



# The use of commercial oxygen probes during the production of high titania slags

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## Synopsis

This work is concerned with studying possible reactions in the ilmenite furnace which may control the product quality of both slag and metal. Two different approaches were followed: comparing actual furnace slag compositions with the calculated equilibrium values and using commercial oxygen probes to measure the effective partial oxygen pressure in the slag and metal. It appears from a comparison of actual furnace slag compositions (in terms of the distribution coefficient of vanadium) with equilibrium values, that the  $\text{TiO}_{1.5}$ - $\text{TiO}_2$  reaction may fix the effective partial oxygen pressure for the vanadium reaction. This possibility was tested using commercial oxygen probes (traditionally applied during steelmaking) to measure the effective oxygen partial pressure of both the slag and liquid iron in Iscor's 3MVA pilot plant ilmenite furnace. From these measurements, it appears that commercial oxygen probes containing zirconia solid electrolytes can be used to measure the effective oxygen potential of both the slag and liquid iron. This oxygen activity correlates well with the FeO content of the slag. The results, furthermore, clearly illustrate that equilibrium conditions are not attained in the ilmenite furnace during the production of high titania slags, since the effective oxygen potential of slag and metal differ substantially.

## Introduction

In the smelting of ilmenite ( $\text{FeO}\cdot\text{TiO}_2$ ), carbon is used as reductant to reduce the FeO to metallic iron, while energy input is supplied by arcing (in a DC or AC furnace). The products are an upgraded  $\text{TiO}_x$ -rich slag (typically containing 85 per cent of titanium expressed as  $\text{TiO}_2$ ) and iron (with some 2 per cent dissolved carbon). For protection of the furnace walls, a side-freeze is formed, and hence the slag temperature is close to its liquidus temperature of around 1700°C. South African examples of this process are the Richards Bay Minerals operation, Namakwa Sands, and the proposed Iscor Heavy Minerals plant.

<sup>†</sup>The  $\text{Ti}^{3+}$  oxide is referred to as  $\text{Ti}_2\text{O}_3$  or  $\text{TiO}_{1.5}$ . The latter description is used in this paper, because available activity data refer to this species.

As indicated, the primary purpose of an ilmenite furnace is to reduce the FeO in ilmenite to metallic iron, thus upgrading the remaining slag to a higher titania content. However, several other reactions occur in parallel with the reduction of FeO. These include partial reduction of  $\text{TiO}_2$  to  $\text{TiO}_{1.5}$ <sup>†</sup>, and partial reduction of reducible impurities such as vanadium and chromium oxides (which are transferred to the metal). These reactions are of importance because the contents of FeO,  $\text{TiO}_{1.5}$ , and impurity oxides in the furnace slag all influence the product quality.

This work is thus concerned with studying possible reactions within the furnace which may control the product quality. Specifically—given the nature of the ilmenite furnace as a reduction unit—reactions which may control the redox conditions within the furnace are of importance. (The redox conditions are commonly expressed in terms of the partial oxygen pressure- $p_{\text{O}_2}$ ).

Two approaches were used in this work—comparing actual furnace slag compositions with the calculated equilibrium values, and using commercial oxygen probes to measure the (effective) partial oxygen pressure in the slag and metal. The slag compositions and oxygen probe measurements were obtained from the 3MVA experimental DC furnace of Iscor (in Pretoria, South Africa).

## Calculated equilibrium compositions

Some data are available on the activities in the binary FeO- $\text{TiO}_2$  and  $\text{TiO}_{1.5}$ - $\text{TiO}_2$  systems, as compiled by Eriksson and Pelton<sup>1</sup>. These data for the binary systems were used to estimate the equilibrium relationship between the %FeO and % $\text{TiO}_{1.5}$  in the slag. In this calculation, it was assumed that the activity of FeO is only

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affected by the molar ratio of  $\text{Fe}^{2+}$  to the total titanium cations (as  $\text{Ti}^{4+}$  or  $\text{Ti}^{3+}$ ) in the slag, using the data for the  $\text{FeO-TiO}_2$  binary to calculate the  $\text{FeO}$  activity. A similar approach was used by Pesl and Eric<sup>2</sup>. Similarly, it was assumed that the ratio of the activity of  $\text{TiO}_2$  to that of  $\text{TiO}_{1.5}$  was not affected by dilution of the slag  $\text{FeO}$ . This appears valid since the activities in the two binary systems approximate ideal behaviour, if the activities are expressed in terms of the species  $\text{TiO}_2$ ,  $\text{TiO}_{1.5}$  and  $\text{FeO}$ , using the pure liquid oxides as reference state<sup>1</sup>. In addition to the activity data, free energy values from the literature<sup>1,3</sup> were used. For these calculations, the slag composition was simplified to a ternary  $\text{TiO}_2\text{-TiO}_{1.5}\text{-FeO}$  combination; typically the total concentration of other impurities in the slag does not exceed some 7 per cent<sup>4</sup>.

The calculated equilibrium compositions are compared in Figure 1 with plant data from previous work<sup>4</sup>, and with measured slag compositions from the present work.

The Figure shows the equilibrium and actual  $\text{FeO}$  and  $\text{TiO}_{1.5}$  contents of the slag; the balance is  $\text{TiO}_2$ . The  $\text{TiO}_2\text{-Fe-TiO}_{1.5}\text{-FeO}$  equilibrium relationship is shown, as well as the slag composition in equilibrium with the dissolved carbon (2 per cent) and pure  $\text{CO}$  (shown as filled circles at the left-hand end of each equilibrium line). The equilibrium is clearly not strongly affected by temperature; this is as expected, since the standard enthalpy change for the reaction  $2\text{TiO}_2 + \text{Fe} = \text{FeO} + 2\text{TiO}_{1.5}$  is only some 163 kJ/mol at 1700°C (with the pure liquid species as the reference states).

Actual slag compositions from previous work<sup>4</sup> (filled diamonds) and the present work (open diamonds) are also shown. The Figure demonstrates that the furnace slag contains less  $\text{FeO}$ , and more  $\text{TiO}_2$ , than the equilibrium amounts. This implies that the iron component of the system is more reduced, and the titanium component less reduced, relative to the equilibrium condition. While it is clear that the  $\text{TiO}_2\text{-Fe-TiO}_{1.5}\text{-FeO}$  reaction in the furnace departs from equilibrium, the question remains whether other reactions in

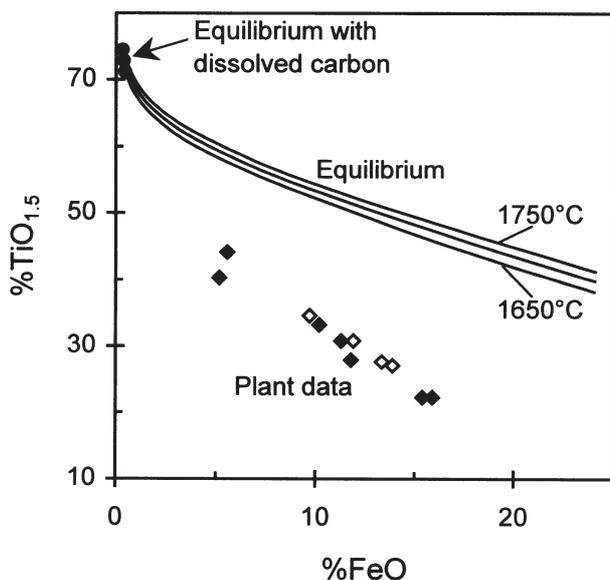


Figure 1—Calculated equilibrium relationship between mass percentages of  $\text{FeO}$  and  $\text{TiO}_{1.5}$  in ilmenite furnace slags (balance of slag is  $\text{TiO}_2$ ), for temperatures ranging from 1650°C to 1750°C (lines on graph)

the furnace reach partial equilibrium—for example with the respective redox pairs  $\text{TiO}_{1.5}\text{-TiO}_2$ ,  $\text{Fe-FeO}$  or  $\text{C-CO}$ . (Each of these redox pairs can be characterized by means of a different effective partial oxygen pressure.)

To explore this possibility, the predicted distribution co-efficient of vanadium between the slag and the metal—expressed as  $(\%V_2O_5)/(\%V)$ —was calculated. This calculation was performed by assuming vanadium to be present in the slag as  $\text{VO}_{1.5}$ , and its activity coefficient to be similar to that of  $\text{TiO}_{1.5}$  (with the pure liquid oxide as reference). These assumptions were made on the basis of the similarity of the behaviour of  $\text{VO}_{1.5}$  in the  $\text{TiO}_2\text{-VO}_{1.5}$  system, to that of  $\text{TiO}_{1.5}$  in the  $\text{TiO}_2\text{-TiO}_{1.5}$  phase system<sup>5</sup>, and the stability of the various vanadium oxides at the range of possible partial oxygen pressures in the ilmenite furnace. Interaction coefficients were used to calculate the activity of vanadium in the metal<sup>6</sup>. The vanadium distribution coefficient was then calculated, given the activity information and assuming the partial oxygen pressure to be fixed in turn by each of the reactions  $\text{C-CO}$ ,  $\text{Fe-FeO}$ , and  $\text{TiO}_2\text{-TiO}_{1.5}$ . The metal was assumed to contain 2 per cent C, and the typical slag composition of 10 per cent  $\text{FeO}$ , 51.8 per cent  $\text{TiO}_2$  and 33.2 per cent  $\text{TiO}_{1.5}$  (mass percentages) was assumed. The activities of  $\text{FeO}$ ,  $\text{TiO}_2$  and  $\text{TiO}_{1.5}$  were again calculated as explained above. Figure 2 compares the resulting equilibrium vanadium distribution coefficients with data from the Iscor 3MVA furnace.

It appears from these results that the  $\text{TiO}_{1.5}\text{-TiO}_2$  reaction may fix the effective partial oxygen pressure for the vanadium reaction: the practically obtained vanadium distribution coefficient lies closest to that predicted by assuming that the  $\text{TiO}_{1.5}\text{-TiO}_2$  couple controls vanadium distribution. To test the possibility that this might also be true for other reactions, oxygen activity measurements were performed at the Iscor 3MVA furnace, using commercial electrochemical oxygen probes. These measurements are described in the next sections.

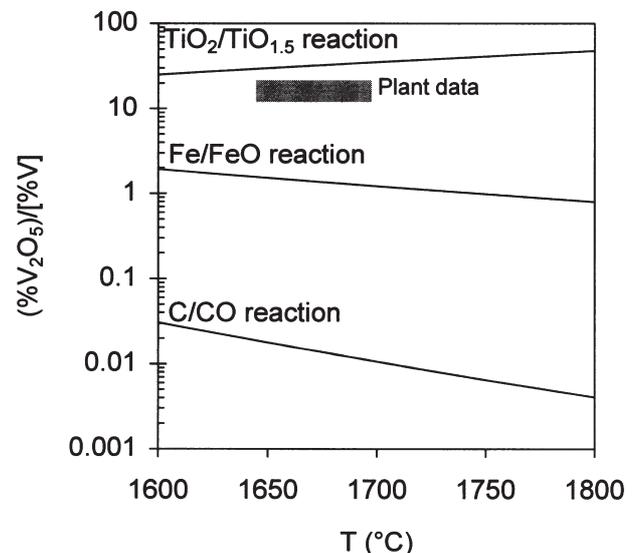


Figure 2—Comparison of calculated vanadium distribution coefficient, if the partial oxygen pressure is fixed by the three different reactions, with plant data

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## Experimental measurements of the effective partial oxygen pressure

It is experimentally almost impossible to simulate the conditions prevailing during steady state operation of an ilmenite smelting furnace in the laboratory, mainly for two reasons: i) An ilmenite furnace is fed continuously which is inherently difficult to do in the laboratory. ii) A freeze lining of solidified slag is used in ilmenite furnaces to protect the furnace refractories from chemical interaction with the titania slag. In the laboratory, all the available oxide crucibles react with the titania slag at these temperatures (1650 to 1750°C). Consequently, oxygen potential measurements had to be performed in an actual ilmenite furnace in order to measure the effective oxygen potential of the system.

Commercial electrochemical oxygen probes are commonly used on steel plants for the determination of the oxygen potential of liquid steel and were also employed here. The design of these probes is shown schematically in Figure 3.

The electrochemical cell arrangement consists of a magnesia stabilized zirconia solid electrolyte (approximately 30 mm in length, outer diameter 5 mm, inner diameter 3 mm), a (Cr+Cr<sub>2</sub>O<sub>3</sub>) reference electrode, a steel tube which serves as contact lead to the steel bath (or electronically conductive titania slag in this case), and a molybdenum wire which serves as contact lead to the reference electrode. The sensor is also equipped with a Pt/Pt-Rh thermocouple contained inside a quartz tube. An outer steel cap protects the zirconia tube and thermocouple from the steelmaking slag during the immersion of the probe into the steel bath. Another inner steel cap covers the zirconia tube and serves mainly as thermal shock absorber, thereby minimizing the chance of the zirconia tube cracking during the immersion process. To complete the oxygen probe, the sensor is attached to an expendable cardboard tube, which encloses electrical connections to a signal-processing unit. Signals of thermoelectric voltage (temperature measurement) and cell potential (oxygen activity measurement) are obtained simultaneously from the probe. When these signals attain stability, they are processed to provide a display and hard copy of the temperature and of the dissolved oxygen content of the steel bath. A hard copy of a graph displaying the thermoelectric voltage and cell potential as a function of time can also be obtained.

In the present investigation, these oxygen probes were evaluated as a possible tool to measure the effective partial

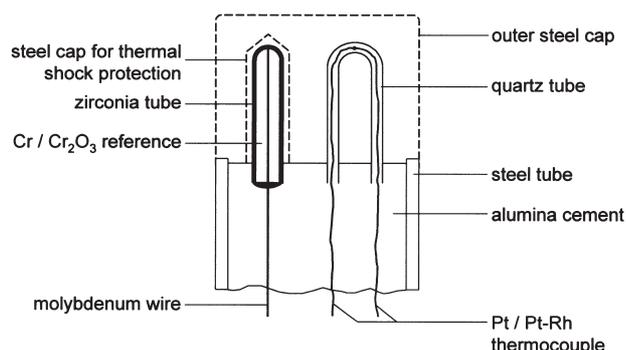


Figure 3—Schematic drawing of a commercial oxygen probe

pressure of oxygen in the titania slag. The electrical conductivity of titania slag is high enough to complete the electrical circuit. For this reason it is possible to measure a cell potential when such a probe is immersed in slag. As far as could be ascertained, such measurements have not been made previously and our measurements could not therefore be compared with existing data. Hence, it is of great importance to evaluate all aspects of these measurements in order to draw meaningful conclusions.

The oxygen measurements were performed during three different stages of ilmenite processing.

- The probes were immersed into the slag (in the slag ladle) in the period during which slag was tapped from the furnace.
- Probes were immersed into the slag while slag and metal were in contact during the production process (in the furnace), and
- one minute later, probes were immersed through the slag layer into the iron bath (in the furnace).

## Measurements in the slag ladle, during tapping

The use of the probes was initially evaluated in the slag during tapping, since these measurements are simple compared with measurements in the furnace. It should be noted that the slag is not in contact with a liquid iron bath after it has been tapped. After the slag tap hole was opened, approximately 1 ton of slag was tapped before it was closed again. The first probe was immersed to a depth of approximately 200 mm below the slag surface, after at least 500 kg slag was tapped. This procedure was followed because a solid slag layer formed in the slag ladle as soon as tapping was terminated. Several oxygen probes were immersed for a period of 12 seconds maximum into the slag. The manufacturers of these probes recommended immersion periods of 12 seconds maximum into the steel, to ensure that the temperature connection between the sensor contact leads and the extension wires to the signal processing unit is kept below 200°C. However, a stable e.m.f. plateau could not be obtained for any of these measurements.

The oxygen probes were dissected after these initial measurements and it was evident that the steel cap, protecting the zirconia tube from excessive thermal shock, was only partially melted during immersion in the slag—the steel cap thus prevented direct contact between the zirconia solid electrolyte and titania slag. Since the liquidus temperature of this slag is in the range of 1650 to 1700°C, the slag temperature is typically less than 50°C above its liquidus temperature. Consequently, when the cold oxygen probe is immersed into the slag, a slag layer freezes on the steel cap covering the solid electrolyte. This slag layer has to melt again before the steel cap melts away. However, the steel cap could not melt in the maximum immersion time period of 12 seconds. Possible ways to overcome this would be to preheat the oxygen probe or to remove the steel cap.

Commercial oxygen probes which do not contain the steel cap for thermal shock protection are available as a standard product. In steelmaking application, these probes are typically applied in the tundish of a continuous caster, where the steel temperature is below 1550°C. Such probes were also immersed into the tapped ilmenite furnace slag for a period of 12 seconds maximum, and yielded a stable, reproducible electromotive force (e.m.f.).

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It is essential that a stable e.m.f. plateau be obtained in order to classify the reading as successful. Several factors could adversely affect oxygen potential measurements when electrochemical oxygen probes are applied in liquid steel or in any slag metal system at high temperatures, including polarization effects at one or both electrodes<sup>8</sup>. As a result of such polarization effects, the e.m.f. signal declines as a function of time. Polarization at the electrodes occurs as a result of one or both of the following causes.

- ▶ The n-type electronic conductivity of the solid electrolyte is relatively high, causing electrons to migrate through the electrolyte from one to the other electrode resulting in polarization effects.
- ▶ A large difference in partial oxygen pressure between the reference electrode and the working electrode results in a large driving force for oxygen anions to migrate from the one electrode to the other.

A typical example of an e.m.f. response as measured in the furnace, in the slag, is shown in Figure 4. The temperature and e.m.f. signals recorded in this case were 1661°C and 78.9 mV, respectively. It is evident from Figure 4 that a stable e.m.f. plateau was obtained although slight polarization effects were indeed present, as was the case with some of the other measurements in this investigation. This affected the accuracy of the measurements, and as a result each measurement was qualitatively analysed to determine the uncertainty in e.m.f., and these values are also indicated in Table II (column 2). The uncertainty in the e.m.f. signal was always smaller than  $\pm 5$  mV.

### Measurements in the slag and iron, in the furnace.

Since stable e.m.f. plateaus were obtained in the slag ladle during slag tapping from the furnace, the measurements could be extended to the furnace, where the slag and metal are in contact. The same type of probe (which was successfully applied into the slag directly after tapping) was immersed in the slag in the furnace. During the immersion process, the probe was moved in a horizontal plane (approximately 1 metre span per second) to ensure that the steel cap for thermal protection melts. The probes were immersed for

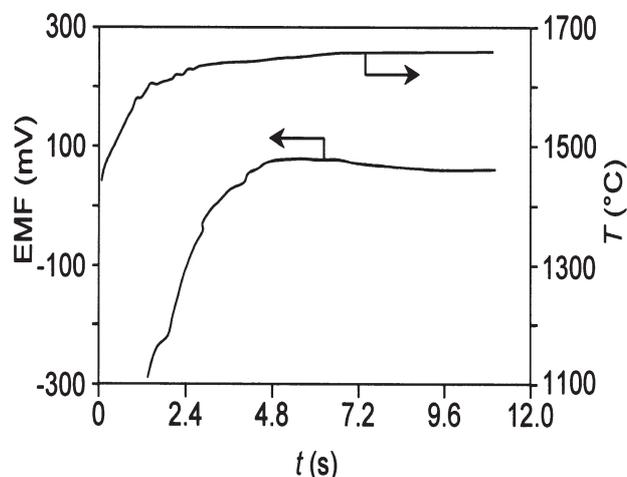


Figure 4—Typical e.m.f. and temperature response of an electrochemical oxygen probe when immersed into the titania slag (in the furnace) during this investigation

periods up to 12 seconds in the slag. Again, stable e.m.f. plateaus were obtained.

Directly after the measurements in the slag, identical probes were immersed through the slag layer into the liquid iron. Again, stable plateaus were obtained during these measurements.

Slag samples were taken directly after each electrochemical measurement (both in the slag ladle and in the furnace). These slag samples were analysed for titanium (expressed as  $TiO_2$ ) and FeO (expressed as FeO) by atomic emission spectroscopy (AES) using an inductively coupled plasma (ICP). The titanium oxide was then analysed by wet chemical analysis to distinguish between  $Ti^{3+}$  and  $Ti^{4+}$ . This slag analysis is summarized in Table II. The total impurity content of the slag (oxides other than those of titanium or iron) was always below 7 per cent; the analyses reported in Table II have hence been normalized to yield a 100 per cent total for the sum of the percentages of  $TiO_2$ ,  $TiO_{1.5}$  and FeO, using the  $Ti^{3+}/Ti^{4+}$  and  $(Ti^{3+}+Ti^{4+})/Fe^{2+}$  molar ratios as obtained from the detailed analyses.

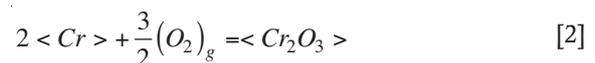
### Results and discussion

Schmalzried<sup>9</sup> analysed the contribution of electronic conduction in the solid electrolyte to the cell potential (e.m.f.) and has proposed that the e.m.f. in the presence of n-type electronic conduction in the solid electrolyte can be expressed as:

$$E + E_t = -\frac{RT}{F} \ln \left( \frac{p_{O_2}^{\oplus \frac{1}{4}} + p_e^{\frac{1}{4}}}{p_{O_2}^{\ominus \frac{1}{4}} + p_e^{\frac{1}{4}}} \right) \quad [1]$$

where  $p_{O_2}^{\oplus}$  and  $p_{O_2}^{\ominus}$  are the partial pressures of oxygen of the titania slag and (Cr+Cr<sub>2</sub>O<sub>3</sub>) reference electrode respectively,  $E$  is the electromotive force,  $E_t$  is the thermal e.m.f. between Mo and Fe (which serve as contact leads to the (Cr+Cr<sub>2</sub>O<sub>3</sub>) reference electrode and the slag/steel respectively),  $R$  is the ideal gas constant,  $F$  is the Faraday constant,  $T$  is the absolute temperature, and  $p_e$  is defined as that partial pressure of oxygen at which the ionic conductivity of the solid electrolyte is equal to its n-type electronic conductivity.

The standard Gibbs energy of formation of solid Cr<sub>2</sub>O<sub>3</sub> as reported by Elliot and Gleiser<sup>10</sup> has been used to calculate the partial oxygen pressure of the reference electrode according to the following equilibrium reaction:



where  $< >$  and  $( )_g$  denote the solid and gas phases respectively.

The thermal e.m.f. between Mo and Fe was determined by Iwase *et al.*<sup>11</sup>, as a function of temperature in the temperature range 1273 to 1623 K yielding the following relationship:

$$E_t = -(14.69 + 1.06) + (0.02227 + 0.0007)T \quad [3]$$

where  $E_t$  is measured in mV and  $T$  in kelvin. It should be noted that  $E_t$  increases linearly with an increase in temperature in this temperature range, and consequently

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there is good reason to believe that Equation 3 is also applicable to the temperature range 1860 to 1950 K. In the probes used in this investigation, the molybdenum lead is connected to a Cu-1% Ni compensating wire which also serves as contact lead to the Pt wire of the Pt/Pt-Rh thermocouple, but the temperature at this junction is always below 200°C. Therefore, Equation 3 has been applied without modification to determine the thermal e.m.f. between the molybdenum and iron contact leads.

An experimental technique was previously developed to determine the  $p_e$  value of short electrolyte tubes<sup>12</sup> (similar to those used in commercial oxygen probes). Using that technique, the  $p_e$  value of commercially available oxygen probes was found to exhibit the following temperature dependence in the temperature range 1400–1600°C<sup>13</sup>.

$$\log p_e = 24.53 - 70083/T \quad [4]$$

where  $p_e$  and  $T$  are measured in atm and kelvin respectively. Since the logarithm of  $p_e$  is a linear function of  $1/T$ , Equation 4 has been assumed to be applicable in the temperature range up to 1680°C. It has, furthermore, been shown that, provided that the chemical composition and impurity content of magnesia stabilized electrolytes are similar, the  $p_e$  value of these electrolytes is also similar<sup>14</sup>. The chemical composition of the commercial zirconia electrolytes studied previously<sup>15</sup> is compared in Table I with that of the zirconia solid electrolytes that were used in this investigation.

It is evident that both the impurity content (primarily, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) and general chemical composition (primarily, MgO as used to stabilize the electrolytes) of the solid electrolytes are in fairly good agreement. There is, therefore, good reason to assume that the  $p_e$  value of these electrolytes is similar and, hence, Equation 4 has been used to estimate the  $p_e$  value of the zirconia solid electrolytes used in the present study.

Chemical interaction between the zirconia solid electrolyte and the slag<sup>16</sup> could result in unsuccessful measurements<sup>17</sup>. In order to determine whether substantial chemical interaction occurred between the titania slag and zirconia solid electrolyte during this study, a solid electrolyte that had been used at a temperature of 1678°C in the slag was examined in a scanning electron microscope. The result is presented in Figure 5, which shows a back-scattered electron image (which yields atomic number contrast).

A reaction layer with a thickness of approximately 30 µm is visible in Figure 5. Chemical analysis (by energy-dispersive X-ray analysis—EDX) of this area indicated that the zirconia content varied from approximately 13 to 29 mass per cent ZrO<sub>2</sub>, while the iron content oxide (expressed as FeO) varied from 7 per cent to 23 per cent—the balance being TiO<sub>x</sub>. Evidently, the zirconia and titania slag did react chemically, yielding a 30 µm thick product layer within a period of approximately 12 seconds. However, this is a small amount of reaction compared with the original wall thickness of the zirconia tube (1 mm). In addition, point analyses (by EDX) in the zirconia matrix immediately adjacent to the areas where zirconia dissolved into the slag, indicated that no slag penetration had occurred. It is thus concluded that chemical reaction between the solid electrolyte and the slag did not affect the measurements adversely.

The (Cr+Cr<sub>2</sub>O<sub>3</sub>) reference electrode consists of Cr and Cr<sub>2</sub>O<sub>3</sub> particles that are intimately mixed and are in contact with each other. The particle size was determined by microscopic analysis and varied between approximately 50 and 250 µm. One concern is that the reference material may have melted during the measurements, since a eutectic reaction is found in the Cr-O system at approximately 1660°C and 80 per cent Cr<sub>2</sub>O<sub>3</sub><sup>18</sup>. Melting of the reference electrode material would cause deviation from the expected relationship between the cell voltage and the oxygen activity.

In order to check whether eutectic melting had occurred, the reference electrode of an oxygen probe that had been immersed at the highest temperature (1678°C), was studied in a scanning electron microscope; a photograph is shown in Figure 6.

Figure 6 shows clearly that the particle sizes are similar to those before immersion, and the particles remain angular, indicating that, at most, very limited liquid formation had occurred. The reasons for little or no liquid formation could be a low reaction rate between the Cr and Cr<sub>2</sub>O<sub>3</sub>, and that the slag sensor temperature was only slightly above the eutectic temperature.

The temperature values measured with the sensor thermocouple were always between 10°C and 20°C lower than that measured at the same time with a dip thermocouple. A dip thermocouple is a disposable Pt-Pt/Rh thermocouple, used to measure the temperature of slag or metal at steelmaking temperatures. Since this thermocouple does not contain an oxygen sensor, the heat capacity of this thermocouple is lower than that of the oxygen probe. Since the slag

Table I

**Comparison of the chemical composition of the solid electrolytes used in the commercial oxygen probes previously investigated<sup>15</sup> and those used in this study (mass percentages; the balance of the compositions is ZrO<sub>2</sub>)**

	No.	%MgO	%CaO	%SiO <sub>2</sub>	%Al <sub>2</sub> O <sub>3</sub>	%TiO <sub>2</sub>	%Fe <sub>2</sub> O <sub>3</sub>	%Na <sub>2</sub> O	%K <sub>2</sub> O
Previous study	1	2.16	0.34	0.50	0.40	0.08	0.25	0.02	<0.01
	2	2.51	0.41	0.49	0.09	0.08	0.17	<0.01	<0.01
	3	2.52	0.39	0.45	0.08	0.09	0.35	<0.01	<0.01
This study	1	2.15	0.21	0.09	0.02	0.06	0.03	0.01	0.016
	2	2.18	0.21	0.17	0.04	0.07	0.07	0.01	0.013
	3	2.18	0.20	0.12	0.02	0.06	0.04	0.01	<0.01

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is only slightly above its liquidus temperature, the small difference in size between the two types of sensors causes the measured temperature to differ as much as 20°C in the worst case. The resulting uncertainty in the accuracy of the temperature measurements measured with the oxygen probe is indicated in Table II (first column).

Given the uncertainties in the measured e.m.f. and the

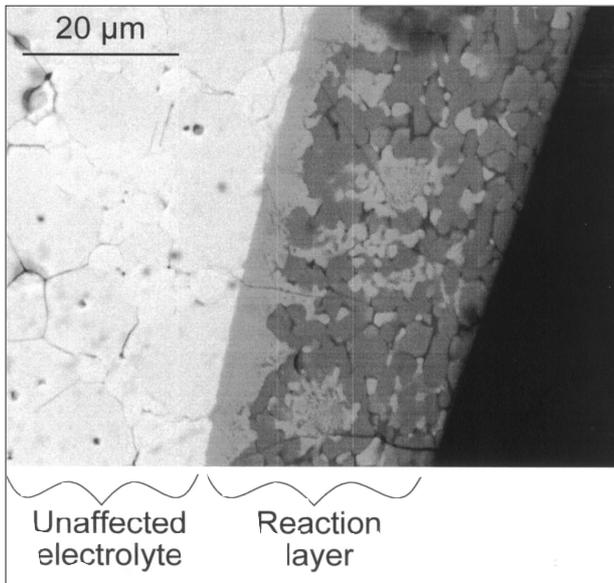


Figure 5—Back-scattered electron image of a cross-section of the zirconia solid electrolyte after immersion in the titania slag at 1678°C, showing the outer part of the electrolyte which had been in contact with the slag

temperature, the maximum total uncertainty in the calculated effective oxygen partial pressure was determined, including the effect of temperature on the partial pressure of oxygen of the reference electrode ( $p_{O_2}$ ), the  $p_e$  value and the thermal e.m.f. ( $E_T$ ). These deviations together with the standard deviation of the e.m.f. signal, were used to calculate the uncertainty in the calculated partial pressure of oxygen of the metal or slag ( $p_{b_2}$ ). This uncertainty is also listed in Table II; it can be seen that the uncertainty was always less than  $8 \times 10^{-12}$  atm.

Figure 7 shows the measured oxygen activities together with the predicted oxygen activity, if this is fixed by respectively the  $TiO_2/TiO_{1.5}$  equilibrium (for slags containing 25 per

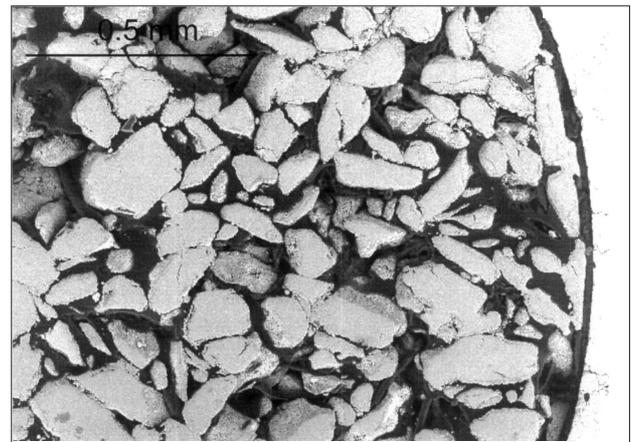


Figure 6—Cr/Cr<sub>2</sub>O<sub>3</sub> reference electrode after immersion for 12 seconds at 1678 °C in the titania slag, as seen in cross-section in a scanning electron microscope

Table II

The measured e.m.f. and temperature for oxygen probe measurements in the slag and metal, together with the calculated  $p_{O_2}$  of the slag and iron, and chemical composition of the slag and carbon content of the iron

Temperature (measured with oxygen probe) (°C)	Electromotive force (e.m.f. signal) (mV)	Calculated partial oxygen pressure of the slag or metal ( $p_{O_2}$ ) [atm]	Carbon content of iron and normalized chemical analysis of slag			
			%C(Fe)	%TiO <sub>2</sub>	%TiO <sub>1.5</sub>	%FeO
• 1671±14	44.1±5	$(8.5±4.6) \times 10^{-12}$	2.37	55.7	34.6	9.7
• 1679±10	47.4±5	$(1.2±0.6) \times 10^{-11}$	2.37	55.7	34.6	9.7
° 1673±6	63.9±2	$(2.0±0.5) \times 10^{-11}$	2.3	57.3	30.8	11.9
° 1672±7	58.5±3	$(1.60±0.5) \times 10^{-11}$	2.3	57.3	30.8	11.9
° 1660±7	73.4±3	$(2.0±0.8) \times 10^{-11}$	1.47	59.0	27.6	13.4
° 1661±6	78.9±4	$(2.6±0.8) \times 10^{-11}$	1.47	59.0	27.6	13.4
▼ 1622±18	-8.2±4	$(2.5±1.6) \times 10^{-13}$	1.47	59.0	27.6	13.4
▼ 1587±18	-10.1±5	$(1.1±0.8) \times 10^{-13}$	1.47	59.0	27.6	13.4
• 1647±3	87.8±5	$(2.4±0.7) \times 10^{-11}$	1.47	59.1	27.0	13.9
• 1642±5	86.1±5	$(2.0±0.8) \times 10^{-11}$	1.47	59.1	27.0	13.0

• Measured in the slag ladle (probe immersed into slag)  
 ° Measured in the furnace (probe immersed into the slag)  
 ▼ Measured in the furnace (probe immersed into the liquid iron)

## The use of commercial oxygen probes during the production of high titania slags

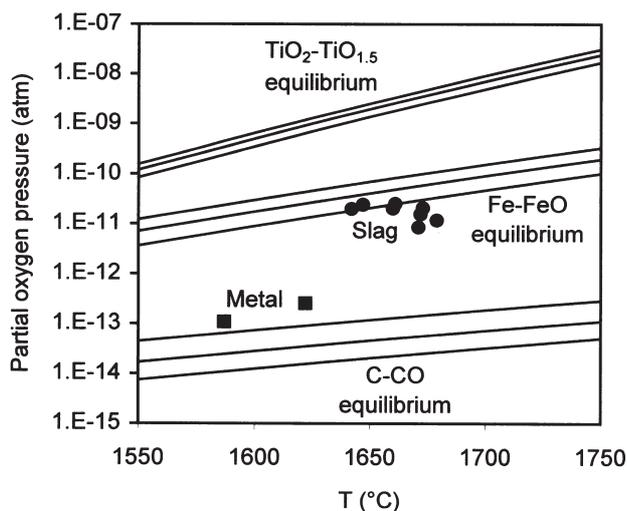


Figure 7—Comparison of the measured partial oxygen pressure in the Iscor 3MVA ilmenite furnace, with the calculated partial oxygen pressure if fixed by each of the three redox couples ( $\text{TiO}_2/\text{TiO}_{1.5}$ ,  $\text{Fe}/\text{FeO}$ , and  $\text{C}/\text{CO}$ ) respectively

cent, 30 per cent and 35 per cent  $\text{TiO}_{1.5}$  respectively, from top to bottom, at constant  $\text{FeO}$  of 12 per cent), the  $\text{Fe}/\text{FeO}$  equilibrium (for slags containing 15 per cent, 12 per cent and 9 per cent  $\text{FeO}$  respectively, from top to bottom, at a constant % $\text{TiO}_{1.5}$  of 30 per cent), and the  $\text{C}/\text{CO}$  equilibrium (for metal containing 1.5 per cent, 2 per cent and 2.5 per cent  $\text{C}$  respectively, from top to bottom, with pure  $\text{CO}$  in the gas phase). The predicted oxygen activity was calculated using the activity data as outlined earlier. From the Figure, it appears that the measured effective oxygen potential of the slag is rather determined by the  $\text{Fe}/\text{FeO}$  reaction and not by the  $\text{TiO}_2/\text{TiO}_{1.5}$  reaction. This is in contrast to the results obtained when the vanadium distribution between slag and metal is compared with that predicted for the different redox couples (Figure 2).

It is also evident that the measured oxygen activity in the iron compares fairly well with the calculated oxygen partial pressure as fixed by the  $\text{C}/\text{CO}$  reaction. It is clear, therefore, that equilibrium is not attained between the metal and the slag, since the effective oxygen potential of slag and metal differ substantially.

### Conclusions

The results obtained during this investigation clearly illustrate that equilibrium conditions are not attained in the ilmenite furnace during the production of high titania slags. However, it appears that commercial oxygen probes containing zirconia solid electrolytes can be used to determine the effective oxygen potential of the slag; this oxygen activity correlates well with the  $\text{FeO}$  content of the slag.

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## Mineral processing '98, Sea Point, South Africa, 6–7 August 1998\*

For the past 17 years, the Universities of Cape Town and Stellenbosch have hosted the Minerals Processing Symposia. The Cape Technicon joined the conference in 1994, enlarging the research base and making a valuable contribution ever since.

About 177 participants from 6 countries attended the conference which was held at the Arthur's Seat Hotel in Sea Point, offering visitors quick access to Cape Town, the Atlantic Seaboard and essentially the whole of the Peninsula.

About 40 papers and 15 posters were presented at the conference and a further 7 presented at the preceding one-day workshop on Mineralogy for Mineral Processing Engineers. The workshop was well attended. Ivan Reynolds, geologist from Rio Tinto, London, opened the day with a discussion on the role of mineralogy in the design process routes for the extraction of complex polymetallic sulphides. Furthermore, Professor Lorenzen from the University of Stellenbosch gave an update on the most recent developments in the field of diagnostic leaching which shows much potential in the field of liberation modelling.

On the first day of the conference, Professor John Ralston of The Ian Wark Research Institute of the University of South Australia gave a plenary lecture on the fundamentals and control of bubble-particle capture. Using a video imaging constructed from high-speed photography, he vividly showed how bubbles and particles interact on a micro scale, also determining if a stable bubble-particle aggregate would form. Moreover, he has shown the current leading edge work being done at the Ian Wark Research Institute regarding bubble particle interactions, a still ill-understood phenomena at a fundamental level.

During the rest of the first day, many research students gave excellent oral presentations on their research. One specific topic which captured the author's attention was a presentation by Mr F. Sawyerr, originally from the U.S. but currently studying at UCT, where he used population balance methods to predict bubble size distributions in mechanical flotation cells and backed up his theoretical work with measurements made by the UCT-developed

bubble-size analyzer.

Thursday was concluded with the Annual Dinner of the Western Cape Branch at the Ritz Plaza Hotel in Sea Point. Mr. John Scott, a distinguished journalist gave a very humorous report-back of his experiences as a reporter on local issues from the Cape, as well as his experiences as a political correspondent. During the dinner, two SAIMM student prizes were awarded by the President of the Institute, Mr. R. Mohring, to Paul Ayers, and Andrew Carr (UCT) and Hanre Rossouw (Stell.) and Maryke Visser (Cape Tech).

Dr. Victor Ross opened the second day of the symposium with a very entertaining plenary lecture on Technological Innovation. In his address he referred to the fact that the men of the future must think in a more feminine way, i.e. be more creative, not only to adapt to the changes of the future, but to *create* the future. He stressed the role of diffusion of technology from the original invention and ideas in the heads of researchers to the implementation so that society can benefit from it.

Two papers were also presented dealing with the high temperature side of minerals processing, with Professor Geldenhuys from the University of Pretoria reporting on the complex non-equilibrium processes during ilmenite smelting and Professor Bradshaw (from the University of Stellenbosch) discussing novel ways of high temperature processing with micro-waves.

It is hoped that the future will bring more research presentations in the pyrometallurgical field as there is such a dire need in South Africa for research in this area and it has lately been treated as the stepchild in mineral and metal extraction research, which has attracted very few researchers from South Africa in the past decade.

Minerals Processing '98 was, as in previous years, a splendid showcase of current process-metallurgical research, maintaining or even improving on the high quality presentations of the past. It is a symposium of which the SAIMM and the symposium contributors can be rightly proud. ♦

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## Aluminum sow casting and charging guidelines

The Aluminium Association's *Guidelines for Aluminum Sow Casting and Charging*, important safety guidelines for companies that produce or melt aluminum sows, is now available.

The publication is intended to assist companies that produce or melt aluminum sows, prevent injuries and equipment damage, resulting from charging wet or contaminated sows into molten aluminum in melting furnaces. It also contains information to assist personnel in handling, transporting, storing and drying sows.

There are nine major sections, including sow casting, storage, transportation, receiving and inspection, drying, charging, incident reporting system, and references. Additionally, the guidelines offer information and

suggestions for individual plants to consider in designing and operating their own safety programmes related to aluminum sow casting, inspection, drying and melting.

Single copies of the *Guidelines for Aluminum Sow Casting and Charging* are \$10 for members of The Aluminum Association and \$20 for non-members, plus shipping and handling. To order, request item GSC and send a cheque or money order payable to The Aluminum Association, Publications Department, P.O. Box 753, Waldorf, Maryland, 20604, or call the association's fulfillment house at 301-645-0756.

For information on all association publications, log on to the association's web site at [www.aluminum.org](http://www.aluminum.org). ♦