The relationship between FeO and Ti_2O_3 in ilmenite smelter slags

P. Chris Pistorius

Department of Material Science and Metallurgical Engineering
University of Pretoria

Abstract

Smelting is used to upgrade ilmenite ($FeO.TiO_2$) to high-titania slags which serve as feedstocks for TiO_2 pigment manufacture. During smelting partial reduction of FeO to liquid iron, and of TiO_2 to Ti_2O_3, occurs. Lower FeO levels in the solidified slag correlate with higher Ti_2O_3. Since some pigment manufacturers limit the allowable Ti_2O_3 level in the slag, the origin of this relationship is of interest. The relationship does not follow equilibrium, nor is there likely to be a simple kinetic cause. The relationship in fact closely follows that required by the stoichiometric M_3O_5 phase, the major component of solidified slag.

1. Background

The purpose of ilmenite smelting is to yield an upgraded titania slag product, by partial reduction of FeO from ilmenite ($FeO.TiO_2$) with carbon as reductant.[1] The upgraded slag, with a typical "equivalent" TiO_2 content of 85% by mass or greater*, is then used in pigment production (by the chloride or sulphate routes).[2]

In parallel with reduction of FeO to Fe, some reduction of TiO_2 to Ti_2O_3 also occurs; hence the two main reactions in ilmenite smelting are:

$$FeO + C = Fe + CO \qquad\qquad (1a)$$
$$2TiO_2 + C = Ti_2O_3 + CO \qquad\qquad (1b)$$

The partial reduction of TiO_2 (reaction 1b) does not contribute to upgrading of the slag, but consumes electrical energy and carbon. The formation of Ti_2O_3 does have the beneficial effect of lowering the liquidus temperature of the slag, as indicated by Figure 1[†].[3] However, slags with low FeO and high Ti_2O_3 are sometimes associated with foaming incidents, perhaps related to a change in the primary phase of the slags from TiO_2 (for higher-FeO slags) to M_3O_5 (for lower-FeO slags).[4] (In the Ti-Fe-O system, M_3O_5 is a solid solution between the end members Ti_3O_5 and $FeTi_2O_5$.[5]) In addition, chloride pigment producers sometimes place a maximum limit on the allowable amount of Ti_2O_3 in the slag,[6] presumably because of the strongly exothermic nature of oxidation of Ti^{3+} to Ti^{4+}, which occurs during chlorination.

For these reasons, it is of importance to understand the factors which control the extent of Ti_2O_3 formation during ilmenite smelting. Previous work indicated that it is not possible to control the relative extents of reactions (1a) and (1b) by manipulating energy and reductant inputs separately.[3] In the work presented here, literature data on ilmenite smelter slag compositions were analysed to determine the changes in FeO and Ti_2O_3 contents in slags after reduction to different degrees; the compositional data were also used to test possible mechanisms which can determine the FeO-Ti_2O_3 relationship. These mechanisms include reaction equilibrium, kinetic effects, and phase chemistry.

2. The FeO-Ti_2O_3 relationship in industrial slags

Figure 2 summarises the changes in levels of FeO, Ti_2O_3 and impurity oxides[‡] as ilmenite slag is upgraded (by reduction) to different equivalent TiO_2 contents. The slag compositions quoted here were taken from those literature data where it appeared that oxidation of the slag during and after tapping was largely avoided.[6,7,8,9,10] (Oxidation of the slag converts some of the Ti_2O_3 in the slag to TiO_2, so distorting the FeO-Ti_2O_3 relationship which had prevailed in the furnace.) Data could be found for two commercial operations in South Africa (at Richards Bay Minerals, which uses six-in-line alternating-current furnaces, and Namakwa Sands, which uses a direct-current hollow-electrode furnace), the Iscor pilot plant operation in South Africa (similar in design to the Namakwa Sands furnace, but smaller by a factor of about 10), and the QIT plant in Canada (which uses similar furnaces to Richards Bay Minerals). The

---

* The "equivalent" TiO_2 content is the total amount of titanium present as TiO_2 and Ti_2O_3, expressed as an equivalent amount of TiO_2.
† Please note that Figure 1 is the corrected version of the diagram presented in previous work,[3] which was subsequently found to contain some inaccuracies.
‡ The "impurity oxides" are here defined to be all oxides other than FeO and TiO_x, including mainly SiO_2, MnO, CaO, MgO, Al_2O_3, Cr_2O_3 and V_2O_3.

main difference between the South African and Canadian ilmenites is the substantially higher alkali earth content of the latter. The slag composition data are summarised in Table 1. The Ti_2O_3 content of the slags was stated in the references cited, except for reference 9, where the Ti_2O_3 content was estimated from the equivalent TiO_2 content and a mass balance (assuming the correct Ti_2O_3 level to be where the slag composition adds up to 100%, with the assumed valencies of impurity oxides as stated below in section 3.3).

The strong increase in Ti_2O_3 content with increased equivalent TiO_2 content (i.e. decreased FeO content) is evident from Figure 2, as is the relatively constant level of impurity oxides (which is as expected, since these oxides are not reduced to the metal bath to any significant extent). Remarkably, the results for the South African furnaces seem to follow a single correlation, despite the very different designs and sizes of the furnaces involved. The solid lines in Figure 2 a) and b) indicate the calculated equilibrium behaviour (as discussed below) for pure TiO_x-FeO slags (with zero impurity levels). The striking correspondence between the different operations suggests that some general mechanism fixes the relative degrees of FeO reduction and TiO_2 reduction; possible mechanisms are considered below.

3. Possible origins of the FeO-Ti_2O_3 relationship
3.1 Equilibrium

Equilibrium between the reduced and unreduced forms of iron and titanium in the smelter is expressed by the following reaction:

$$FeO + Ti_2O_3 = Fe + 2TiO_2 \tag{2}$$

To calculate the slag compositions in equilibrium with metallic iron (assumed to have an activity of 1.0), the parameters for the quasichemical models for the FeO-TiO_2 and TiO_2-$TiO_{1.5}$ binaries as assessed by Eriksson and Pelton were used,[11] using the procedure proposed by those authors for estimating the activities in the ternary FeO-TiO_2-$TiO_{1.5}$ mixture.[5]

The calculated activities in the liquid slag are not far from ideal, as shown by the summary given in Figure 3 (which depicts the calculated activities at 1650°C). The equilibrium relationship between FeO and Ti_2O_3 which is predicted with these activity data is shown as Figure 4. Clearly, the Ti_2O_3 content of the slag is higher and the FeO content lower than these would be at equilibrium; reaction (2) is out of equilibrium to the right.

3.2 Kinetic effects

It would seem reasonable to invoke kinetic effects for the departure of reaction (2) from equilibrium – for example, it may be proposed that the reduction of FeO to Fe (reaction [1a]) is more efficient ("faster") than the reduction of TiO_2 to Ti_2O_3 (reaction [1b]). Given the lack of any kinetic data, it is not possible to test this possibility rigorously. However, some observations serve to cast some doubt on a dominant kinetic effect. Firstly, the FeO-Ti_2O_3 relationship is remarkably consistent between furnaces of very different sizes and electrical design (see for example Figure 4), despite the very different degree of stirring (mass transfer) in these furnaces. Secondly, given the much higher TiO_2 concentration in the slag and the likelihood of slag mass transfer control effects, one would expect TiO_2 to be reduced preferentially, followed by reduction of FeO; this is the *opposite* of the real effect. Lastly, the slags produced from the Canadian ilmenites show a consistently lower Ti_2O_3 content at a given FeO content (Figure 2) – a difficult effect to explain on the basis of kinetics, given that

the only major difference between the two Canadian and South African ilmenites is the level of alkali earth oxides.

It is hence concluded that – while absence of kinetic data rule out any direct assessment – it appears unlikely that kinetic effects are the primary origin of the observed FeO-Ti_2O_3 relationship.

3.3 Phase chemistry

As observed by others,[6,9,12] the solidified titania slag consists largely of a single phase – the M_3O_5 solid solution – together with much smaller amounts of rutile, metallic iron, and a silicate glass phase. If this M_3O_5 solid solution is simply a mixture of the stoichiometric end members Ti_3O_5 and $FeTi_2O_5$, a simple linear relationship between the amounts of FeO and Ti_2O_3 in the solidified slag is expected. This predicted relationship is shown in Figure 5, together with the actual trend. Clearly, the real slag compositions lie well below the composition line of Ti_3O_5–$FeTi_2O_5$ mixtures.

However, this difference is apparently not due to a departure from stoichiometry in the M_3O_5 phase, but is caused by the impurity oxides which form a significant component of the slag (see Figure 2). Of the impurity oxides, nearly all the SiO_2 and CaO are contained in the glass phase, the amount of Al_2O_3 in the glass phase is about a third (by mass) of the amount of SiO_2, and the other impurity oxides are accommodated in the M_3O_5 solid solution.[9] Specifically, the divalent impurities (Mg^{2+} and Mn^{2+}) substitute for Fe^{2+}, and the trivalent impurities (Al^{3+}, Cr^{3+} and V^{3+}) substitute for Ti^{3+}. The higher content of both divalent and trivalent ions in the slag (relative to the tetravalent Ti^{4+}) than given by only Fe^{2+} and Ti^{3+} implies that the slag composition in fact lies closer to the stoichiometric M_3O_5 line.

To quantify the effects of the impurity oxides, the following procedure was followed:

Given that MnO and MgO are taken to be equivalent to FeO on a molar basis,[§] the equivalent FeO content is calculated as:

$$(\%FeO)_{eq} = (\%FeO) + (M_{FeO}/M_{MgO})(\%MgO) + (M_{FeO}/M_{MnO})(\%MnO) \tag{3a}$$

where M_i is the molar mass of oxide i, and the amounts of the oxides are in mass percentages.

Similarly, the equivalent Ti_2O_3 content is calculated as:

$$(\%Ti_2O_3)_{eq} = (\%Ti_2O_3) + (M_{Ti_2O_3}/M_{V_2O_5})(\%V_2O_5) + (M_{Ti_2O_3}/M_{Cr_2O_3})(\%Cr_2O_3)$$
$$+ (M_{Ti_2O_3}/M_{Al_2O_3})[(\%Al_2O_3) - (\%SiO_2)/3] \tag{3b}$$

In expression (3b), the vanadium content of slag is expressed as V_2O_5 since this is the convention for the analyses, although the vanadium is expected to be present in the trivalent form.[13] As the expression shows, part of the Al_2O_3 is not taken into account when the equivalent Ti_2O_3 content is calculated, because some Al_2O_3 (a mass taken to be one-third of that of the silica) reports to the separate glass phase.

The sum of $(\%FeO)_{eq}$, $(\%Ti_2O_3)_{eq}$ and $(\%TiO_2)$ is then normalised to 100%, where $(\%TiO_2)$ is the Ti^{4+} content of the slag, expressed as a mass of TiO_2.

[§] CaO and SiO_2 are not taken into account in this calculation since these oxides are assumed to report fully to the separate glass phase.

The result of this normalisation procedure is given in Figure 6, which demonstrates that – when the effect of the impurity oxides is taken into account – the slag composition closely follows that expected for stoichiometric M_3O_5. This is the case for slags produced from both the lower-impurity (South African) and higher-impurity (Canadian) ilmenites. The former slags generally lie slightly below the stoichiometric line, probably reflecting a slight degree of oxidation of these slags (which is not unexpected, since these slags contain a higher amount of Ti_2O_3 than those produced from the Canadian ilmenite – see Figure 2).

It is worth noting that simply normalising the FeO, Ti_2O_3 and TiO_2 content of the slag to a total of 100% (i.e. neglecting any effect of the impurity oxides other than dilution) does not improve agreement between the slag composition and M_3O_5 stoichiometry or equilibrium, as shown by Figure 7.

4. Conclusion

The FeO-Ti_2O_3 relationship in ilmenite smelter slags appears to follow a single pattern for different smelter furnace sizes and designs, and is apparently only altered by the impurity content of the ilmenite feed. Of the possible origins of this consistent relationship, equilibrium does not hold, and kinetic effects are not expected to play the dominant role. Rather, it appears that the amount of Ti_2O_3 for a given amount of FeO is fixed by the tendency of the slag to solidify as essentially a single phase (M_3O_5). The deterministic nature of this relationship implies that, given the degree of reduction (determined by the amount of reductant fed to the furnace), and the impurity content of the ilmenite and reductant, it should be possible to predict the tap composition (%FeO, %Ti_2O_3 and %TiO_2^{equiv}) of the smelter slag.

References

1. T Rosenqvist: "Ilmenite smelting." *Transactions of the Technical University of Košice*, vol. 2 (special issue), pp. 40-46 (1992).
2. JA Kahn: "Non-rutile feedstocks for the production of titanium." *Journal of Metals*, July, pp. 33-38 (1984).
3. PC Pistorius: "Limits on energy and reductant inputs in the control of ilmenite smelters." *Heavy Minerals 1999*. Johannesburg, South African Institute of Mining and Metallurgy. pp. 183-188 (1999).
4. J Nell: "An overview of the phase-chemistry involved in the production of high-titanium slag from ilmenite feedstock." *Heavy Minerals 1999*. Johannesburg, South African Institute of Mining and Metallurgy. pp. 137-145 (1999).
5. G Eriksson, AD Pelton, E Woermann, and A Ender: "Measurement and thermodynamic evaluation of phase equilibria in the Fe-Ti-O system." *Ber. Bunsenges. Phys Chem.* vol. 100, pp. 1839-1849 (1996).
6. D Bessinger, H du Plooy, PC Pistorius, and C Visser: "Characteristics of some high titania slags." *Heavy Minerals 1997*. Robinson, RE (ed.). Johannesburg, South African Institute of Mining and Metallurgy. pp. 151-156 (1997).
7. R Desrosiers, F Ajersch and A Grau: "Electrical conductivity of industrial slags of high titania content." 19th Annual Conference of Metallurgists, 24-27 August 1980, Halifax, Nova Scotia.
8. J Pesl and H Eric: "Phase equilibria and thermodynamics in the Fe-Ti-O system at 1500°C and 1600°C." *Metals and Minerals 1995*, Cape Town. South African Institute of Mining and Metallurgy, pp. 59-66.

9. K Borowiec, AE Grau, M Gueguin, and J-F Turgeon: "Method to upgrade titania slag and resulting product." *United States Patent* 5830420, 3 November 1998.
10. JMA Geldenhuis and PC Pistorius: "The use of commercial oxygen probes during the production of high titania slags." *Journal of the South African Institute of Mining and Metallurgy*, vol. 99, pp. 41-47 (1999).
11. G Eriksson and AD Pelton: "Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the $MnO\text{-}TiO_2$, $MgO\text{-}TiO_2$, $FeO\text{-}TiO_2$, $Ti_2O_3\text{-}TiO_2$, $Na_2O\text{-}TiO_2$, and $K_2O\text{-}TiO_2$ systems." *Metallurgical Transactions Series B*, vol. 24B, pp. 795-805 (1993).
12. I Toromanoff and F Habahsi: "The composition of titanium slag from Sorel." *Journal of the less-common metals*, vol. 97, pp. 317-329 (1984).
13. T Coetsee and PC Pistorius: "Preliminary Observations on Phase Relations in the $V_2O_3\text{-}FeO$ and $V_2O_3\text{-}TiO_2$ Systems from 1400°C to 1600°C in Reducing Atmospheres." *Journal of the American Ceramic Society* (in press).

Table 1. Slag compositions from the literature, as used to analyse the FeO-Ti_2O_3 relationships. Compositions are in mass percentages; " TiO_2^{equiv}" gives the total Ti^{4+} and Ti^{3+} of the slag, expressed as an equivalent amount of TiO_2.

Plant	Ref.	TiO_2^{equiv}	FeO	TiO_2	Ti_2O_3	SiO_2	Al_2O_3	CaO	MgO	MnO	Cr_2O_3	V_2O_5
RBM	7	80.4	15.3	54.9	23.0	1.61	1.43	0.14	0.95	1.37	-	-
		84.8	11.7	54.7	27.1	1.88	1.58	0.16	1.04	1.48	-	-
		88.1	7.7	50.7	33.7	2.30	1.83	0.23	1.38	1.56	-	-
NS	8	86.0	10.0	54.9	28.0	1.80	1.80	0.16	0.85	1.50	0.07	0.42
IP	6	92.2	5.2	47.4	40.3	2.22	1.57	0.49	0.76	1.14	0.10	0.42
		91.9	5.6	42.9	44.1	2.33	1.67	0.44	0.83	1.15	0.10	0.44
		88.7	10.2	51.8	33.2	1.23	1.07	0.12	0.97	1.22	0.12	0.46
		84.1	11.3	49.9	30.8	2.94	1.57	0.41	0.50	1.29	0.08	0.37
		86.0	11.8	55.0	27.9	1.26	0.98	0.10	0.94	1.25	0.13	0.47
		80.2	15.4	55.4	22.3	2.23	1.51	0.43	0.99	1.08	0.09	0.42
		80.2	15.9	55.4	22.3	1.97	1.42	0.26	0.86	1.04	0.06	0.43
	10	87.9	9.1	52.0	32.3	1.90	1.00	0.26	1.15	1.16	0.03	0.44
		86.4	11.3	54.1	29.1	1.24	0.81	0.31	1.01	1.13	0.05	0.45
		84.8	12.6	55.8	26.1	1.34	0.86	0.25	0.86	1.23	0.05	0.45
		83.7	13.0	55.5	25.4	1.27	0.77	0.24	0.99	1.23	0.06	0.44
QIT	7	66.1	20.3	55.6	9.4	4.44	4.45	0.89	4.95	0.28	-	-
		69.1	15.3	54.2	13.4	4.92	3.66	1.07	5.10	0.27	0.18	-
		74.3	9.8	54.5	17.9	4.99	4.94	1.13	5.30	0.28	0.17	-
		77.5	9.4	50.6	24.2	4.14	4.58	0.93	5.20	0.31	0.17	-
		79.0	6.9	50.2	26.0	4.71	5.43	1.17	5.10	0.26	0.16	-
	8	77.5	10.9	59.7	16.0	3.00	3.50	0.60	5.30	0.20	0.17	0.30
	9	82.6	8.2	54.8	25.0	2.09	2.98	0.47	5.56	0.26	0.18	0.63
		84.8	4.8	49.8	31.5	3.06	3.62	0.47	5.89	0.26	0.03	0.65
		78.3	10.4	59.1	17.3	2.73	3.82	0.50	5.21	0.25	0.21	0.59

Plant: RBM - Richards Bay Minerals; NS - Namakwa Sands; IP - Iscor pilot plant
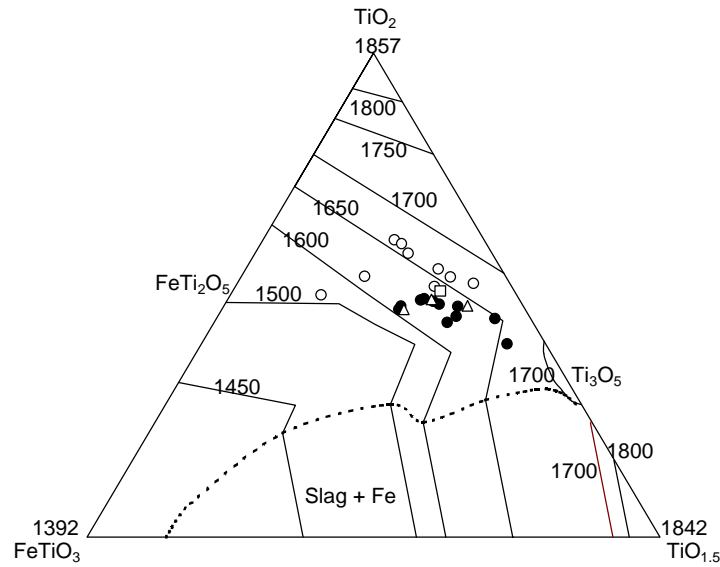
Figure 1. Conjectural liquidus diagram of ilmenite smelter slags, based on the TiO_2-$TiO_{1.5}$ and TiO_2-FeO binaries,[11] 1500°C and 1600°C isotherms,[8] and quasichemical model parameters for the liquid slag region, to calculate the slag composition in equilibrium with iron.[5,11] Compositions are plotted as mole fractions, and temperatures are in °C. Corrected form of diagram presented earlier.[3] Data points show compositions of slags produced with South African ilmenites, with the $FeO+TiO_2+Ti_2O_3$ content normalised to 100% (see compositions in Table 1). Symbols: ● Iscor pilot plant,[6,10] Δ Richards Bay Minerals,[7] □ Namakwa Sands,[8] ⊙ QIT.[7,8,9]
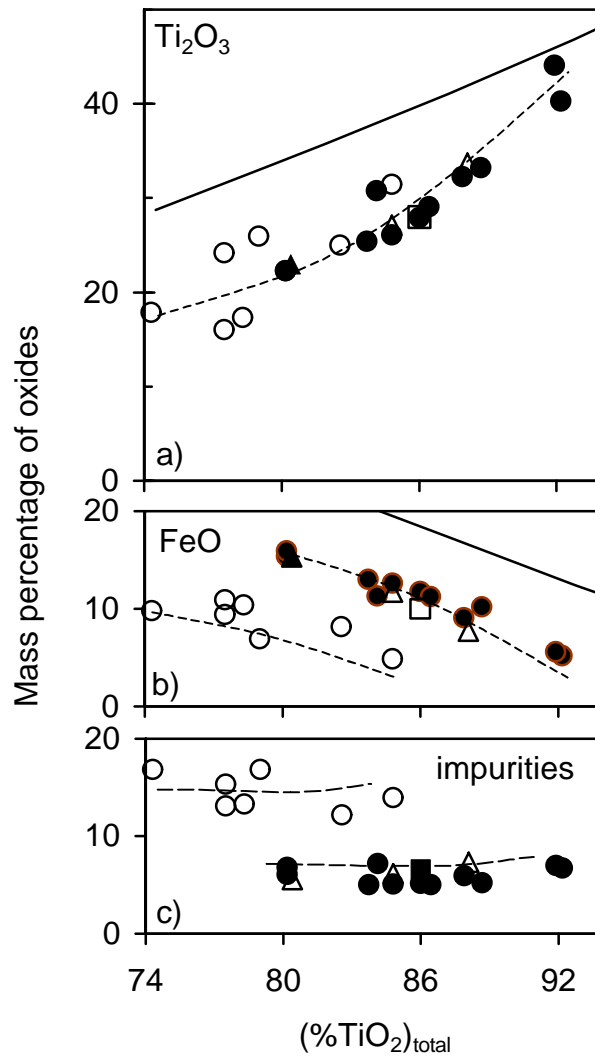
Figure 2. Changes in FeO, Ti$_2$O$_3$ and impurity oxide content with increased equivalent total TiO$_2$ content, for slag produced from Canadian ilmenite (open circles) and South African ilmenite (others) (see Figure 1 for references). Solid lines in a) and b) given calculated relationship for pure FeO-Ti$_2$O$_3$-TiO$_2$ slag in equilibrium with pure liquid iron at 1650°C.
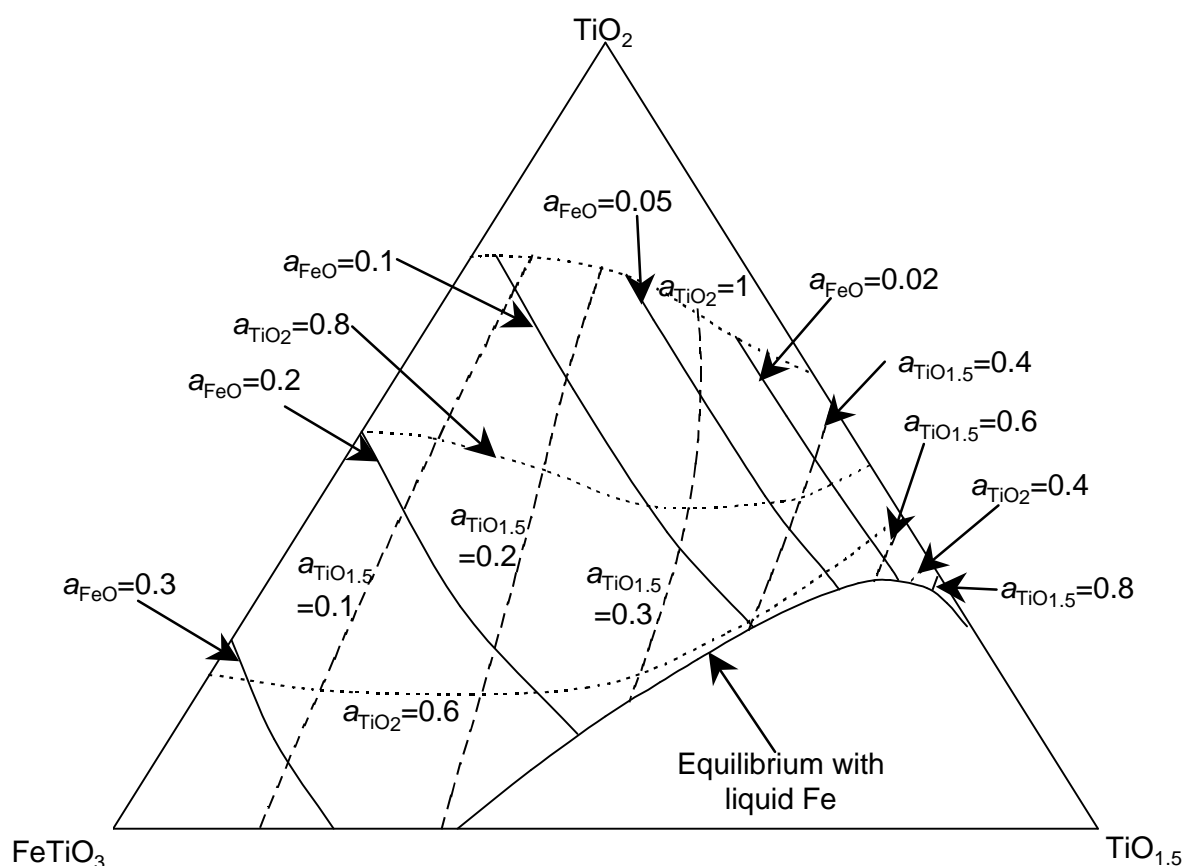
**Figure 3.** Calculated activities in pure liquid FeO-TiO$_2$-TiO$_{1.5}$ slag at 1650°C. Reference states are pure solid TiO$_2$ and TiO$_{1.5}$, and pure liquid FeO. Compositions plotted as mole fractions of TiO$_2$, TiO$_{1.5}$ and FeO. Calculated using literature values of the quasichemical model parameters.[5,11]
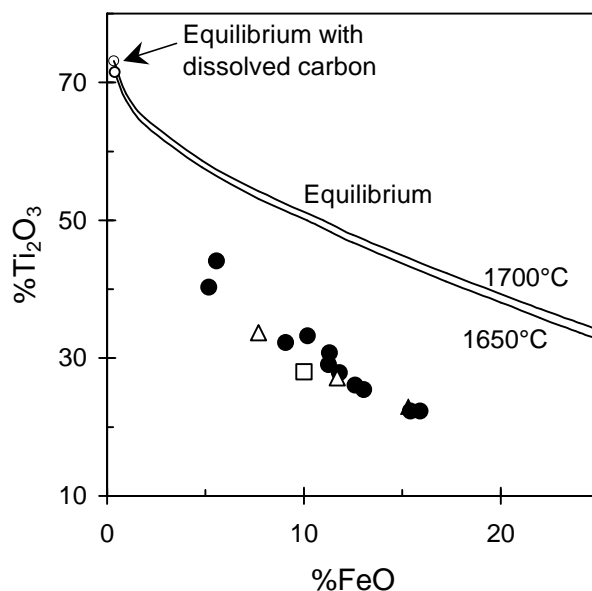

Figure 4. Calculated relationship between FeO and Ti$_2$O$_3$ (mass percentages) in pure FeO-TiO$_2$-TiO$_{1.5}$ slags in equilibrium with pure liquid iron (lines) and liquid iron containing 2%C under an atmosphere with p_{CO}=1 atm (open circles), compared with the real FeO-Ti$_2$O$_3$ trend. Activities calculated as in Figure 3, and symbols as in Figure 1.
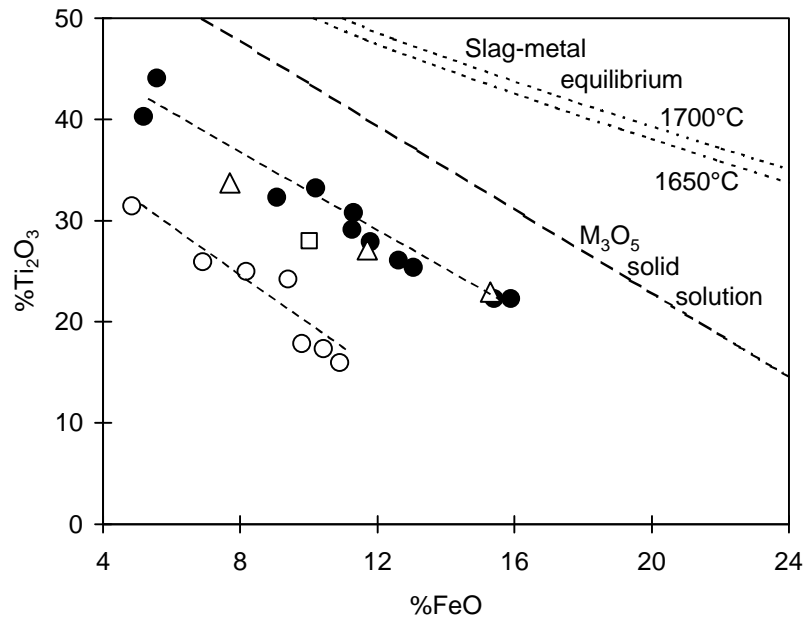
Figure 5. Comparison of the actual FeO-Ti_2O_3 trend in slags produced from Canadian ilmenite (open circles) and South African ilmenite (others) (symbols as in Figure 1) with the expected relationship in a solid solution ("M_3O_5") between stoichiometric Ti_3O_5 and $FeTi_2O_5$, and for equilibrium with liquid iron.
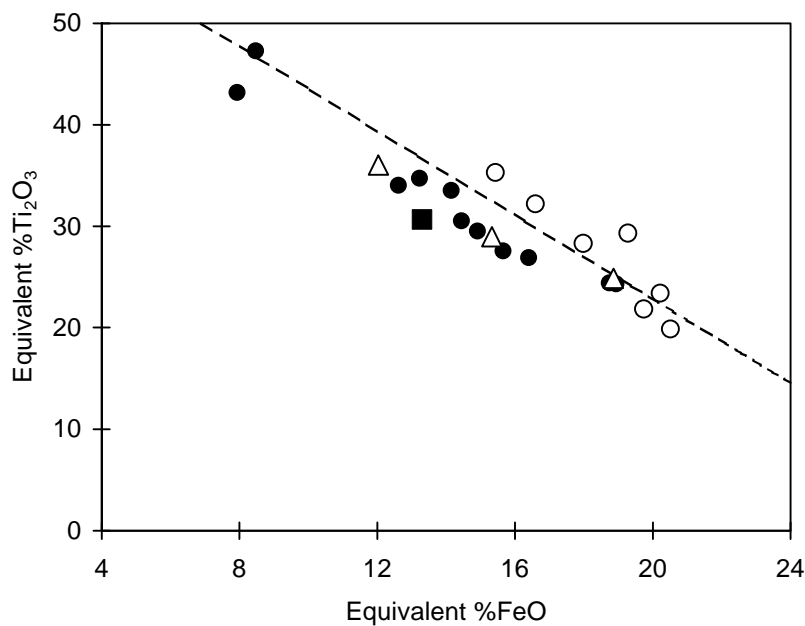
Figure 6. Comparison of the actual trend of "equivalent FeO" (including substitution of FeO by MgO and MnO) with "equivalent Ti_2O_3" (including substitution of Ti_2O_3 by Al_2O_3, Cr_2O_3 and V_2O_3) for slags produced from Canadian ilmenite (open circles) and South African ilmenite (others) (symbols as in Figure 1) with the expected relationship for stoichiometric M_3O_5 (broken line).
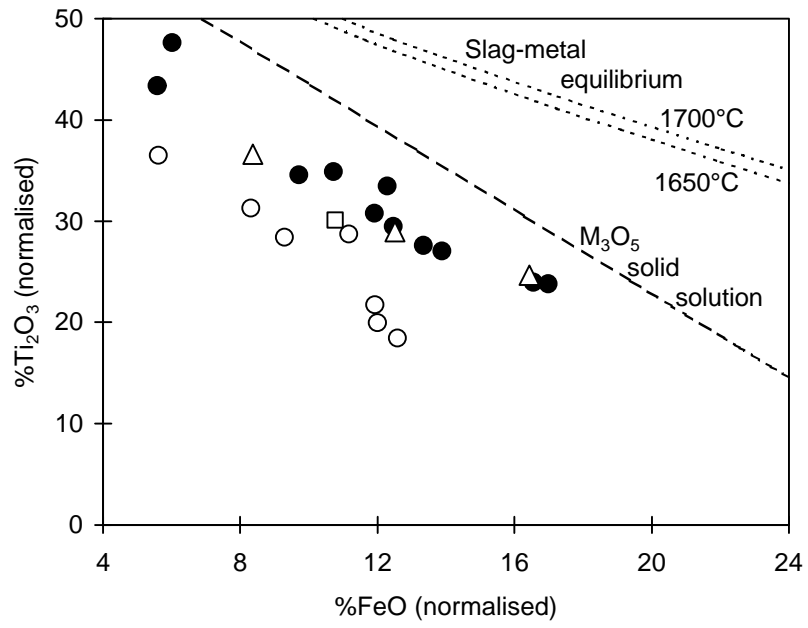
Figure 7. Data of Figure 5, but with the total of FeO, Ti_2O_3 and TiO_2 normalised to 100% (i.e. neglecting the effect of impurity oxides).