

## Thermochemical Modelling of the Isasmelt Process

James S. Edwards  
Mount Isa Mines Limited  
Mount Isa, Qld 4825, Australia  
Telephone (077) 442011

### ABSTRACT

A thermochemical model of the Isasmelt process as applied to copper smelting has been developed. The model uses a commercial free energy minimisation method and thermodynamic databases. The slag is assumed to be a regular solution; The matte solution model is based on published activity coefficient correlations.

For a 60% Cu matte the calculated Fe and S in matte were 16% and 23% respectively. Plant control samples contained 15.7% Fe and 23.5% S. The dissolved oxidic copper in slag was calculated as 0.14%; The total dissolved copper in slag (oxidic and sulfidic) was measured as 0.3%.

The composition of melts produced in the Isasmelt process are closely approximated by an equilibrium model. Differences arise with several reaction zones present in the furnace, and the difficulty of matching published solution models with plant conditions.

### 1. INTRODUCTION

The Isasmelt process is a bath smelting process utilising a top entry, submerged, lance. The process is a joint development of the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO) and Mount Isa Mines Limited (MIM).

Pelletized concentrate, flux and coal are continuously fed into the Isasmelt furnace through a port in the furnace roof. Matte and slag are tapped from the furnace through a single taphole into a settling furnace.

A thermochemical model of the Isasmelt process is an essential tool for the plant metallurgist at Mount Isa. The feed to the plant is of variable composition; It consists of chalcopyrite concentrate produced at Mount Isa, slag concentrate produced by flotation of converter slag, and other purchased concentrates with a range of mineralogies. The thermochemical model is used to predict the air, flux and fuel required to treat a concentrate blend.

A thermochemical model is also essential to determine the process conditions when comparing processing options.

Since 1992 a model of the Isasmelt process has been under development which uses a spreadsheet as the front end for the CHEMIX module of the CSIRO Thermochemistry System<sup>1</sup> and the following solution models:

- The activity coefficient correlations of Shimpo et al<sup>2</sup> for the matte phase, and
- The Regular Solution Model (RSM)<sup>3</sup> for the slag phase.

Thermodynamic data for all species, except  $\text{Al}_2\text{O}_3$ , is taken from the CSIRO Thermochemistry System. Thermodynamic data for  $\text{Al}_2\text{O}_3$  is taken from Barin, Knacke and Kubaschewski<sup>4</sup>.

The CHEMIX model has been verified against plant control samples and campaign heat and mass balances<sup>5</sup>. A good fit is obtained between the model and plant above a 55% Cu matte grade. Shortcomings of the model include:

- FeS as the iron sulfide species in the matte rather than  $\text{FeS}_{1.09}$ .
- All condensed species in the liquid standard state, i.e. thermodynamic data for some species has been extrapolated over several hundred degrees.
- Oxidised  $\text{Fe}^{3+}$  /oxidised  $\text{Fe}^{2+}$  \* in matte as calculated using the model is greater than 1.5 compared to a usual value of 1<sup>6</sup>.
- Product phases are at equilibrium, whereas it appears there are 3 reaction zones which are not in equilibrium with each other:
  1. Lance gas/melt reaction zone.
  2. Melt/coal reaction zone.
  3. Coal/Offgas reaction zone.

### 2. THERMOCHEMICAL MODEL

The thermochemical model consists of:

- A spreadsheet containing:
  - User input
  - CHEMIX input file,
  - Regular Solution Model,
  - CHEMIX output file, and
  - Macro controlling CHEMIX execution.
- The CSIRO Thermochemistry System.

The product phases and species in the system are specified as:

- Gas;  $\text{O}_2(\text{g})$ ,  $\text{N}_2(\text{g})$ ,  $\text{CO}(\text{g})$ ,  $\text{CO}_2(\text{g})$ ,  $\text{H}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$ ,  $\text{SO}_2(\text{g})$
- Matte;  $\text{Cu}(\text{l})$ ,  $\text{Cu}_2\text{S}(\text{l})$ ,  $\text{FeS}(\text{l})$ ,  $\text{FeO}(\text{l})$ ,  $\text{Fe}_3\text{O}_4(\text{l})$
- Slag;  $\text{SiO}_2(\text{l})$ ,  $\text{FeO}(\text{l})$ ,  $\text{Fe}_3\text{O}_4(\text{l})$ ,  $\text{Cu}_2\text{O}(\text{l})$ ,  $\text{Al}_2\text{O}_3(\text{l})$ ,  $\text{MgO}(\text{l})$ ,  $\text{CaO}(\text{l})$

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\* Oxidised  $\text{Fe}^{3+}$  /oxidised  $\text{Fe}^{2+}$  in matte is the ratio of iron in matte as  $\text{Fe}_2\text{O}_3$  to iron in matte as  $\text{FeO}$ .

The thermodynamic data for species in the liquid standard state, at the system temperature of 1473K, is obtained by extending heat capacity data for the liquid phase to 298K. The exceptions to this are Cu and Cu<sub>2</sub>S.

As a consequence of the above:

- A heat of fusion at the system temperature of 1473K is included in the heat balance for all condensed species, and
- The free energy of each condensed species at 1473K is extrapolated from the liquid standard state.

The free energy and free enthalpy of magnetite calculated using the standard data set is compared with that calculated using the extrapolated data set in Fig. 1 and Fig. 2. The results for the two data sets agree above the melting point of magnetite. If the heat capacity data for the liquid phase is only extrapolated to 1473K the free energy for the liquid phase does not agree with that calculated from the standard data set, Fig. 3.

It is not standard practice to use the liquid standard state for all condensed species. However, if a heat of fusion is not included for all condensed species the a priori heat balance does not match the measured heat balance. If Cu, Cu<sub>2</sub>S, Cu<sub>2</sub>O, FeS and FeO are the only species in the liquid standard state, as is standard practice, the excess enthalpy (calculated heat loss - measured heat loss<sup>3</sup>) from the a priori heat balance increases from 4.0% of the system enthalpy to 11.2%, equivalent to a temperature increase of 50°C.

Fe<sub>3</sub>O<sub>4</sub> is used as the ferric ion species instead of Fe<sub>2</sub>O<sub>3</sub> because thermodynamic data is available for Fe<sub>3</sub>O<sub>4</sub> as a liquid phase, but not for Fe<sub>2</sub>O<sub>3</sub>.

### 2.1 Matte solution model

Activity coefficients of the matte species are calculated using the correlations of Shimpo et al, which have been incorporated into the spreadsheet. The activity coefficients are then passed to the CHEMIX input file as fixed values.

The thermodynamic data listed by Shimpo et al does not include a heat capacity correlation for Fe<sub>3</sub>O<sub>4</sub> as a liquid. However, when matte is modelled with Fe<sub>3</sub>O<sub>4</sub> as a solid species the calculated Fe<sub>3</sub>O<sub>4</sub> in matte is 22% for a 53 % Cu matte grade. A solution to the free energy minimisation cannot be obtained at higher matte grades.

When thermodynamic data for Fe<sub>3</sub>O<sub>4</sub> as a liquid is used the calculated Fe<sub>3</sub>O<sub>4</sub> in matte for a 60% Cu matte is 2.6% compared to a measured Fe<sub>3</sub>O<sub>4</sub> in matte of 2.2%. Therefore the matte is modelled with Fe<sub>3</sub>O<sub>4</sub> as a liquid, without applying a conversion to the activity coefficient of Shimpo et al.

The activity correlations for FeO and Fe<sub>3</sub>O<sub>4</sub> are based on the work of Korakas<sup>6</sup> who blew air into matte, whereas the lance gas in the Isasmelt process varies between 21 and 55% oxygen.

### 2.2 Slag solution model

Activity coefficients of the slag species, and the heat of mixing, are calculated using the RSM which is incorporated into the spreadsheet. The activity coefficients are then passed to the CHEMIX input file as fixed values, and the heat of mixing is added to the system heat loss.

After each CHEMIX run the CHEMIX output file is imported into the spreadsheet and the slag composition in the CHEMIX output file is compared with the slag composition in the input file. If the slag composition has changed CHEMIX is rerun.

With each iteration of the [spreadsheet-CHEMIX] loop the activity coefficients and heat of mixing are recalculated using the most recent calculated slag composition. Iteration continues until the composition of the product phases is constant.

Concentrate assays typically add to 95 to 97%. In the CHEMIX model the remaining 3 to 5% of the concentrate is assumed to be a diluent having the same properties as MgO. In this manner an estimate of the heat load placed on the furnace by the diluent is included in the heat balance.

Calculation of activity coefficients is done on the basis that only assayed species report to the slag. The diluent is treated as a separate phase. The diluent is included in the slag composition in the spreadsheet at the completion of the CHEMIX run.

## 3. COMPARISON WITH PLANT DATA

### 3.1 Plant control samples

Matte and slag samples are taken in the plant for control purposes. The samples are collected in a mild steel spoon, 165mm in diameter and 65mm deep, from melt flowing in a launder. Each sample is split into matte and slag fractions and the fractions submitted to the on site chemical laboratory for analysis.

In Fig. 4 a comparison is made between Fe<sub>3</sub>O<sub>4</sub> in slag that has been quenched in water and then annealed<sup>7</sup>, Fe<sub>3</sub>O<sub>4</sub> in slag quenched in water, and Fe<sub>3</sub>O<sub>4</sub> in spoon samples. As the Fe<sub>3</sub>O<sub>4</sub> content of the annealed slag spans the same range as the Fe<sub>3</sub>O<sub>4</sub> content of the spoon samples of slag, all Fe<sup>3+</sup> in spoon samples is assumed to have precipitated as Fe<sub>3</sub>O<sub>4</sub>.

Fe<sub>3</sub>O<sub>4</sub> is measured in both matte and slag using a magnetic susceptibility meter. It is assumed that all magnetism measured is due to Fe<sub>3</sub>O<sub>4</sub>.

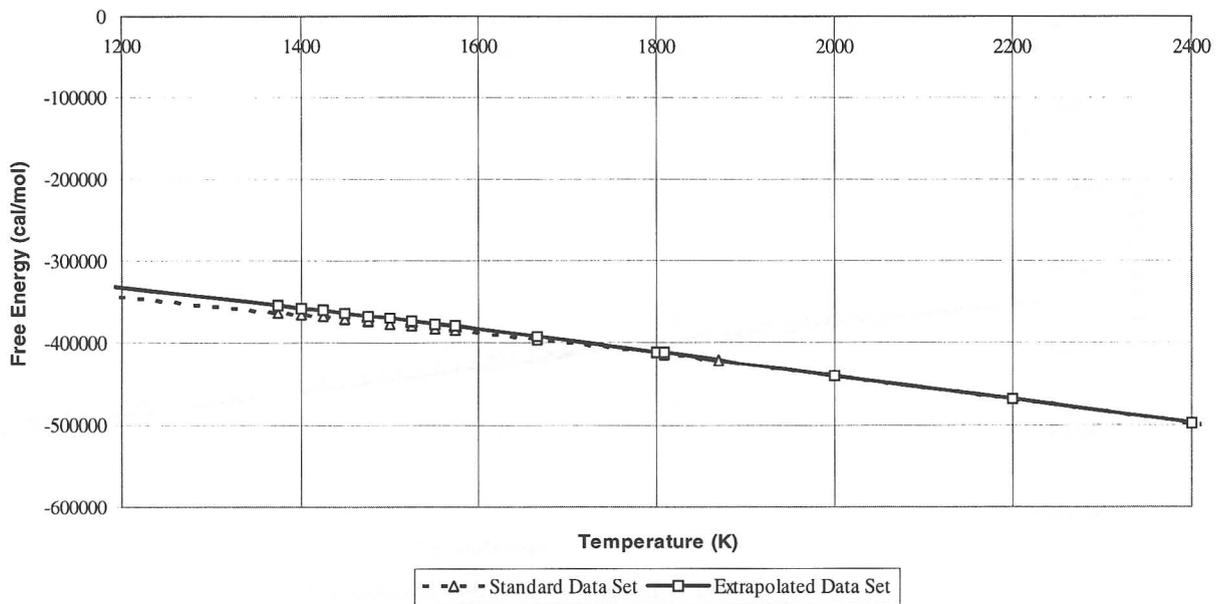


Fig. 1. Comparison between the free energy of Fe<sub>3</sub>O<sub>4</sub> calculated from: (1) The CSIRO Thermochemistry System Data Set, and (2) The Extrapolated Data Set.

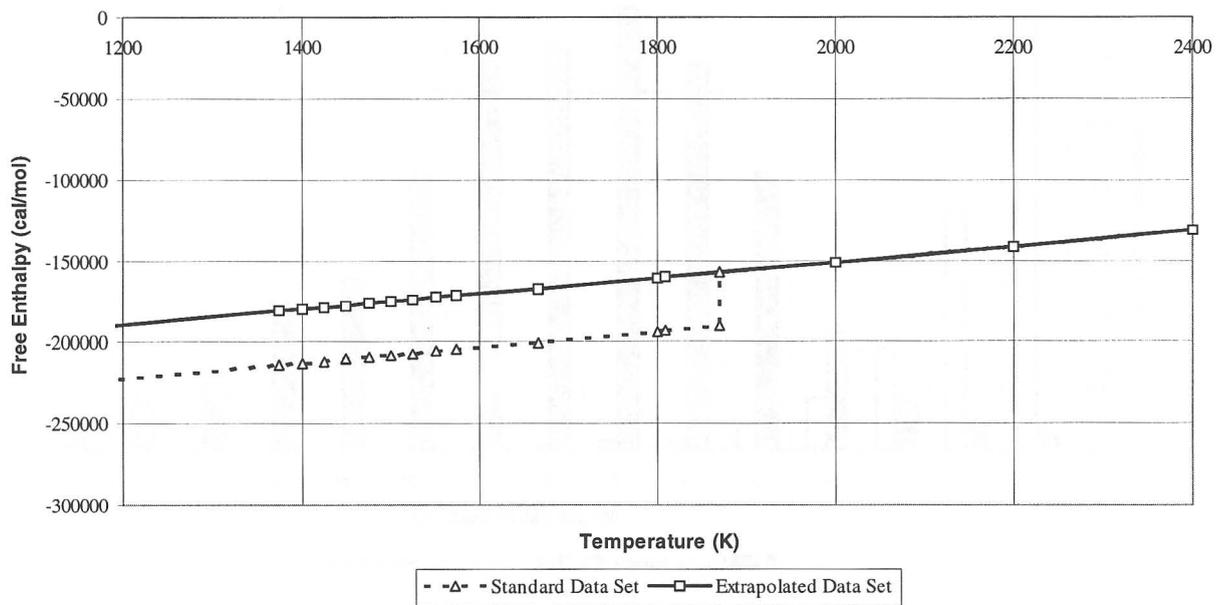


Fig. 2. Comparison between the free enthalpy of Fe<sub>3</sub>O<sub>4</sub> calculated from: (1) The CSIRO Thermochemistry System Data Set, and (2) The Extrapolated Data Set.

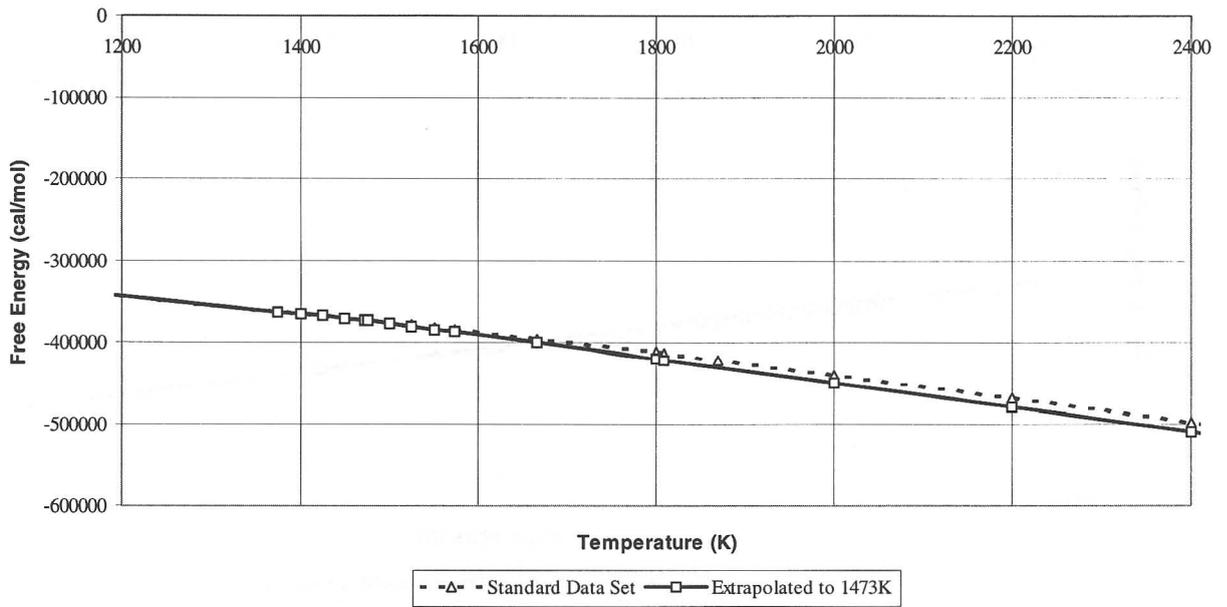


Fig. 3. Comparison between the free energy of  $\text{Fe}_3\text{O}_4$  calculated from: (1) The CSIRO Thermochemistry System Data Set, and (2) A data set where data for the liquid phase was extrapolated to 1473K.

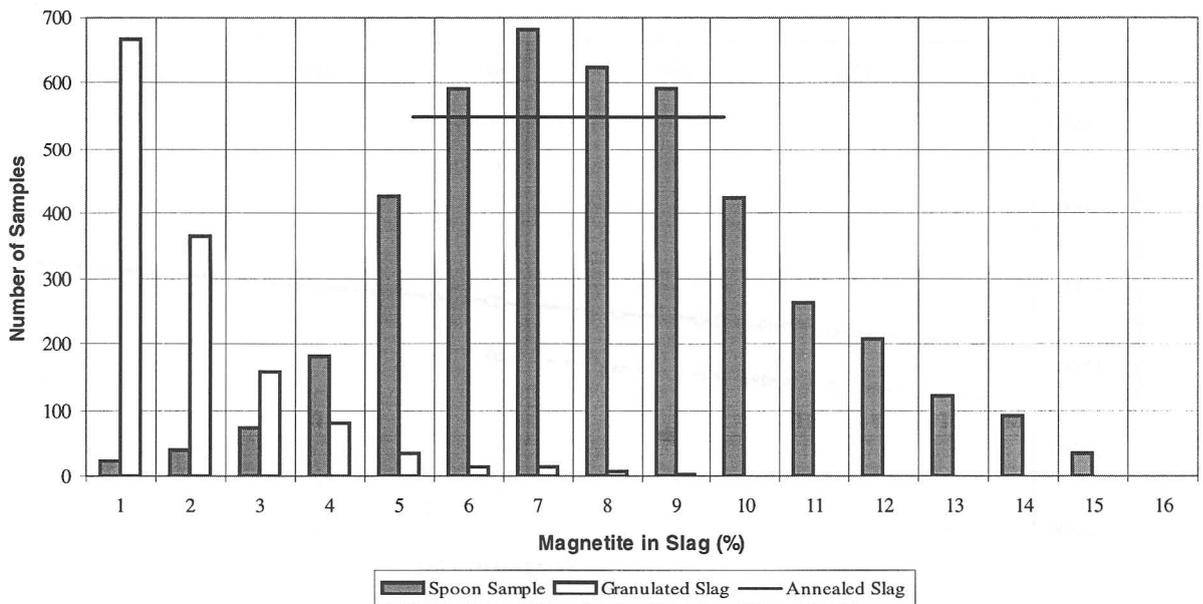


Fig. 4. Comparison between the magnetite content of annealed slag, quenched slag and spoon sample slag.

X-ray fluorescence is used to measure Cu, Fe, S and Si in matte, and Fe, Si, Al, Mg and Ca in slag.

### 3.2 Matte solution model

The matte composition calculated using the CHEMIX model is compared with plant control samples in Fig. 5, Fig. 6 and Fig. 7. The plant analyses represent furnace operation over a range of conditions:

- Oxygen content of the lance air ranged between 21% and 55%.
- Furnace temperature varied over a 50°C range.
- SiO<sub>2</sub>/Fe in the slag varied between 0.8 and 1.0.

Plant matte analyses have been modified in the following manner:

- Sulfur content of the matte has been reduced by an amount equal to the sulfur associated with lead as PbS and zinc as ZnS; Typical lead and zinc levels in matte are 0.15% and 0.1% respectively.
- The oxygen content of matte is calculated assuming all ferric ions precipitate as Fe<sub>3</sub>O<sub>4</sub> and oxidised Fe<sup>3+</sup>/oxidised Fe<sup>2+</sup> = 1<sup>6</sup>.
- The copper, iron, sulfur and oxygen have been ratioed so %Cu + %Fe + %S + %O = 100%.

The correlations describing the matte composition are:

$$\%[\text{Fe}] = 63.89 - 0.8036 \times \%[\text{Cu}] \quad (1)$$

$$\%[\text{S}] = 30.65 - 0.1190 \times \%[\text{Cu}] \quad (2)$$

$$\%[\text{O}] = 5.46 - 0.0774 \times \%[\text{Cu}] \quad (3)$$

When percent copper in matte equals zero, and assuming oxidised Fe<sup>3+</sup>/oxidised Fe<sup>2+</sup> = 1, then the FeS<sub>x</sub> species is FeS<sub>1.09</sub>. Up to a matte grade of 70.5% the Cu<sub>y</sub>S species is, then, Cu<sub>2.00</sub>S. The formulae FeS<sub>1.09</sub> is in agreement with the composition of the maximum melting point for the FeS liquidus<sup>8</sup>, and indicates there is no sulfur deficiency.

A close fit is obtained between calculated and measured iron in matte, Fig. 5. The difference between the calculated and measured Fe content of matte decreases with increasing matte grade.

Calculated sulfur in matte deviates from the measured sulfur in matte at the lower matte grades. For a 45% Cu matte the calculated sulfur content of the matte is 22.9%, 2.4% lower than the sulfur content of plant matte.

Matte has been shown to contain the non-stoichiometric species FeS<sub>1.09</sub>, whereas the matte solution

model contains the stoichiometric species FeS. At a 45% Cu matte grade the difference in sulfur in matte due to the use of FeS in the model, rather than FeS<sub>1.09</sub>, is 1.4%.

The low calculated sulfur in matte for a 45% Cu matte occurs with high calculated oxygen levels. Oxygen levels in the plant matte samples are calculated assuming oxidised Fe<sup>3+</sup>/oxidised Fe<sup>2+</sup> = 1, whereas the calculated ratio from the model is greater than 1, and increases as matte grade decreases, Fig. 8.

For matte grades greater than 55% Cu, good agreement is obtained between the model and the plant matte compositions.

There are several problems with the matte solution model:

- Selection of matte species.
- Selection of standard state.
- Oxidised Fe<sup>3+</sup>/oxidised Fe<sup>2+</sup> ratio.

### 3.3 Slag solution model

Plant measurements of slag p<sub>O2</sub> have been taken using a Leeds and Northrup Temp-O-Tip with a stabilised zirconia electrolyte and Ni/NiO reference<sup>9</sup>.

Over a 3 day period at a matte grade of 50% Cu, the average measured p<sub>O2</sub> was 0.99×10<sup>-9</sup> with a standard deviation of 0.48×10<sup>-9</sup>, Fig. 9. The calculated p<sub>O2</sub> using the CHEMIX model is 1.95×10<sup>-9</sup>. As this is within two standard deviations of the average measured p<sub>O2</sub>, the calculated p<sub>O2</sub> appears to match the measured p<sub>O2</sub>.

However, the calculated Fe<sub>3</sub>O<sub>4</sub> in slag at a 50% Cu matte grade is 9.5% compared to the measured Fe<sub>3</sub>O<sub>4</sub> in slag of 3.3%. This indicates the slag is reduced, and the difference between calculated and measured p<sub>O2</sub> may be significant.

The difference in calculated and measured Fe<sub>3</sub>O<sub>4</sub> in slag is attributed to the presence of coal in the furnace forming melt/coal and coal/offgas reaction zones which are not in equilibrium with each other, or with the lance gas/melt reaction zone.

Within the gas cavity at the lance tip O<sub>2</sub> from the lance gas reacts with FeO in the slag to form Fe<sub>3</sub>O<sub>4</sub>, which in turn reacts with FeS in the feed dropped into the melt to produce FeO and SO<sub>2</sub>. As the melt circulates coal floating on the surface of the melt reduces Fe<sub>3</sub>O<sub>4</sub>, shifting the p<sub>O2</sub> of the melt lower.

The interaction between coal and melt forms one reaction zone, the interaction between coal and offgas forms another. In Fig. 10 the difference between calculated heat loss and measured heat loss for four plant sampling campaigns are plotted against coal rate<sup>5</sup>. With increasing coal rate the excess enthalpy increases due to

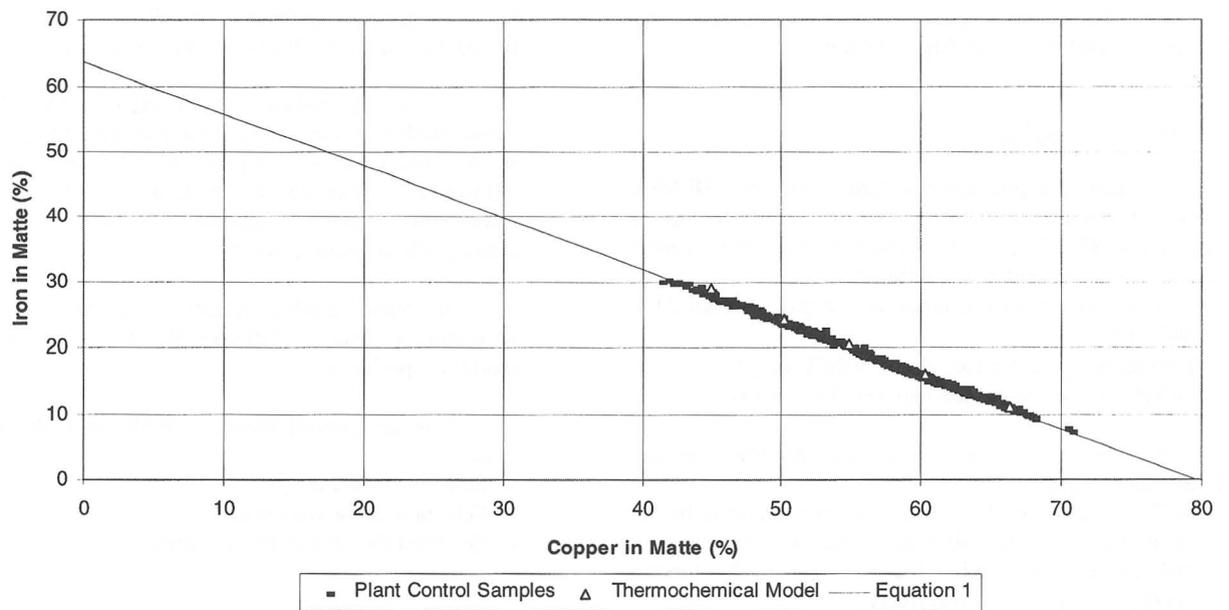


Fig. 5. Relationship between the copper and iron content of matte.

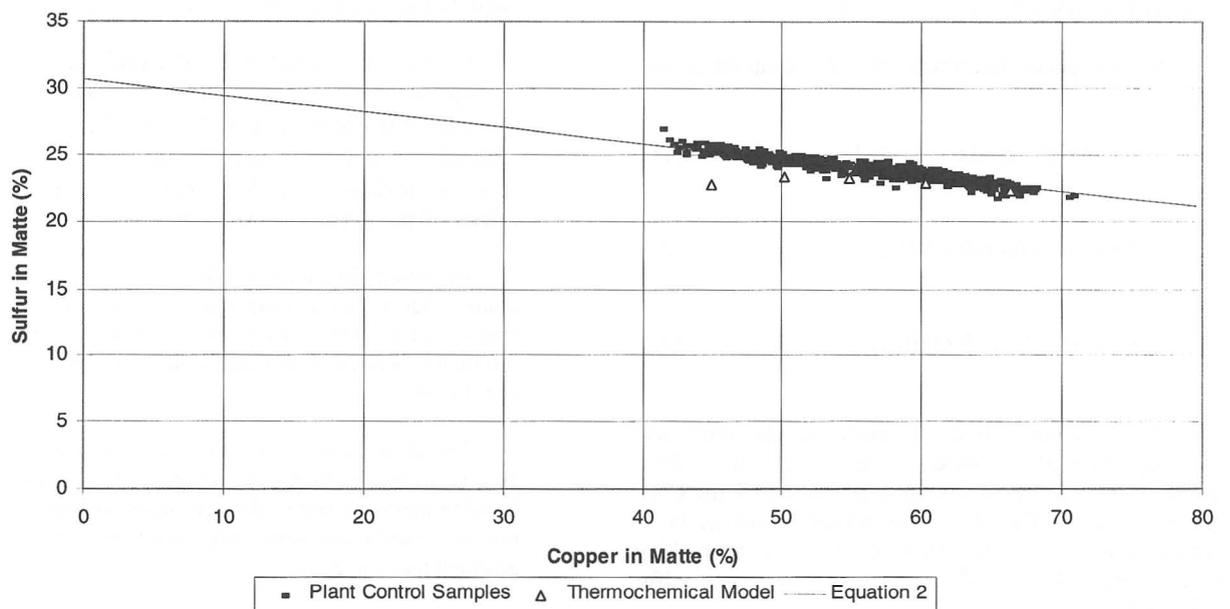


Fig. 6. Relationship between the copper and sulfur content of matte.

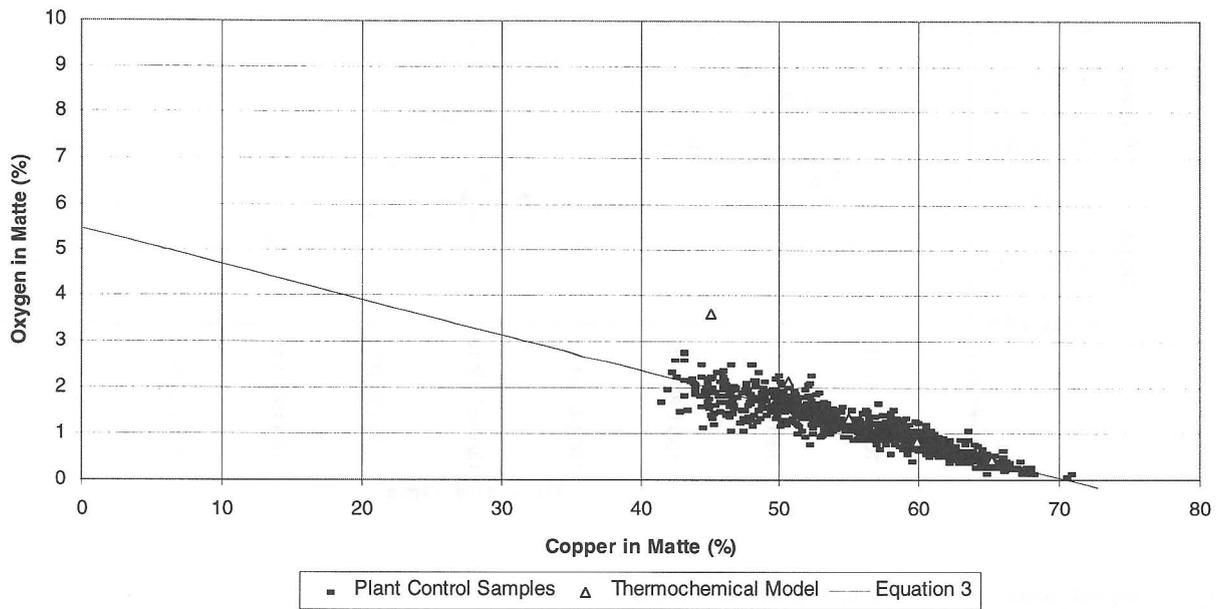


Fig. 7. Relationship between the copper and oxygen content of matte.

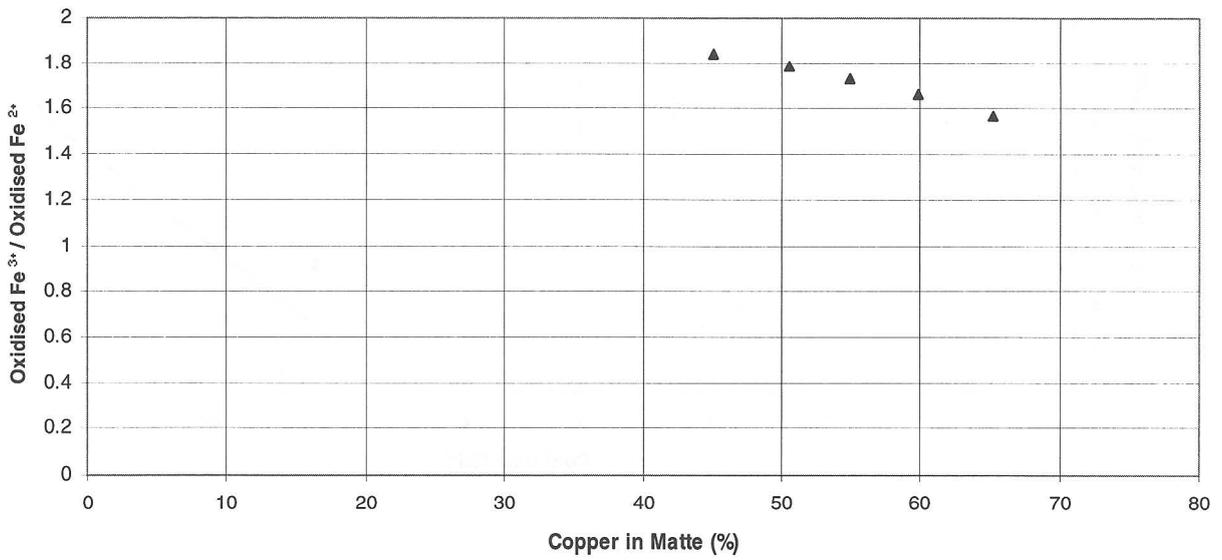


Fig. 8. Calculated oxidised Fe<sup>3+</sup>/oxidised Fe<sup>2+</sup> vs matte grade.

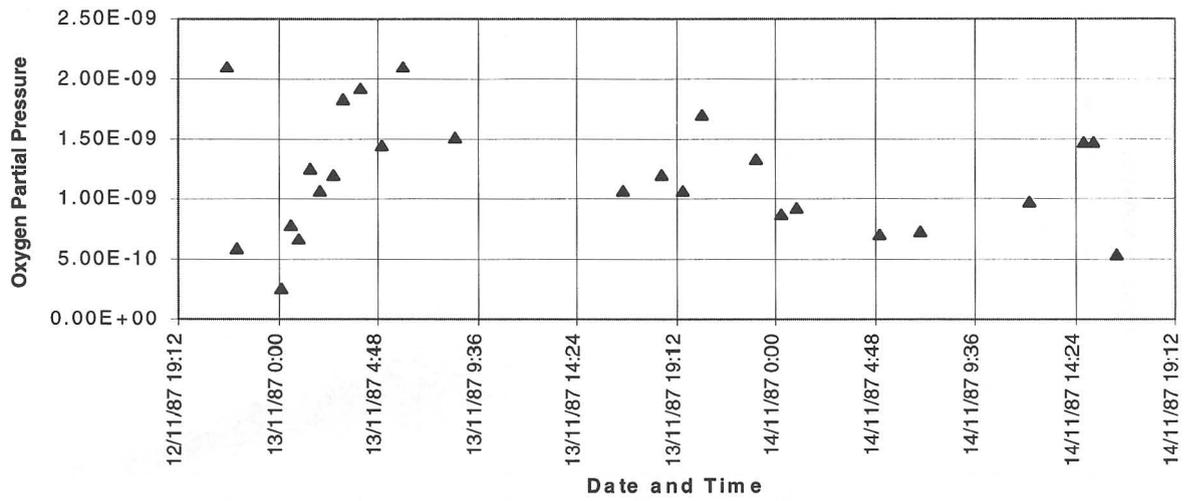


Fig. 9. Oxygen partial pressure at a matte grade of 50% Cu.

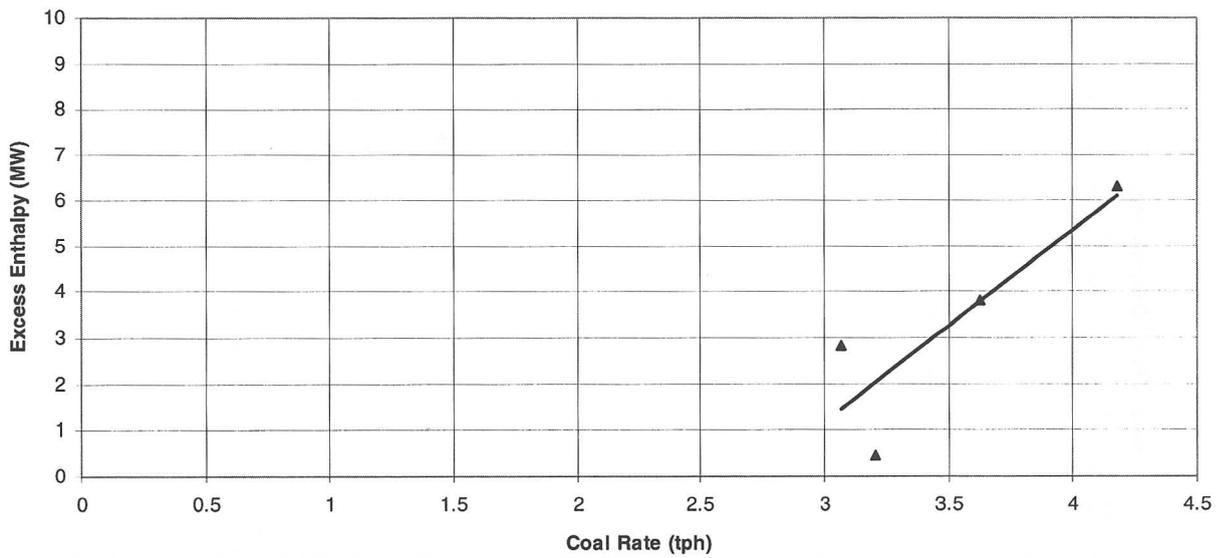


Fig. 10. Excess enthalpy vs coal rate.

inefficient coal combustion. The excess enthalpy represents less than 10% of the total system enthalpy.

At high coal rates offgas produced when coal reacts with the melt is reduced when CO<sub>2</sub> in the offgas reacts with the coal forming CO. The reduced offgas then does not come to equilibrium with the melt as it leaves the furnace.

0.3 to 0.4% Cu is dissolved in Isasmelt slag at a matte grade of 60% Cu<sup>7</sup>. The calculated % Cu in the slag is 0.14% (0.16% Cu<sub>2</sub>O). This is lower than the 0.245% oxidic copper in slag calculated by Nagamori<sup>10</sup>.

#### 4. CONCLUSIONS

- The thermochemical model of the Isasmelt process developed using the CHEMIX module of the CSIRO Thermochemistry System agrees with plant data above a 55% Cu matte grade.
- Species used in the matte solution model do not correspond to species present in the plant matte.
- There is no sulfur deficiency in mattes produced using the Isasmelt process.
- Modelling of the Isasmelt heat balance improves with the use of the liquid standard state for all species.
- It appears there are separate reaction zones within the furnace, with coal shifting both the slag and offgas equilibrium.

#### ACKNOWLEDGEMENT

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