



# Mineralogical solutions for pyrometallurgical problems

by L. Andrews\* and P. den Hoed\*

## Synopsis

Mineralogy, traditionally associated with concentrator studies, is being increasingly applied to problems in pyrometallurgy. Such investigations commonly make use of a number of techniques, and the results are combined for a meaningful interpretation, which can lead to a successful solution for the problem.

Mineralogical techniques are described for various pyrometallurgical operations. Examples are given of studies and investigations involving mineralogy in chemical-looping combustion, feed monitoring to platinum-smelting furnaces, and losses to slag in base metal and platinum smelting.

## Keywords

mineralogy, phase-chemical, chemical-looping combustion, XRD, SEM, EDS, QEMSCAN, PGM, slag, matte, ilmenite.

## Introduction

Mineralogy can be thought of as an extra dimension in metallurgical planning and investigations, especially when combined with chemical or metallurgical information. Strictly defined as the study of minerals, including their distribution, identification, physical properties, and chemical composition, mineralogy is traditionally associated with the geosciences and concentrator studies, but can equally be applied to problems encountered in metallurgy<sup>1,2</sup>.

The most basic technique used in mineralogy is optical microscopy; in addition, modern phase characterization relies on the measurement of crystal structure and orientation by means of techniques such as X-ray diffractometry (XRD) and electron-backscattered diffractometry (EBSD), and the determination of phase shape, size, modal abundance, and composition with electron-beam techniques such as scanning electron microscopy and electron-probe micro-analysis. A mineralogical assessment will usually rely on a combination of several techniques.

## Mineralogical applications in pyrometallurgy

Mineralogy can be used to characterize solid phases in furnace or roaster feeds and in the products of roasting, smelting, and converting. Some of the processes in which mineralogy can contribute are outlined below, and specific applications are described.

### Roasting

Knowledge of the phase-chemical compositions and structures of roaster feed and products, and their variations over time, allows processes to be designed. The benefit of this knowledge can be seen, for example, when evaluating the performance of the oxygen carrier in chemical-looping combustion (CLC).

### Application: chemical-looping combustion

CLC is a technology being developed in laboratories round the world. It addresses the matter of CO<sub>2</sub> emissions to atmosphere by inherently separating the greenhouse gas during combustion<sup>3</sup>. A pure CO<sub>2</sub> stream can be sequestered. In a CLC process an oxygen carrier—an oxide, either natural or synthesized—is made to circulate between two fluidized-bed reactors, an 'air reactor' and a 'fuel reactor'. Fuel (e.g. natural gas or coal) is introduced to the fuel reactor, where it reduces the oxygen carrier and forms CO<sub>2</sub> and H<sub>2</sub>O.

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(Equation [1] describes the reaction in schematic form). Condensation separates H<sub>2</sub>O from CO<sub>2</sub>. The reduced oxygen carrier is then transferred to the air reactor where, in contact with air diluted by nitrogen, it is re-oxidized (Equation [2])<sup>3</sup>. Temperatures in the two units run at about 950°C. Reaction 1 is often endothermic; reaction 2 is exothermic. Nevertheless, the total heat evolved from both reactions equals that released under normal combustion, where oxygen is in direct contact with the fuel. Thus, without losing energy, but achieving a separation of CO<sub>2</sub> from N<sub>2</sub>, CLC has an emission advantage over normal combustion.

C<sub>n</sub>H<sub>2m</sub> + (2n + m)Me<sub>x</sub>O<sub>y</sub> = (2n + m)Me<sub>x</sub>O<sub>y-1</sub> + nCO<sub>2</sub> + mH<sub>2</sub>O [1]

O<sub>2</sub> + 2Me<sub>x</sub>O<sub>y-1</sub> = 2Me<sub>x</sub>O<sub>y</sub> [2]

The matter that concerns us here, however, is the behaviour of the oxygen carrier. A first requirement is the selection of a good carrier. Carriers are required to exhibit high reactivity, good mechanical strength, and resistance to attrition and agglomeration. The carrier particles should also retain their integrity during many cycles of oxidation and reduction. Candidates have included oxides of iron, manganese, cobalt, nickel, and copper<sup>4,5</sup>. Ilmenite (FeTiO<sub>3</sub>) has become a popular oxygen carrier, because it is abundant and comparatively cheap. It has been tested for a number of years, now, but it has never been fully examined; its effectiveness has been determined by such measures as how much fuel it can convert and how quickly and, in doing so, what its oxygen-carrying capacity is. That is not to say that there have not been reports characterizing the oxygen carrier: phases have been identified, but their distribution in particles has not been examined. In recent years studies have

published images of the internal structures of particles, but these have not been tied to the distribution of phases. Some of the images nevertheless point to the performance of the oxygen carrier over the long term. So, for example, ‘ilmenite’ particles after a number of cycles show an iron-enriched (oxide) rim on the surface of particles and an exfoliation shell<sup>6</sup>. The shell appears somewhat fragile; it is very likely that the mechanical forces in a fluidized bed will, in time, break this shell from the rest of the particle. Each subsequent shell will, in all likelihood, meet the same fate. This possibility warrants investigating.

The changes that iron-titanium oxides undergo during redox cycles in CLC can be evaluated in an informative manner by referring to the chemical thermodynamics of the oxide system. A useful tool in this regard is the equilibrium phase diagram, which is well documented for the Fe-Ti-O system. The phases and their relations described by the diagram can be compared with those observed in samples of actual oxygen carriers at different stages in the process. Using XRD, and by examining (polished) sections of particles under the electron microscope and measuring phase compositions with energy-dispersive X-ray spectroscopy (EDS), one can determine phase-chemical compositions in the samples and compare them with those described in the appropriate phase diagrams. A first step in this direction has been made with the application of phase relations in the system Fe-Ti-O to the performance of ‘ilmenite’ in CLC<sup>7</sup>. The chemical thermodynamics predict that FeTiO<sub>3</sub> oxidizes to Fe<sub>2</sub>TiO<sub>5</sub> (pseudobrookite) and TiO<sub>2</sub> (rutile), a condition reflected by a move on the oxygen reaction line XY towards Y (see Figure 1). Subsequent reduction returns the oxide either to FeTiO<sub>3</sub> (ilmenite) if the system is held at equilibrium or to Fe<sub>2</sub>TiO<sub>4</sub> (ulvöspinel) if conditions prevent TiO<sub>2</sub> (rutile) from taking part in the reduction. Which of the oxides actually

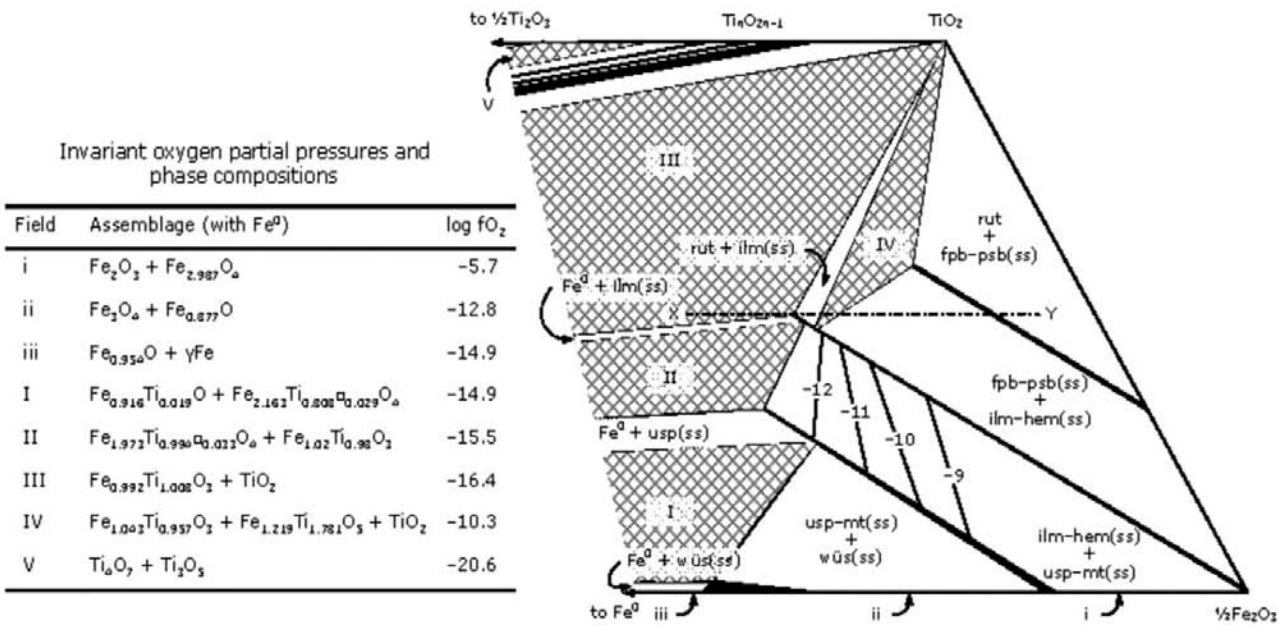


Figure 1—Phase relations in the system Fe-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-Ti<sub>2</sub>O<sub>3</sub> at 1000°C<sup>8</sup>

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forms, how much of it forms, and how it is distributed has yet to be confirmed. Once we know this, a comparison of predicted and observed outcomes will allow us to evaluate an aspect of the performance of the oxygen carrier: how close to the limit (where metallic iron is formed—an undesirable outcome) the oxygen carrier can be pushed in the fuel reactor, and therefore the extent to which the oxygen transport capacity of the carrier is diminished (if at all).

The oxygen transport capacity is defined as

$$R_o = \frac{m_{ox} - m_{red}}{m_{ox}} \quad [3]$$

where  $m_{ox}$  is the mass of a carrier in its oxidized state and  $m_{red}$  is its mass in the reduced state. The higher the oxygen transport capacity, the less the oxygen carrier required for the job. The oxygen transport capacity of  $\text{FeTiO}_3$  (ilmenite) is 5.0%, which compares with 21.4% for Ni-NiO and 20.1% for Cu-CuO. If  $\text{TiO}_2$  (rutile), once formed, remains inert in subsequent cycles, then one can improve the oxygen transport capacity for iron-titanium oxides only slightly by synthesizing either  $\text{Fe}_2\text{TiO}_5$  (pseudobrookite) or  $\text{Fe}_2\text{TiO}_4$  (ulvöspinel).  $R_o$  rises to 6.7%, which remains a comparatively low value. Any diminished capacity, by not reducing or oxidizing the carrier to its full extent, only makes matters worse. Confirmation of the phases formed, their individual compositions, and distributions throughout the carrier particles will help identify the nature of any diminished capacity. It will provide an important piece in the puzzle and do much to establish the full potential of ilmenite as an oxygen carrier in chemical-looping combustion.

### Smelting/converting

#### Feed

Several types of furnace feed (ore concentrates or flash-dryer products) may possess very similar chemical compositions, but display completely different melting characteristics. Accurate knowledge of the mineral content allows prediction of the energy requirements, the melting temperature, and the matte fall.

#### Application (furnace feed)

Concentrates (smelter feeds) produced from the Bushveld Complex in North West and Limpopo provinces by Anglo Platinum Ltd are routinely monitored by means of mineralogical and chemical analysis. Merensky Reef, UG-2, and Platreef final concentrates are sampled at the concentrators; flash-dryer feeds are sampled at the smelters<sup>9</sup>. Automated mineralogy techniques (QEMSCAN® or MLA) determine the mineralogy of the concentrates, specifically the modal percentage and type of gangue minerals and base metal sulfides (Figure 2). Mineralogical and compositional results may be combined to predict the smelting characteristics of the feed—parameters such as the matte fall, slag viscosity, and smelting energy requirements can be calculated

by modelling. The information is databased so that trends can be identified. Feed concentrates can be blended to reduce potential problems, such as spinel formation in the furnace, variable sulfur levels, and the need for flux addition. These are dealt with in more detail below.

Many problems encountered in the furnaces are feed-related. High levels of chromium in feed lead to chromium saturation of the slag (at  $\text{Cr}_2\text{O}_3$  levels around 2% during normal furnace operation)<sup>10</sup>. This leads to crystallization of slag spinel ( $[\text{Cr,Fe,Mg}]_3\text{O}_4$ ), which has a relatively high melting point. The spinel can form a layer between the slag and matte, one that hinders matte droplets in the slag from settling into the matte bath. Figure 3 shows the microtexture



Figure 2—One of the QEMSCAN® instruments at Anglo American Research

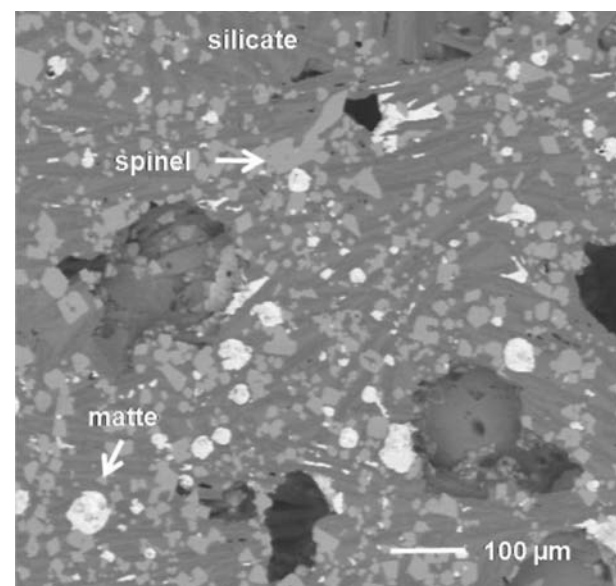


Figure 3—Backscattered-electron image showing 'intermediate layer' material from a sounding-bar sample. The proliferation of slag spinel crystals has impeded matte settling



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of a sounding-bar (dip) sample taken from a six-in-line furnace when spinel had formed just above the slag–matte interface. The semi-solid layer is more viscous than normal slag, and this causes problems for tapping and level control. Spoon samples from the slag taphole can also confirm the high spinel levels, but are not so easy to relate to depth in the furnace.

In sulfide smelting, a certain amount of sulfur in furnace feed facilitates matte fall and collection of value metals. Sulfide minerals in furnace feed melt to provide sulfur, but the amount of sulfur produced and the temperature at which it is released depend on the sulfide mineralogy of the feed. In a melting furnace, pyrite ( $\text{FeS}_2$ ) decomposes below the smelting temperature to produce FeS with a release of sulfur vapour (Figure 4). In a similar manner, chalcopyrite ( $\text{CuFeS}_2$ ) decomposes to produce FeS,  $\text{Cu}_5\text{FeS}_4$  (bornite), and sulfur vapour (Figure 5).  $\text{Cu}_5\text{FeS}_4$  can thermally decompose further to FeS and  $\text{Cu}_2\text{S}$ , releasing additional sulfur vapour. These reactions can occur while the feed is situated over the slag bath as a ‘black top’, and can result in sulfur loss and sulfidation corrosion of various furnace structures.

The problems outlined above may be controlled to some extent by blending the final concentrates to balance the feed characteristics. Samples of flash-dryer feed (blended furnace feed) are taken from the belt and composited. Dried samples are later sent for chemical and QEMSCAN® analysis, and these results are reported to the smelters and included in the database.

### *Furnace/converter products—matte*

Problems in processing or refining of furnace or converter mattes may be prevented by defining the mineralogy and composition of the matte after it has been cast or quenched. Studies of platinum converter mattes, for example, reveal that the mineralogy of constituent phases has a direct bearing on the choice of downstream recovery process, and is affected by even small changes in upstream (feed) metallurgy<sup>11,12</sup>. The phases which form in slow-cooled and quenched mattes are related not only to the cooling rate, but also to the major-element composition of the melt. If the matte is to be slow cooled and then concentrated by magnetic separation, the size, shape, and magnetic susceptibility of the PGE-bearing alloy phases has to be optimized, and this is done by controlling iron and sulfur levels for a given nickel-to-copper ratio.

### *Furnace/converter products—slag*

It is essential we understand the type of losses to a furnace or converter slag if the slag is to be treated further or cleaned successfully. In base metal and platinum smelting, values can be trapped in slag as mechanically entrained matte or metal, or chemically bound in oxides or silicates. The size and relative amounts of the phases involved can be inferred from the mineralogy, and the most suitable cleaning process can be used. Take, for example, relatively large particles of matte

or metal entrained in the slag and low solubilities of base metals in these slag silicates. The entrained particles bearing the base metals can be recovered by milling and flotation. Fine matte- or metal-size distributions and high base-metal solubilities in silicates, on the other hand, would require pyrometallurgical slag cleaning in a slag-cleaning furnace. The use of reductant and suitable settling times would aid recovery.

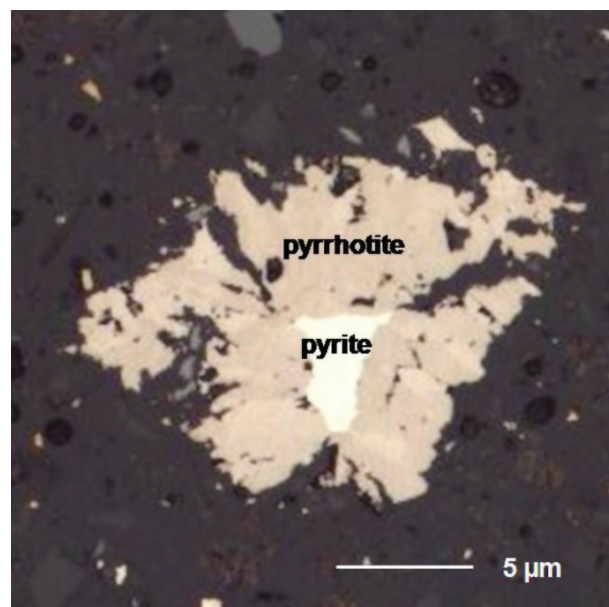


Figure 4—A photomicrograph illustrating the decomposition of a pyrite particle in furnace feed to form pyrrhotite (or troilite – FeS) with low temperature emission of sulfur

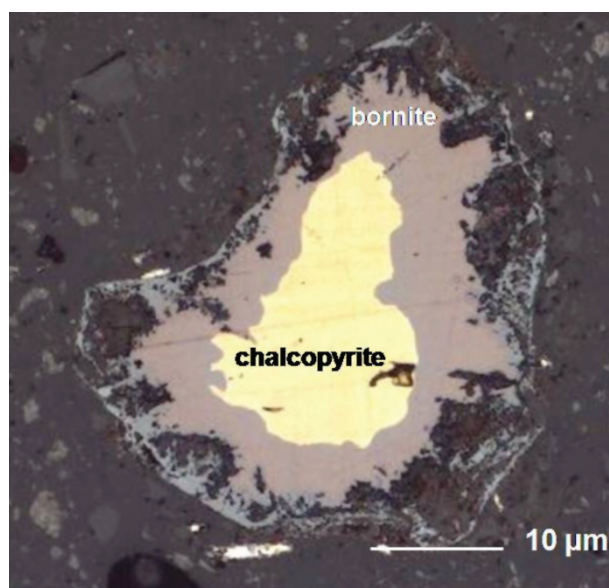


Figure 5—The partial decomposition of a chalcopyrite particle in furnace feed. Bornite forms with low temperature emission of sulfur

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### Application—slag losses

Losses of PGEs and base metals (nickel, copper, and cobalt) to slags from the six-in-line and slag-cleaning furnaces of Anglo Platinum Ltd are monitored regularly at Anglo American Research. The smelting parameters that affect and control base-metal losses are numerous<sup>13</sup>; they include slag composition, basicity ratio, smelting temperature, and oxygen potential. The factor found to be the most important in determining base-metal dissolution into furnace slag at Anglo Platinum Ltd is the degree of oxidation, or slag  $pO_2$ . Prior to 2001, converter slag was returned regularly to the six-in-line furnaces. This raised the furnace-slag  $pO_2$  and gave rise to higher base-metal dissolution in, and therefore losses to, the slag. A study of slag samples taken five years apart combined techniques, such as chemical analysis (for bulk slag composition), electron-probe microanalysis (to measure small amounts of dissolved, or chemically-bound, base metals in slag), scanning electron microscopy (to examine mechanically entrained matte droplets in slag), and Mössbauer Spectroscopy (to measure slag  $Fe^{3+}/Fe^{2+}$  and hence calculate  $pO_2$ )<sup>14,15</sup>. Images of quenched furnace slag and the instrument currently used for the microanalysis of dissolved base metals are shown in Figures 6 and 7. Base metals are concentrated in the entrained matte sulfides. The amounts of these metals dissolved in slag silicate glass are much lower (Table I), but the high ratio of silicate to entrained matte, combined with the small size of entrained matte inclusions, leads to more base metals being lost in discarded silicate than are recovered by sulfide flotation (Table II).

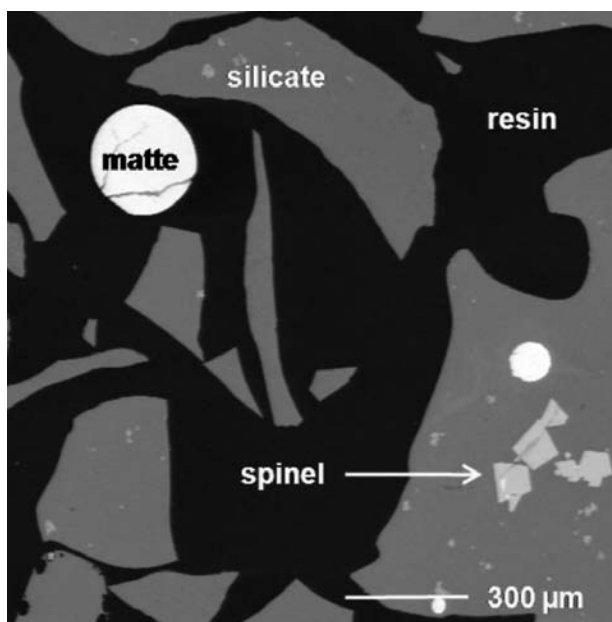


Figure 6—A backscattered-electron image showing granulated furnace slag in section. Matte may be present as a free phase or enclosed in the silicate glass. Slag spinel crystals may also be enclosed, especially in higher-chromium slags

As well as demonstrating the higher dissolved base-metal losses introduced by converter slag return, the investigation showed that tapped slag is not in equilibrium with bulk

Table I

Levels of nickel and copper in slag for the six-in-line furnaces

Source†	Nickel (%)	Copper (%)
Early data		
Dissolved in slag silicate	0.123	0.073
Bulk slag‡	0.170	0.080
Later data		
Dissolved in slag silicate	0.075	0.055
Bulk slag‡	0.138	0.071

†Early data was acquired from samples taken during converter slag return to the furnaces; the later data, from samples taken when this practice had been discontinued

‡Bulk slag results were determined by 'chemistry' (base-metal fusion and ICP-MS). Dissolved base-metal results are averaged from 160 electron-probe microanalyses on samples taken over a month

Table II

Proportion of base-metal loss to slag (loss by dissolution rather than matte entrainment)

Sample†	Nickel (%)	Copper (%)
Early	71	76
Later	56	78

†The early samples were taken during converter-slag return; the later, when no slag was being returned



Figure 7—The Cameca SX-100 electron microprobe at the University of Johannesburg. This instrument is being used to determine small amounts of dissolved base metals in slag samples from the six-in-line furnaces and the slag-cleaning furnace

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matte. One aspect of this is that modelling software underestimates base-metal losses to slag, because equilibrium is usually assumed. It is likely that the same applies to base-metal smelting.

### Other applications

Mineralogy is helpful in many other areas of pyrometallurgy, such as flux or furnace additive and off-gas solids characterization, and refractory failure and compatibility investigations.

### Conclusions

Mineralogy and the techniques in mineral phase analysis are being applied in a wide variety of pyrometallurgical investigations, where they assist in process design, problem-solving, and model validation. The paper considers four examples:

- The performance of  $\text{FeTiO}_3$  (ilmenite) as an oxygen carrier in chemical-looping combustion. The phase chemistry of the Fe-Ti-O system shows that  $\text{FeTi}_2\text{O}_5$  (pseudobrookite) and  $\text{TiO}_2$  (rutile) are formed during oxidation; that subsequent reduction forms either  $\text{FeTiO}_3$  (ilmenite) or  $\text{Fe}_2\text{TiO}_4$  (ulvöspinel), depending on whether the  $\text{TiO}_2$  (rutile) formed takes part in further reaction or not. Identifying phases, their compositions, and morphologies by means of XRD, SEM, and EDS will confirm which course the redox reactions follow, and in turn answer questions about the performance and potential of ilmenite as an oxygen carrier
- Problems related to the phase-chemical composition of furnace feed to the smelters at Anglo Platinum Ltd can be alleviated by blending according to concentrate composition and mineralogy
- Difficulties encountered in the processing of furnace and converter mattes may be avoided by careful control of matte composition and monitoring of the product mineralogy
- The losses of PGEs and base metals to furnace slag at Anglo Platinum Ltd have been characterized, and it has been established that current modelling practises must be validated by mineralogical analysis.

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