

Development of alternative techniques for matte level measurements in sulphide smelting furnaces

J.M.A. GELDENHUIS*, D. MILLER†, B. VAN BEEK‡, J. NDLOVU**, and K.T. HARA§

*HATCH. Gallo Manor, South Africa

†Heraeus Electro-Nite, Dunswart, South Africa

‡LONMIN. Marikana, South Africa

**AngloPlatinum, Polokwane Smelter, Polokwane, South Africa

§Anglo Platinum Research Centre

This paper describes the development of an alternative technique for measuring the matte level height in sulphide smelting furnaces. The initial studies involved applying electrochemical oxygen probes in a smelting furnace to measure the oxygen potentials of the matte and slag phases. However, these measurements were not successful as a result of low temperatures, preventing the reference electrode from attaining equilibrium during the measurements. These trials were followed up by using oxygen probes containing a (Mo + MoO₂) reference electrode instead of the (Cr + Cr₂O₃) reference electrode used previously. It was shown that with some further development work, it should be possible to measure the oxygen potential of these mattes accurately.

Further measurements were performed with a magnetic sensor in sulphide mattes. It was shown that an electronic signal, which is proportional to the magnetic susceptibility of the surrounding material, was generated during immersion into liquid matte. These measurements were extended and done in a smelting furnace. Initial results indicated that when the magnetic sensor was dipped through the slag layer into the matte, a signal was generated as soon as the sensor came in contact with the matte. Measurements are ongoing in order to record (on a computer for improved accuracy) the signal as a function of distance when the sensor is immersed through the slag layer into the matte phase. The magnetic sensor measurements may be the solution to a matte level measurement problem that has existed for a few decades in matte smelting furnaces.

Introduction

During the production of value metals such as nickel, copper, cobalt, and platinum from sulphide ores, the first metallurgical treatment step typically involves flotation to increase the sulphide grade by removing gangue material from the sulphides. This flotation concentrate is then typically dried and smelted in a smelting furnace to further increase the sulphide grade. The oxides formed report to the slag (which is either discarded or processed further to recover value metals), while the desired metal accumulates as sulphides in the matte phase. During the smelting process, the slag and matte phases are tapped through separate furnace tap holes.

The density of the matte phase is typically in the order of 4.5 g/cm³ while that of the slag might vary between 2.8 and 3.2 g/cm³. Accordingly, the matte phase accumulates on the furnace floor (bottom layer), while the slag forms a layer on top of the matte. From a production viewpoint, it is important to know where the interface between matte and slag is, in order to optimize the tapping schedules for matte and slag. This slag/matte interface level changes continuously between tapping events and the rate is determined by different factors, which include the smelting rate, 'matte fall' of the concentrate feed (which might vary quite substantially over a 24 hour period), the power input

and the concentrate feed rate into the furnace. It is important to be able to physically measure the matte-slag interface level. Matte tapping decisions are based on these measurements and reliable measurements could contribute to better overall control of the process and the determination of the bottom build-ups, which reduce furnace capacity.

Sounding bars have been used to measure matte/slag interface levels (matte bath level) since the development of matte smelting furnaces. This method is based on the different interaction/reaction of matte and slag, respectively, with a steel rod when dipped into the smelting furnace. Typical visible differences on the steel rod, after the rod has been dipped into the furnace, are used to distinguish between the slag and matte levels. The differences include:

- difference in colour induced onto the steel rod by matte and slag
- attachment characteristics of matte and slag to the steel rod
- difference in texture of the steel rod surface after removal of the slag and matte layer from the steel rod as a result of the chemical reaction, which occurs between the matte and the steel rod (slag does not react with steel rod).

In general the accuracy and repeatability of matte level measurements performed with sounding bars are poor and prone to human error, due to the following factors:

- interpretation of results by individual shift operators since the matte/slag interaction with the steel rod is not always the same
- the matte and slag composition (as well as temperature) varies continuously and affects the interaction with the sounding bar.

This paper describes the development of an alternative technique to measure the matte-slag interface level in sulphide smelting furnaces .

Theoretical background

Oxygen potential

The difference in physico-chemical properties between the matte and slag phases in a smelting furnace can be utilized to determine the level of the interface between the phases. One such variable is the oxygen potential of the slag and matte. It has previously been suggested to further develop the application of electrochemical oxygen probes in order to determine the matte level in sulphide smelting furnaces¹ . Electrochemical oxygen probes are used extensively in the steel industry to measure the oxygen potential of liquid steel. The application of these types of sensors includes the optimization of the deoxidation process of steel when aluminium is added to react with the dissolved oxygen content of the steel. The design of these probes is shown schematically in Figure 1.

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+Cr₂O₃) or (Mo+MoO₂) reference electrode, a steel tube that serves as a contact lead to the steel bath (or electronically conductive sulphide matte in this case), and a molybdenum wire that serves as a 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 liquid slag during the immersion of the probe into the bath. Another inner steel cap covers the zirconia tube and serves mainly as a 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 graph displaying the thermoelectric voltage and cell potential (e.m.f.) as a function of time.

It is essential that a stable e.m.f. plateau is obtained in order to classify the reading as successful in terms of the exact oxygen potential of the melt. Several factors could adversely affect oxygen potential measurements when electrochemical oxygen probes are applied in slag-matte systems at high temperatures, including polarization effects at one or both electrodes². 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:

- 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 oxygen partial pressure (PO₂) 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.

Schmalzried 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 as³:

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

where p'_{O_2} and p''_{O_2} are the partial pressures of oxygen of the matte and (Cr+Cr₂O₃) or (Mo+MoO₂) 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+Cr₂O₃) 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

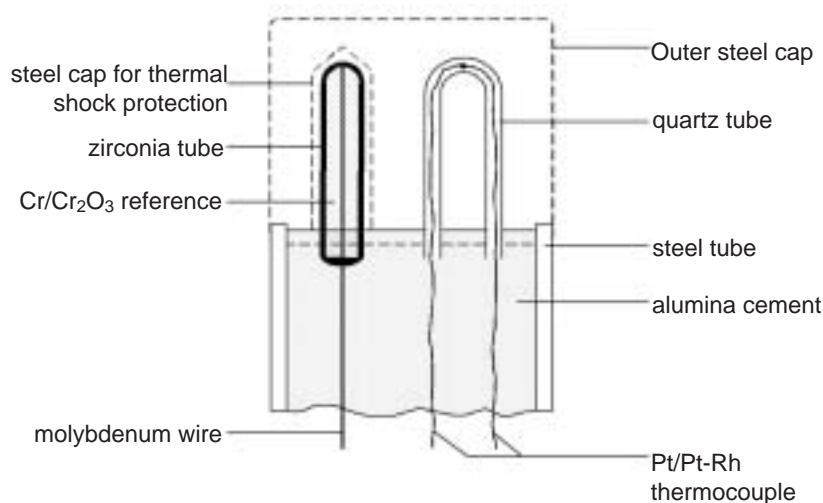
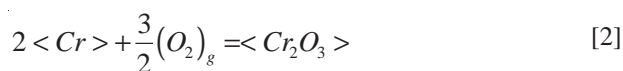


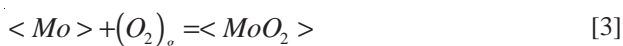
Figure 1. Schematic diagram of electrochemical oxygen probe

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_2O_3 and MoO_2 respectively, as reported by Elliot and Gleiser⁴ has been used to calculate the partial oxygen pressure of the reference electrode according to one of the following reactions:



or



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.*⁵ as a function of temperature in the temperature range 1000 to 1350°C yielding the following relationship:

$$E_t = -(14.69) + (0.02227)T \quad [4]$$

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 there is good reason to believe that Equation [4] is also applicable to the temperature range 1350 to 1500°C. 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 [4] has been applied without modification to determine the thermal e.m.f. between the molybdenum and iron contact leads.

One of the applications in the steel industry is as follows: In order to measure the slag/steel interface level of liquid steel and slag contained in a ladle, these probes are dipped through the slag layer into the liquid steel. The probe is then slowly lifted from the liquid steel while the e.m.f. is recorded. As soon as the probe makes contact with the slag layer, the e.m.f. signal changes as a result of the oxygen potential of the slag, which differs from that of the steel. This change in e.m.f. signal is used to measure the steel/slag interface level.

Magnetic susceptibility

Industrial applications

It is well known that there is a major difference in the magnetic susceptibility between steel and steelmaking slags at typical steel production temperatures (1550 to 1650°C). This principal is utilized to measure the steel level in steel ladles. A lance containing a sensor, which is sensitive to changes in induced magnetic susceptibility, is utilized during these measurements. As soon as the sensor comes in contact with material, which is magnetically susceptible, a signal is generated. The intensity of this signal is proportional to the induced magnetic susceptibility of the material.

The steel and slag contained in the ladle during treatment at a ladle furnace, separate to form a liquid slag layer on top of the liquid steel bath surface. When this lance containing the sensor (which is sensitive when in contact with magnetic susceptible material) is dipped through the slag layer into the liquid steel bath, the electronic signal that is generated changes instantaneously when it enters the liquid

steel bath, as a result of the difference in the induced magnetic susceptibility (slag versus steel). This change in the intensity of the signal is then used to determine the level of the steel bath in the ladle.

Another industrial example where the magnetic characteristics of liquid steel is utilized for process control, is the continuous casting process of liquid steel. Electromagnetic stirring, which is applied to control the casting structure, is based on the magnetic susceptibility of the liquid steel before solidification in the steel slab or billet. Another example where the magnetic characteristics of liquid steel is utilized, is the control of the steel level in the mould of a continuous casting machine (eddy currents).

Matte level application

At the time of the current tests, data were not available on the magnetic susceptibility of liquid matte typically produced during the smelting of sulphide ores. However, based on the fact that the chemical composition of the slag and matte produced in a smelting furnace vary significantly, trials were performed to investigate the possibility of utilizing the magnetic characteristics of matte and slag to measure the matte level in such a furnace.

Plant trials

Electrochemical oxygen probes

In a Ni-Cu matte smelting furnace, concentrate feed is smelted and separates into a sulphide-rich matte phase (containing the base metals and PGMs) and oxide-rich slag phase (containing mainly gangue material). If slag-matte equilibrium is achieved, the oxygen potential of the matte and slag would be the same. However, it is to be expected that equilibrium between slag and matte is not fully achieved and therefore there should be a difference in oxygen potential between the slag and matte. Furthermore, it is also well known that the temperature of the slag is typically 50 to 150°C higher than the matte in these furnaces. Accordingly, trials were initiated to test if the expected difference in oxygen potential and temperature between slag and matte could be used to determine the interface between slag and matte. These trials were conducted originally at the new rectangular smelting furnace of Anglo Platinum (Polokwane smelter) as well as on the Mortimer plant of Anglo Platinum.

Trial procedure

The sounding bar, which is usually used to measure the matte level in the Polokwane smelting furnace, is attached to a cable that is lowered by means of an electric motor. During a sounding measurement, the sounding bar is lowered into the furnace by manually starting the electric motor. The steel sounding bar is lowered until it reaches the bottom of the furnace. The sounding bar is kept in the furnace for a while before the electric motor is manually prompted to turn in the reverse direction in order to pull the sounding bar out of the furnace. The sounding bar is then visually inspected to determine the height of the matte level.

This same device was used to lower the oxygen probes into the furnace. The sounding bar (steel rod) was replaced by the oxygen probe lance (which was attached to the cable in a similar manner as the sounding bar). However, it should be noted that the sounding bar could only be replaced by the oxygen probe lance during a shut-down when the furnace power was off. The reason is that the sounding bar mechanism is installed on the electrode floor,

inside the cage, which surrounds the electrodes. In order to maintain high safety standards, access to this area is only permitted when the furnace power is off. In order to minimize production disturbance, these trials were performed at the end of a 36-hour shut-down (before the power was switched on again). It was to be expected that the matte and slag temperatures would be slightly lower and more similar to each other than normal.

A disposable probe was put onto the oxygen lance, which was connected to the electronic unit, which recorded the e.m.f. signal of both the probe and the thermocouple as a function of time. The lance was lowered at a rate of approximately 100 mm per second through the slag layer until it was in contact with the matte. It was ensured that the probe did not touch the furnace floor because of potential damage that could be done to the probe. The probe was then kept in the matte for a few seconds before it was slowly pulled out through the slag layer until it was in its original position (out of the furnace). The procedure was then repeated with a new disposable probe.

Results and discussion

Eight measurements were done, all showing similar tendencies. Figure 2 shows the results of the second measurement and it is evident that the temperature signal between 2 and 6 seconds after immersion (period that the probe was in contact with the matte) was fairly stable at 1275°C. However, the e.m.f. signal (which is a function of the oxygen potential of the matte), increased continuously from 0 mV to approximately 200 mV over the same time period. This was probably a result of the fact that equilibrium between the Cr and Cr₂O₃ (which served as reference electrode) was not attained fully within this period as a result of the temperature, which was below 1350°C (the furnace being in shut-down state, was also colder than normal, and this would not have helped the situation). It is also likely that the reaction rate between Cr and Cr₂O₃ to establish an equilibrium oxygen potential (according to Reaction 2) was too slow to ensure equilibrium in this time (4 to 8 seconds) and hence caused the oxygen potential of the reference electrode to change continuously; and, as a result, the e.m.f. signal changed as well.

After a period of 5 to 7 seconds, the probe was lifted from the matte and made contact with the slag. Hence, the temperature signal increased during this period (from 7 seconds onwards). The e.m.f. signal also changed in this period. However, the inflection point is not uniquely defined on the e.m.f. curve, since a stable plateau has not been established while the probe was immersed into the matte. Figures 3 and 4 show similar tendencies. The temperature measured in Figure 3 was approximately 1320°C and the relatively low temperature probably caused the reference electrode not to reach equilibrium in time. When the probe was lifted and came in contact with the slag, both curves changed. Again, it is not possible to define the exact inflection point that should be correlated with the interface between matte and slag. A temperature reading of 1215°C is displayed in Figure 4, which in general causes the same tendency when compared to the previous 2 measurements.

The results obtained during the first trial with oxygen probes dipped into platinum containing sulphide matte and slags are summarized as follows:

- the temperature of the matte was too low to establish equilibrium within the reference electrode of the probe. Accordingly, a stable e.m.f. plateau could not be obtained
- the temperature measured by the different probes inserted into the matte, varied between 1215 and 1320°C. This was probably as a result of the fact that no power was put into the furnace during the 36-hour period preceding the oxygen measurements. Accordingly, the matte temperature was not homogeneous, but stratified, resulting in varying temperatures. Furthermore, it should be noted that the oxygen probes were not lowered to exactly the same depth into the matte.

The trials at Polokwane were followed up by measurements in the smelting furnace situated on the Mortimer site. However, in this case oxygen probes containing an Mo and MoO₂ oxide as reference electrode, were used. The equilibrium oxygen potential of this electrode is higher than that of a Cr and Cr₂O₃ electrode. Accordingly, depending on the oxygen potential of the

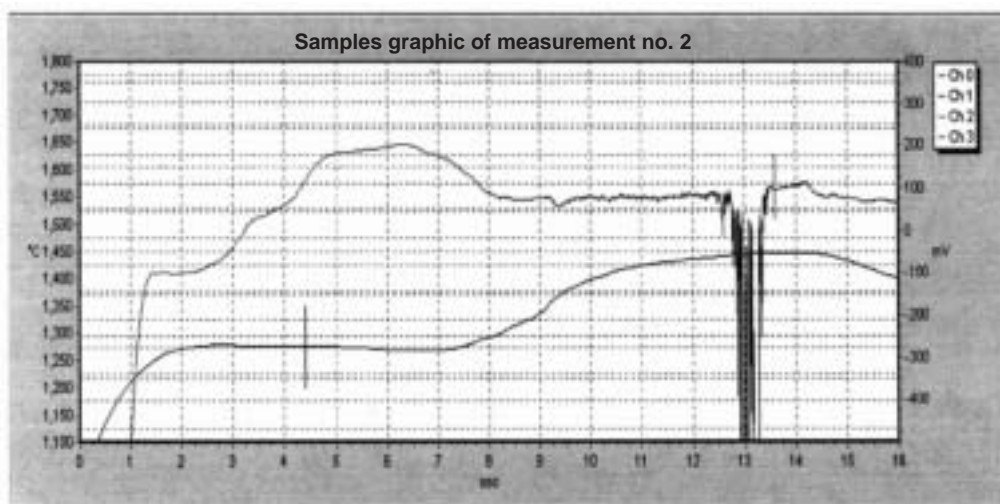


Figure 2. Electromotive force (EMF) signal (related to the oxygen potential) and temperature signal as a function of time during immersion into the Polokwane sulphide smelting furnace

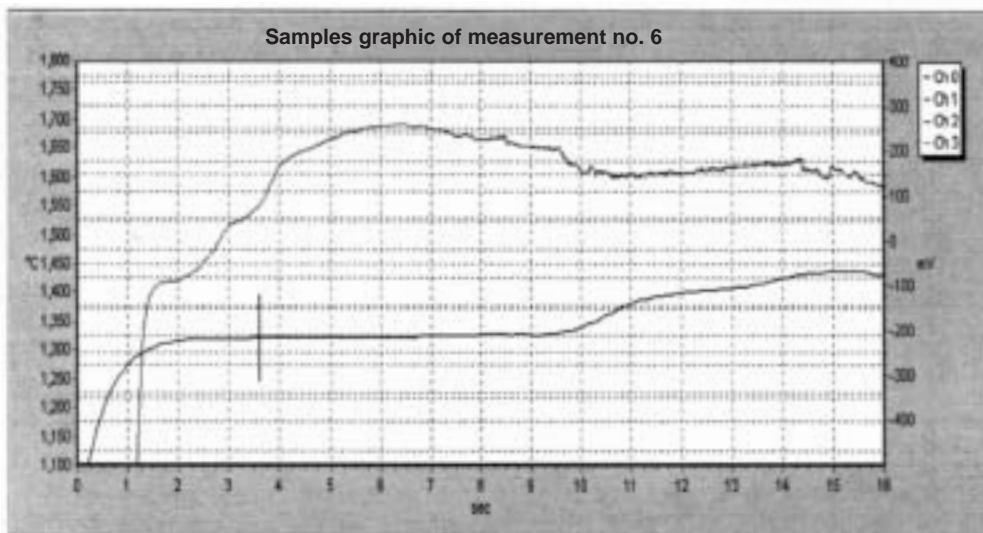


Figure 3. Electromotive force (EMF) signal (related to the oxygen potential) and temperature signal as a function of time during immersion into the Polokwane sulphide smelting furnace

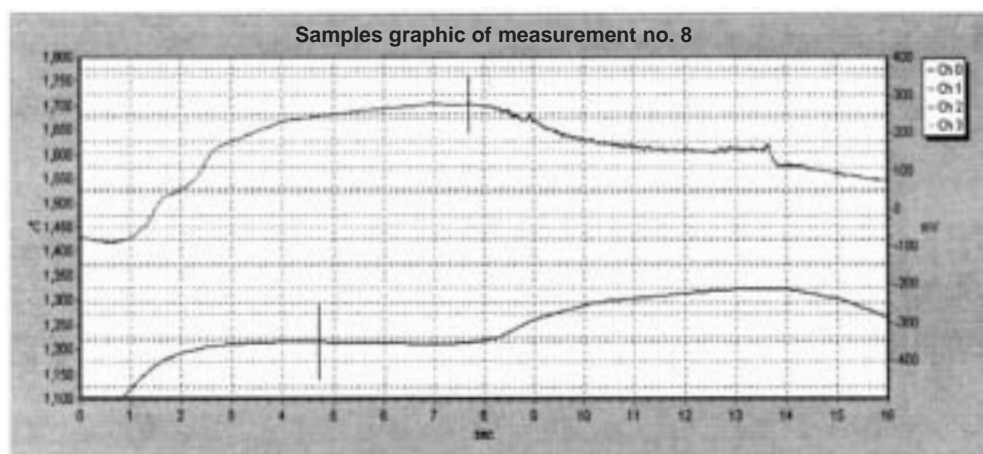


Figure 4. Electromotive force (EMF) signal (related to the oxygen potential) and temperature signal as a function of time during immersion into the Polokwane sulphide smelting furnace

matte, the difference in partial oxygen pressure between the matte and electrode could be lower, which could be a benefit for limiting possible polarization effects that might occur. Unfortunately, the measurements in the furnace had to be discarded because of technical set-up problems.

However, in order to test the application of these probes in the matte phase, the oxygen measurements were done in the furnace launder. Four different measurements were done. The first two measurements were discarded since the immersion technique was still being developed. The results of the last 2 measurements are displayed in Figures 5 and 6. It is evident from Figure 5 that an e.m.f. plateau was obtained (-226 mV). This is an indication that equilibrium was attained in the reference electrode. The temperature curve is not displayed, but was measured to be 1501°C. The calculated partial oxygen pressure, by using Equations [1], [3] and [4], is 4.6×10^{-12} atm. The e.m.f. curve of the last measurement is shown in Figure 6 as a function of time. Based on the corresponding e.m.f. at the plateau (-250 mV) and the measured temperature of 1553°C, a PO_2 value of 1.4×10^{-12} atm is calculated.

It is important to note that the e.m.f. plateaux were not as

stable as they should be. The reason can most probably be ascribed to the fact that the contact between the sensor and the matte was not very stable since the sensor was dipped into the shallow stream of matte in the launder. Accordingly, the accuracy of these measurements is not good (estimated deviation of ± 30 mV, which relates to a deviation of $\pm 2.5 \times 10^{-12}$ atm) in the measured PO_2 . However, these trials showed that, by further optimizing the immersion technique, it should be possible to measure the oxygen potential of the matte produced in a sulphide smelting furnace. In fact, similar successful measurements have been performed in copper flash smelting furnaces 6-8. Furthermore, these results suggest that it might be possible to determine the matte level in the furnace when these probes are used to measure the oxygen potential while the probe is removed from the matte to be in contact with the slag in such a furnace. The temperature of the matte and slag should be higher than 1400°C to ensure that equilibrium is attained between the metal and metal oxide, which serves as reference electrode. This technique has not been further optimized during this project, since another alternative method has also been investigated.

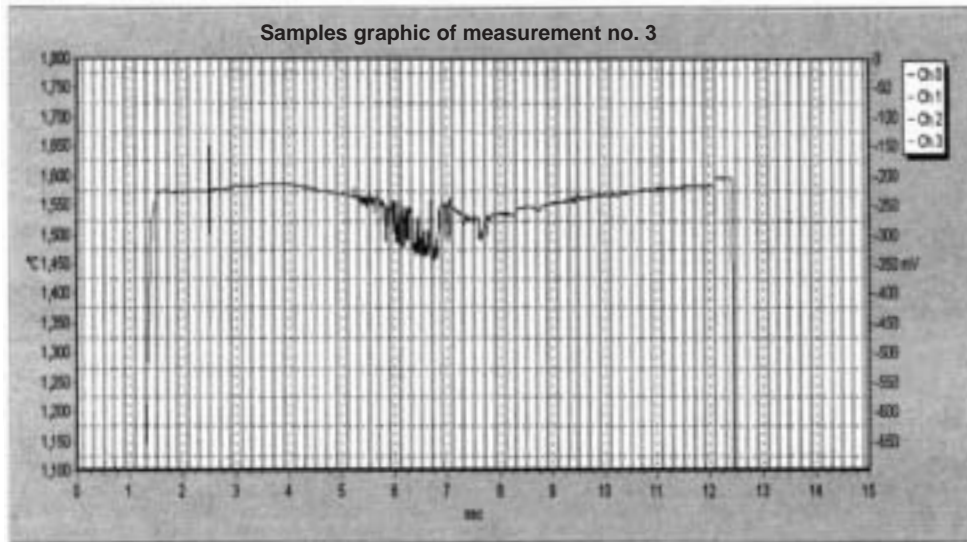


Figure 5. Electromotive force (EMF) signal (related to the oxygen potential) as a function of time during immersion into the furnace launder of the Mortimer smelter (temperature of 1501°C)

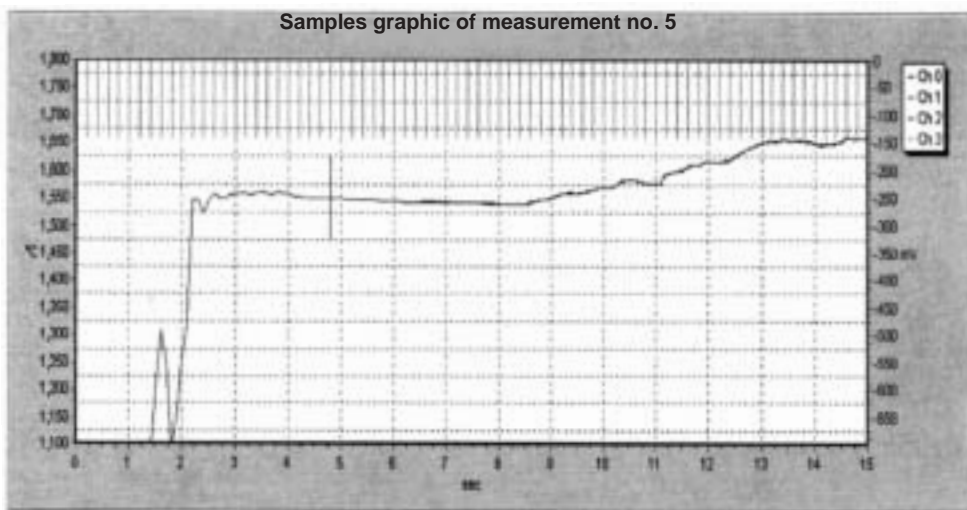


Figure 6. Electromotive force (EMF) signal (related to the oxygen potential) as a function of time during immersion into the furnace launder of the Mortimer smelter (temperature of 1553°C)

Magnetic sensor

It is well known that the electrical conductivity of the matte and slag differs. However, the difference in magnetic susceptibility of matte and slag at high temperatures is not well known. In order to test the idea of possibly utilizing the magnetic characteristics of matte and slag for matte level measurements, samples of slag and matte were obtained from Lonmin. These samples were milled to form a fine powder. The slag and matte powder was brought in contact with a static magnet in order to determine if there is a difference in magnetic susceptibility at room temperature. However, the magnetic domains of a powder may differ from a bulk material. No noticeable visual difference was observed.

Nonetheless, it was decided to do trials in order to determine if there was not a noticeable difference in magnetic susceptibility when these phases are in the liquid state (higher temperatures).

Trial procedure

Lonmin agreed that tests could be done in the ladle directly after tapping matte from a smelting furnace. These ladles contain approximately 7 tons of liquid matte after tapping. A lance containing a magnetic sensor was dipped into the liquid matte to a depth of approximately 300 mm below the matte surface. Two electrical wires were connected the magnetic sensor (contained in a lance) and an electronic black box. As soon as the sensor is in contact with magnetically susceptible material, a signal is generated and is displayed by a light bulb which starts glowing in the electronic black box.

Two measurements were made and it was evident that an electronic signal was generated the moment the sensor was dipped into the matte. Accordingly, it was decided to extend the trials to measurements in the new 60 MVA smelting furnace of Lonmin. The trial in the new furnace was performed by attaching the electronic probe (replacing

the sounding bar) to the sounding cable at the slag side of the furnace. The probe was lowered into the furnace through the slag layer and mushy layer without generating a signal. As soon as the probe came into contact with the matte, a signal was generated (indicated by a light on the control box) and the probe was removed again. Two measurements were taken and in both cases, the level detected was in agreement with the levels measured by a sounding bar directly before the trial. These results could not be recorded electronically and were only visually detected. Furthermore, only two measurements could be taken since the travel speed of the sounding winch motor was too low, which caused the lance containing the magnetic sensor and electrical wires to overheat, damaging the electrical wires.

Based on the results obtained, it was recommended that the travel speed of the winch motor (slag side of the furnace) be increased in order to minimize damage to the electronic probe. Lonmin increased the winch motor speed to 400 mm/s in a downward and upward direction, before the next trial was performed.

Before the electronic measurements were pursued, the following manual sounding measurements were obtained at the slag side of the furnace:

- Matte thickness: 140 mm
- Slag thickness: 1380 mm
- Concentrate thickness: 600 mm.

A protecting cardboard of 1700 mm was slipped onto the bottom end of the lance before each electronic measurement in order to protect the electronic sounding bar from overheating. Furthermore, the electronic sounding bar was marked at the top end with markings 50 mm apart. This assisted in determining, visually, at which level the light bulb started to glow (signal generated when the probe hits the matte). It should be noted that one person (person A) watches the light bulb (to determine at which moment it starts glowing), while the other person (person B) observes the probe travelling at 400 mm/s into the furnace. As soon as the light bulb starts to glow, person A gives a signal to person B to mark the electronic sounding bar relative to a reference point. Accordingly, it is evident that the accuracy of these measurements is influenced by the response time of human beings, which will not be the case if the signal is electronically recorded.

Results and discussion

- *First measurement*—the electronic signal was generated in the vicinity of the matte level, but was not determined accurately because of coordination problems between person A and person B
- *Second measurement*—the electronic signal was generated, indicating a matte level of approximately 150 mm
- *Third measurement*—the electronic signal was generated, indicating a matte level of approximately 110 mm
- *Fourth measurement*—the electronic signal generated indicating a matte level of approximately 140 mm.

The reason for the seemingly varying results, is that the accuracy is determined by the coordination between two people, while the sensor is travelling at 400 mm/s. The important aspect is that no signal was generated while the sensor was travelling through the slag layer, and that the

signal was generated only when it came into contact with the matte.

After the fourth measurement, a portion of the sounding bar (just above the point where the cardboard sleeve stopped) glowed red. This caused the electrical leads (which were not specifically protected for the trial) to overheat. Accordingly, no further measurements were done.

Conclusions

- The application of electrochemical oxygen probes for the measurement of the oxygen potential in the sulphide mattes, seems to be possible. However, it should be ensured that equilibrium between the metal and metal oxide of the reference electrode is attained. Preliminary results indicate that a reference electrode containing (Mo + MoO₂) might be the best choice. This application should be further optimized by performing more trials, before final conclusions are reached
- Initial results obtained during the application of magnetic sensors for the measurement of the matte level in smelting furnaces, indicate that it should be possible to measure the matte level in the matte smelting furnace accurately. These measurements are being extended and will shortly be performed routinely at Lonmin. The system is being upgraded, which will enable the recording of the electronic signal as a function of distance on a computer, which will more accurately reflect the matte level in the furnace
- The magnetic sensor measurements may be the solution to a matte level measurement problem that has existed for a few decades in matte smelting furnaces.

Acknowledgements

The authors would like to extend their appreciation to the respective companies (Hatch, Heraeus-Electronite, Lonmin and Anglo Platinum) for permission to publish this paper. The assistance of Clive Watkins and Alpheus Moshokwa during the trials is also appreciated as well as fruitful discussions with Lloyd Nelson.

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