbon are fed to the furnace cold, and that liquid Fe and CO are produced at the liquidus temperature. The enthalpies of these species were found from a literature compilation. The liquid iron was assumed to contain 2% dissolved carbon. Heat losses were neglected in the calculation.

Results

The calculated inputs to maintain constant slag compositions with different FeO contents, along the eutectic groove, are shown in Figure 4. As observed before², the requirement that the reductant and energy inputs are matched to achieve the

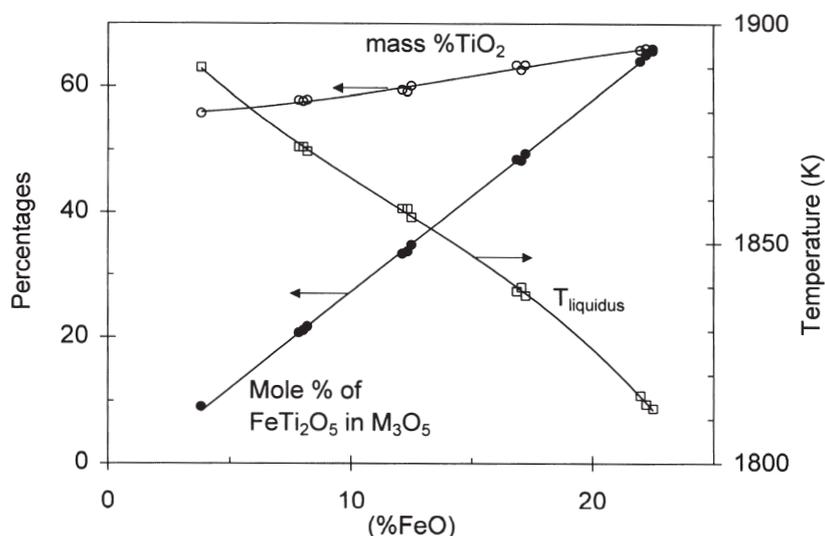


Figure 3—Conditions along the eutectic groove, plotted as functions of the mass percentage of FeO in the liquid slag. The curve labelled '%TiO₂' gives the mass percentage of TiO₂ in the liquid slag (the balance of the TiO₂ and FeO is TiO_{1.5}). The curve labelled 'mole % of FeTi₂O₅ in M₃O₅' gives the composition of the solid, and the curve labelled 'T_{liquidus}' gives the upper-temperature limit of three-phase equilibrium (between rutile, liquid slag, and M₃O₅)

Table I

Equilibrium relationships along the eutectic groove, as fitted to the data of Figure 3 (valid for FeO contents from 4% to 23%). The percentage of FeO is on a mass basis in all cases

Liquid slag composition	$(\%TiO_2) \text{ (mass basis)} = -1.061 \times 10^{-3}(\%FeO)^3 + 0.04912(\%FeO)^2 - 0.1031(\%FeO) + 55.71$
Liquidus temperature (in kelvin)	$T_{liquidus} = -7.333 \times 10^{-3}(\%FeO)^3 + 0.2558(\%FeO)^2 - 6.430(\%FeO) + 1911$
Mole fraction of FeTi ₂ O ₅ in M ₃ O ₅ (solid solution between Ti ₃ O ₅ and FeTi ₂ O ₅)	$X_{FeTi_2O_5} = 3.0609(\%FeO) - 3.4012$

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Table II

Correlation for the enthalpy (in kJ/g-atom) of molten slag. X_i is the mole fraction of species i in the slag (which is taken to be a mixture of FeO, TiO₂ and TiO_{1.5}); T is the temperature in kelvin

$$H = -236.3X_{\text{TiO}_{1.5}} - 106.8X_{\text{FeO}} - 257X_{\text{TiO}_2} + 0.0275(T - 2023)$$

required slag composition has the result that changes in energy input and carbon input need to be made in a constant ratio. The parallel trend of the two curves in Figure 4 implies that, for each 1 kg change in carbon input, the energy input needs to be changed by 5 kWh.

Figure 4 illustrates the inputs required to maintain a constant slag composition. However, if it is necessary to move from a current slag composition to a new composition, it will be necessary to depart from this steady-state relationship—for the simple reason that the furnace acts as an 'integrator', with the new slag composition being the result of both the current composition in the furnace and the current inputs into the furnace. If, for example, it is desired to increase the FeO content of the slag (which implies an decrease in the steady-state carbon and energy inputs), the carbon and energy inputs (per ilmenite fed) need to be decreased to well *below* the new steady-state level to arrive at the new slag composition. This effect is illustrated in Figure 5, for the cases where the FeO content is respectively increased (Figures 5 a and b), and decreased (Figures 5 c and d). In each case, the original slag mass is taken as 1 000 kg, and the carbon and energy inputs were calculated (from a mass and energy balance) to be those required to move along the eutectic groove, from 8% FeO to 15% FeO (Figures 5 a and b), and from 15% FeO to 8% FeO (Figures 5 c and d). The first step change in inputs (at 1 000 kg of slag mass) is where the change in FeO content starts, and the second step change is where the new steady-state FeO content is achieved.

The difference between Figure 5 a and Figure 5 b is the amount of slag produced during the time that the slag composition is being changed. Obviously, the faster the change in slag composition, the more drastic the change in inputs needs to be—hence the carbon and energy inputs are cut more drastically in the case of Figure 5 a (about 585 kg of slag produced while the composition changes) than in the case of Figure 5 b (about 950 kg of slag produced while the composition changes). Similar observations apply to the difference between Figures 5 c and 5 d.

What is also evident from Figure 5 is that the energy and carbon inputs must not be constant during the period of change in slag composition—as the slag composition changes, the inputs need to be adjusted to keep the slag composition and temperature within the eutectic groove. This is illustrated in another form in Figure 6, which shows the changes in inputs with slag composition for three situations: steady-state (the same data as in Figure 4), a decrease in FeO content, and an increase in FeO content (the latter two are for a specific rate of slag composition change, taken to be a 1 per cent absolute change in FeO content for a 15 per cent change in slag mass). The curves in Figure 6 are nearly parallel, which implies an approximately constant offset between the steady-state settings of the inputs for the *current* (changing) slag composition in the furnace, and their required settings to effect the change in composition. So, to change the slag composition at a given rate, the inputs must not be constant, by they must *differ* by a roughly constant offset from the steady-state settings for the current slag composition.

As mentioned earlier, the sizes of these offsets depend on the desired rate of change of the slag composition. This effect is shown in more detail in Figure 7, which gives the required average deviations from steady-state settings to adjust the slag composition at a given rate. (The data are for composition changes from 8% FeO to 12% FeO or the reverse, but since the curves in Figure 6 are nearly parallel, similar results are found for larger changes in composition.) The offsets are plotted as functions of the percentage change in slag mass per one per cent change in FeO content (this is

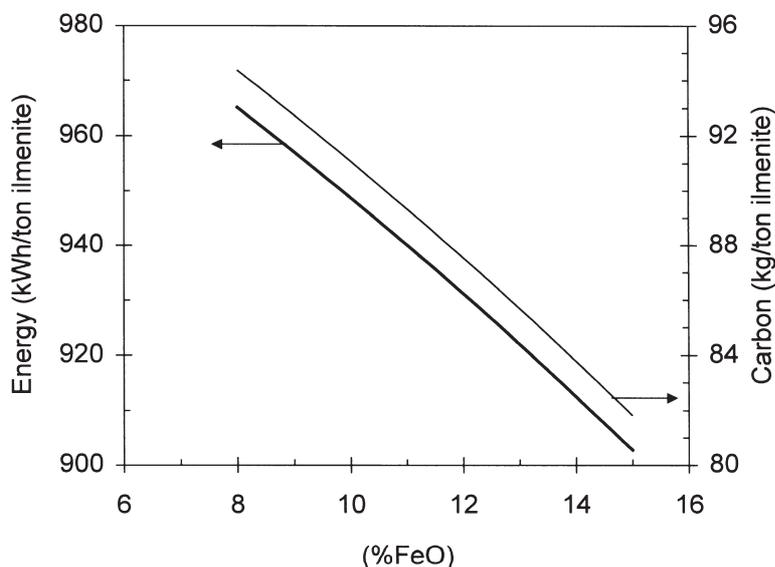


Figure 4—Calculated steady-state inputs of carbon and energy required to produce slags with different FeO contents (plotted as mass percentages). Heat losses excluded. Inputs assumed to be pure FeTiO₃ and C, off-gas assumed to be pure CO, and iron assumed to contain 2 mass per cent carbon

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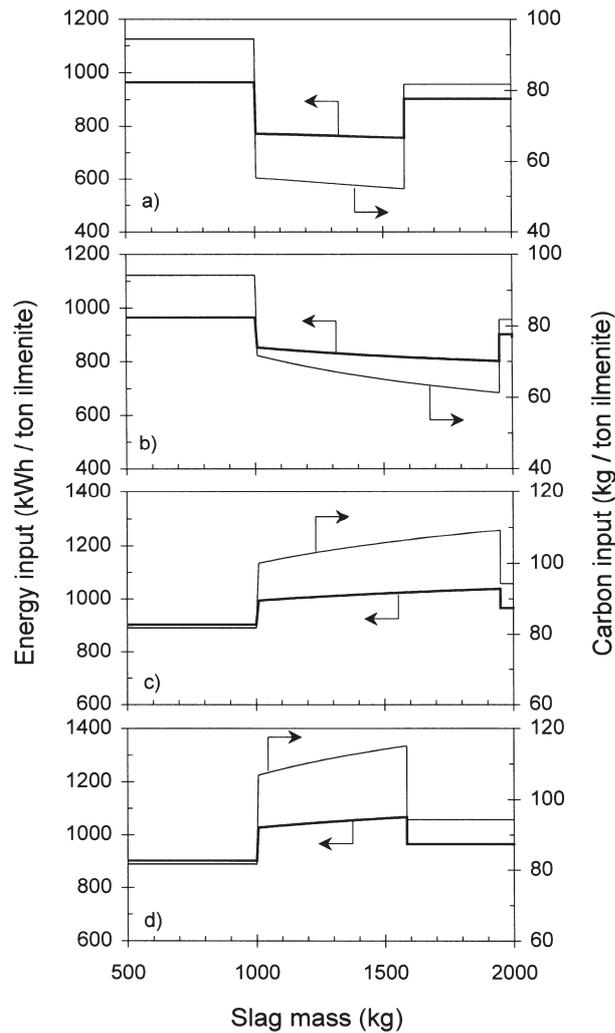


Figure 5—Calculated changes in energy and carbon inputs required to change the slag composition along the eutectic groove. Cases a) and b) are for an increase in FeO content from 8% to 15%, with, respectively, a faster and a slower change in slag composition. Cases c) and d) are for a decrease in FeO content from 15% to 8%, with a slower and faster change in slag composition respectively. The slag mass when the change in FeO content starts is 1000 kg in all cases; the slag mass when the change in FeO content ceases is indicated by the step change in inputs

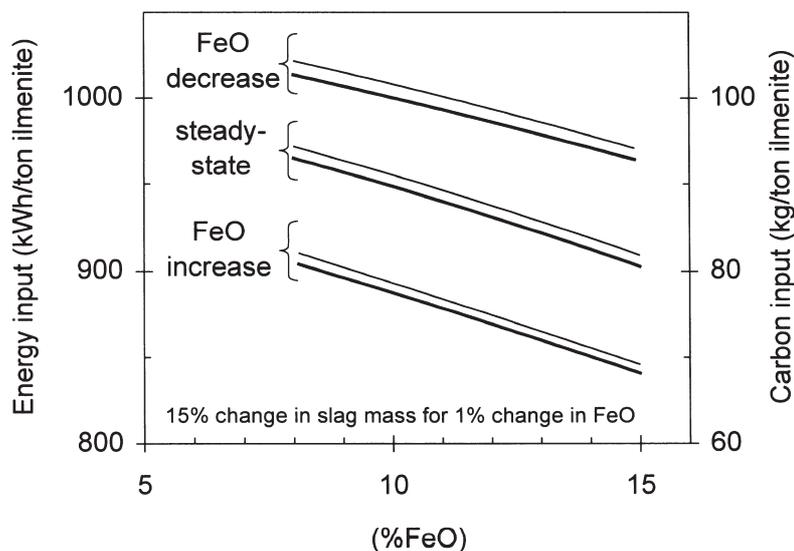


Figure 6—Required inputs of carbon and energy, respectively for steady-state conditions, during a decrease in FeO content (while the slag mass increases by 15 per cent for each per cent decrease in FeO), and during an increase in FeO content (while the slag mass similarly increases by 15 per cent for each per cent increase in FeO). The heavier lines give the energy input, and the lighter lines the carbon input

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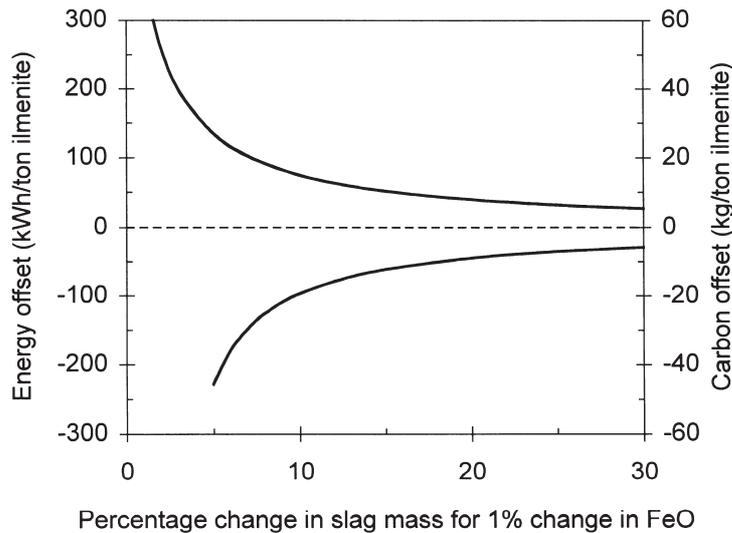


Figure 7—Required average difference between the energy and carbon inputs during a decrease in FeO content (upper half of figure), and an increase in FeO (lower half of figure), as functions of the relative change in slag mass per one per cent change in FeO content. The curves for energy and carbon inputs are exactly superimposed

termed the 'mass increment ratio' below). It should be noted that the slag mass changes are cumulative; hence the final slag mass depends as follows on the change in FeO content and the mass increment ratio:

$$m_{\text{final}} = m_{\text{start}} (1 + f)^{[(\% \text{FeO})_{\text{final}} - (\% \text{FeO})_{\text{start}}]}$$

where m_{final} is the slag mass after the change in FeO content, m_{start} is the initial slag mass, f is the mass increment ratio, $(\% \text{FeO})_{\text{final}}$ is the final FeO content, and $(\% \text{FeO})_{\text{start}}$ is the initial FeO content. For example, if the initial slag mass is 1 tonne, if the slag mass changes by 15% for 1% change in FeO content, and if the FeO content increases from 8% to 15%, then the final slag mass is $1\,000(1+0.15)^{(15-8)} = 2\,660$ kg.

Evidently, rapid changes in slag composition (towards the left in Figure 7) require drastic changes in the energy and reductant inputs. An interesting and useful observation is that the same ratio between changes in energy and carbon inputs as found for steady-state conditions (5 kWh for 1 kg; see Figure 4) also holds for these transient offsets: the curves for the changes in energy and in carbon are exactly superimposed when the choice of scales in the graph are in the ratio of 5 kWh for 1 kg.

Conclusions

This work (which represents only a small part of the larger project on freeze lining dynamics) illustrates that the reductant and energy inputs need to be changed drastically from their steady-state values to effect changes in slag composition. If executed incorrectly, such changes may destabilize the furnace. For example, if during an attempt to increase the FeO content of the slag, the carbon content is decreased, but the energy input is not decreased sufficiently, the effect will be to superheat the slag to above the eutectic temperature (the slag may become superheated without any increase in actual temperature since the melting point of the slag drops as the FeO content increases—see Figure 3). This means that the slag will tend to dissolve some of the freeze lining. Such dissolution can be beneficial, since it would tend

to restabilize the slag composition at the eutectic groove (this feedback is indeed the proposed mechanism behind the observed pervasive slag composition relationship⁵). However, large-scale dissolution of the freeze lining would not be a desired result. Similarly, if during a decrease in the FeO content the energy input is too small to match the required increase in carbon input, the slag temperature will decrease to below the liquidus temperature. The resulting partial solidification can take place on the freeze lining, or may precipitate solids in the slag—increasing the apparent viscosity, and so increasing the chances of foaming.

It would hence be necessary to monitor the furnace carefully for loss of stability during deliberate changes in slag composition. Monitoring methods need to be able to detect the onset of foaming, and also changes in freeze lining thickness; detecting the latter is hindered by the inherently large reaction time of thermocouples in the furnace wall.

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