

# Integrated experimental and thermodynamic modelling research methodology for metallurgical slags with examples in the copper production field

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**Abstract:** Recent advances of coupled experimental and thermodynamic modelling research on phase equilibria, thermodynamics and viscosities of copper and other metallurgical slag systems, and experiences of implementation of the advanced research outcomes into industrial practice are summarised. An outline of key issues derived from many years experience in continuing development and application of both experimental, thermodynamic and viscosity modelling research is presented. Particular emphasis is given to the details of the research methodologies, analysis of reasons for uncertainties and the ways to continuously improve the accuracy of both studies. The ways how the advanced research tools can be implemented into industrial operations are presented with examples on copper production slag systems.

Experimental part of the study involves high temperature equilibration in controlled gas atmospheres, rapid quenching and direct measurement of equilibrium phases with electron probe X-ray microanalysis (EPMA). Thermodynamic modelling undertaken using computer package FactSage with the quasi-chemical model for the liquid slag phase is closely integrated with the parallel experimental research. Experiments are planned to provide specific data for thermodynamic model development as well as for pseudo-ternary liquidus diagrams which can be used directly by process operators. Thermodynamic assessments are used to identify priorities for experiments. Experimental and modelling studies are combined into an integrated research program contributing to and enhancing outcomes of each other and of the overall program.

The continuous development of experimental methodologies have brought significant advances. Importantly, these novel approaches enable measurements to be made in systems that could not previously be characterised, for example, due to uncontrollable reactions with container materials or changes in bulk composition due to vapour phase reactions. The approach, however, requires particular attention to ensure accurate information is obtained. An ongoing dedicated program of improving accuracy of all possible elements of the research revealed a number of possible sources of uncertainties and the ways developed to mitigate those shortcomings are systematically summarised in this paper.

The thermodynamic modelling has progressed significantly, and achieved a level of prediction of phase equilibria and thermodynamics of complex multi-component multi-phase systems with improved accuracy. The adequate description of the systems however requires a combination of various types of data and still demands continuous further development.

The outcomes of both experimental and modelling studies are applied to assist in improvements of the industrial copper production. High certainty of the predictions of the behaviour of complex industrial processes provides a strong basis for optimisation of operations. The stage of implementation of the outcomes of the laboratory experimental and

theoretical thermodynamic modelling, however, is frequently overlooked, but requires high level of research expertise to establish the actual conditions in the real industrial process and relate them to the advanced laboratory and theoretical research tools. Examples of the applications are given in the paper.

**Keywords:** copper smelting, slag, phase equilibria, thermodynamic modelling, liquidus, minor elements distribution.

## 1. Introduction

Significant gaps in knowledge on slag properties still exist – these are due to difficulties associated with high temperature research. *The demand* for the accurate fundamental information on phase equilibria, thermodynamic and physicochemical properties of the complex multi-component systems from metallurgical and recycling industries is growing due to a) stronger economical competition, b) stricter environmental regulations, and c) better equipment and options in process control. Many other factors also contribute, including increasing complexity of ores, the number of available smelting technology options. *The supply* of the so needed fundamental data on the chemistry of the processes is becoming possible since a) new experimental techniques are becoming available due to the developments of modern advanced analytical techniques, dramatic improvement of their capabilities and availability, and b) new theoretical modelling approaches appear due to the significantly increased computer power. This demand / supply combination is the basis for *the renaissance in research on chemistry for metallurgical applications*. Recent trends determine the new challenges for the scientists including a) stricter demand for the accuracy of the data, and b) more difficult systems for research and c) more components of chemical systems. Relatively easy availability of the advanced analytical and computer-power-driven theoretical tools and the recent emphasis on the number of publications common for many universities and scientific organisations make it particularly important to stress the importance of the accuracy of the fundamental scientific data. More powerful and advanced research tools in combination with the significantly improved control of the operations introduce new opportunities, but implementation of research outcomes into practice requires high level of expertise from the technologists and in many cases requires close involvement of researchers.

The present paper attempts to outline the whole range from fundamental and applied research through the expert analysis of processes of the industrial processes to the implementation of the results of the research outcomes into industrial operations with an emphasis on the copper production.

The plan of the paper is as follows. The experimental and thermodynamic modelling research methodologies are briefly outlined first with focus on the practical measures essential to maintain adequate accuracy. The advantages of the integrated experimental and modelling approach are highlighted. The application of the new advanced research tools to the analysis of the metallurgical operations are then discussed with the focus on copper smelting. Example is given of the possibility to use new data and new treatment to examine a long-standing thermochemistry issue of the role of sulphur in copper solubility. Further analysis of the metallurgical processes starts from predominance diagram level and progresses to more detailed investigation of the trends between key input and output operational parameters. In summary, an attempt is made in this paper to outline the research capabilities that have recently become available, to highlight the opportunities to implement these to improve outcomes of the metallurgical operations, and to provide some views on possible ways to progress further in all these directions.

## 2. Research Tools

### 2.1. Experimental Methodology

#### Brief description of principal details of the procedure

The equilibration/quenching/EPMA experimental approach that is being continuously developed and applied to the increasingly complex systems is explained with reference to Figure 1 [1].

An artificial oxide mixture is prepared from the analytically pure powders or pre-sintered solids or pre-melted master slags to obtain after equilibration a predetermined bulk composition X. The starting materials thoroughly mixed using an agate mortar and pestle, and then pelletised in a die using a press. The starting composition is selected to obtain two or more phases in the final sample after equilibration. Excess of a pure metal powder is added for systems in equilibrium with particular metal (e.g. Cu, Fe or other). The sample is placed in a crucible, in a thin foil envelope or on a substrate made of a primary phase, and then suspended on a wire to be equilibrated at controlled gas atmospheres usually in a vertical impervious ceramic tube in a resistance furnace. The gas atmosphere is maintained by mixture of pure gases such as CO, CO<sub>2</sub>, H<sub>2</sub>, Ar, SO<sub>2</sub> etc added in proportions calculated using reliable thermodynamic information (e.g. FactSage package). The required gas flow-rates are usually maintained with the U-tube capillary flow-meters.

The output gas from the equilibration furnace in some experiments is directed into a consecutive vertical tube furnace at controlled temperature equipped with a DS-type oxygen probe (supplied by Australian Oxygen Fabricators, AOF, Melbourne, Australia) with the accuracy of  $\pm 0.1 \text{ Log}(P_{O_2})$  units to test accuracy of the oxygen partial pressure control. Alternative tests confirmed that the actual accuracy of the  $P_{O_2}$  control is better than the  $\pm 0.1 \text{ Log}(P_{O_2})$  units.

The furnace temperature is controlled within  $\pm 1 \text{ K}$  by an alumina-shielded Pt/Pt-Rh 13% thermocouple placed immediately adjacent to the sample, and is periodically calibrated against a standard thermocouple (supplied by National Measurement Institute, West Lindfield, NSW, Australia). The overall temperature accuracy is estimated to be within 5 K or better.

After equilibration for predetermined time the samples are quenched into cold water or brine solution so that the phases present at high temperature and their compositions are retained at room temperature. The liquid slag phase is converted to glass, and the solid crystals existed at the temperature are frozen in place on quenching. The final microstructure and phases (see example in Figure 1) therefore represent equilibria existed at the temperature.

The samples are mounted, polished and then examined initially using optical microscopy, and then Scanning Electron Microscopy (SEM) with Energy Dispersive Detector (EDS). Various types of images are used, including secondary and backscattered electron images and other available.

The compositions of the phases (glass and solids) are then measured using a JEOL JXA 8200L (trademark of Japan Electron Optics Ltd., Tokyo) electron probe X-ray microanalyzer (EPMA) with Wavelength Dispersive Detectors (WDD). An acceleration voltage of 15 kV and a probe current of 15 nA are usually used. The Duncumb-Philibert ZAF correction procedure supplied with the probe is applied. The appropriate standards are selected to the oxide, sulphide or metal phases. The phase compositions are measured with EPMA with accuracy within 1 wt % or better. EPMA is used

to measure the total metal cation concentrations; no information on the proportions of the same element having different oxidation states are usually acquired, all metal concentrations are recalculated to selected oxidation state for convenience of presentation and to unambiguously report the compositions of phases.

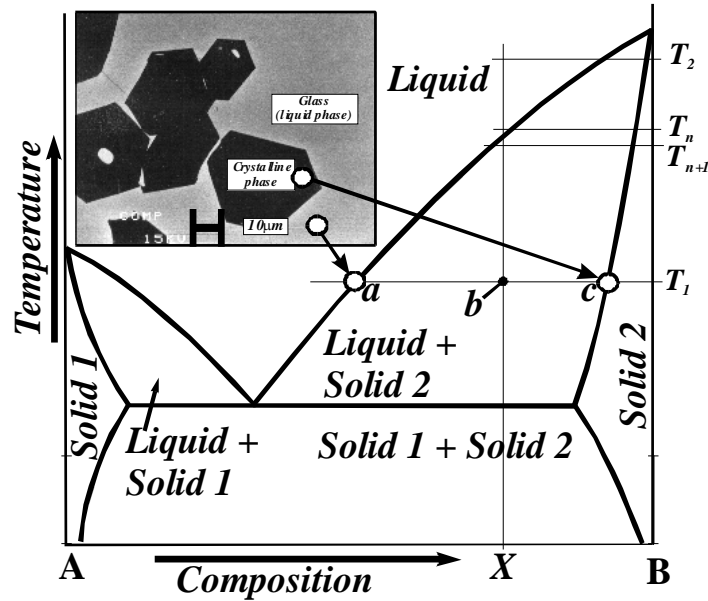


Figure 1. Hypothetical diagram to illustrate experimental technique for determination of phase equilibria.

#### Advantages of the technique

The fact that the compositions of phases are measured after rather than before the experiment make the accuracy of results independent from the changes of bulk composition during the experiment provided the achievement of equilibrium between phases is confirmed. The results therefore are not affected by interaction with the containment material (crucible, substrate), vaporisation of some elements during equilibration and uncertainties in the initial mixture composition. Moreover, this independence from the changes in bulk composition enables to extend the technique to the gas / metal (or matte) / slag / solid(s) systems as well as to the use of the substrate or levitation techniques. The small size of the liquid slag phase used in the suspension technique (down to the several micron liquid film) enhances achievement of a) equilibrium of condensed phases with the gas phase as well as b) high quenching rates (as the liquid contacts quenching media first without crucible interference), thus extending the applications to the systems where these factors are the limitations for research, such as Ca-ferrite slag and slag / matte systems.

The compositions of all phases at equilibrium are measured enabling for determination of not only liquid compositions, but, importantly, the compositions of solid solutions coexisting with these liquids. The crystal phases are reliably identified from their compositions.

The achievement of equilibrium and other factors affecting accuracy and reliability of the results can be directly investigated by observation of the microstructure and measuring compositions of phases in multiple places; details are discussed below.

### Some possible uncertainties

The equilibration / quenching / EPMA technique has proven to be superior in terms of the accuracy, reliability and productivity in a large variety of systems and studies and is currently applied wider in phase equilibria. Although some researchers may take it as a relatively simple and straight forward, there are many underlying uncertainties that have to be seriously confronted. Below is the list of major uncertainties derived and summarised from many years experience of the systematic application and development of this technique.

Achievement of equilibrium is by far the most important and common uncertainty in the equilibria studies, but is not always obvious and not always given sufficient attention to eliminate errors. It is relatively easy to make a wrong conclusion from undetected changes in the samples with time, and the probability of this type of error is high.

Temperature uncertainties include possible inaccuracy of any, even new thermocouple, contamination of the thermocouple during experiment by diffusion through the gas and through the ceramic shield, the fact that the sample is not adequately close to the thermocouple, effects of radiation and gas convective heat transfer, and the heat conduction through the shield from the tip of the thermocouple to a colder zone. Common declarations in papers that the temperature accuracy is within 1°C at over 1000°C are usually overstatements based on the observation of the temperature controller unless special measures are taken.

Quenching is important source of uncertainties and is the limitation of this experimental technique. Critical examination of microstructures is essential to minimise the uncertainty. The homogeneity of the glass phase is usually a good indication, but even observation of a homogeneous glass in some cases does not guarantee absence of the uncertainty. On the other side, in many cases EPMA measurements of the heterogeneous (microcrystalline) product of the quenching can give accurate composition of a phase (usually, a liquid phase) at the temperature – special investigation though has to be undertaken to ensure the validity of such measurements. For example, in the study on the Ca-ferrite slags the accuracy of the EPMA measurements of the microcrystalline quenched liquid was confirmed by independent analysis of the bulk composition of the quenched fully liquid sample using alternative chemical analysis by ICP and by XRF.

The measurement of the composition has uncertainties. The ZAF correction is quite frequently introduces inaccuracies. Vaporisation of elements during measurements (e.g. Na, K, S) takes place, although rarely. It is essential to select appropriate standards, for example, to use standards of similar chemical origine (e.g. oxides for oxides, and metals for metals). Uncertainty of the oxygen concentration in phases with transition metals (e.g. FeO / Fe<sub>2</sub>O<sub>3</sub>) can introduce corresponding uncertainties into the following ZAF correction. Important is to ensure the take-off volume is within the phase (it is not possible to guarantee that there is sufficient depth under the surface for the light matrixes with larger take-off volumes looking at the 2D image); this is particularly important for the phases with low average atomic number.

### Measures to minimise uncertainties

Important: the “principle of presumption of innocence” should not be applied in the research, better is to follow the “presumption of guilt” – always assume result is uncertain unless proved accurate. It is important to always try to prove result is within acceptable accuracy, and accept result as accurate only if failed to prove otherwise.

Hypothesis must pre-empt the experiment, not visa versa. A theory-based analysis of results after a series of experiments had been completed is a common case, however this first theoretical description cannot be taken as the final unless independently checked because there are usually many other theoretical descriptions that could be fitted into the same experimental dataset, and the initial theory may not be the correct one. In some cases such “theoretical” description of the experimental results could become as exercise in logic and result in incorrect conclusions.

Common available reference sources (e.g. [2-4]) must be used initially, followed up by collection and review of original papers. Particularly useful is the Powder Diffraction File [2] that contains very comprehensive list of compounds ever found and investigated.

The collection and review of the original papers is important – secondary references frequently change “dashed lines” indicating expert guesses in the original papers into “solid lines” in the secondary references – the latter could be wrongly understood as reliable experimental information.

All experiments must be undertaken in several cycles, each iteration starting from the initial series followed up by confirmation. The practice to run large matrix of experiments followed up by interpretation and analysis of results for a large set of experiments is inappropriate practice; it excludes the stage of investigation of properties of the system, its behaviour and can introduce significant uncertainties in the final results.

A systematic and comprehensive analysis with possible developments of appropriate and relevant classifications is a common scientific approach that must also be used in the minimisation of uncertainties. As an example, identification of particular categories or types of uncertainties, such as uncertainties of EPMA measurements, uncertainties of equilibration, uncertainties related to quenching etc, can assist to better focus on each detail to ensure a possible source of error is not overlooked.

Independent confirmations where possible are essential, these can include independent researcher, alternative approach or technique (e.g. theoretical analysis).

The application of existing theoretical knowledge and tools are important, and these include the phase rule [4], Alkemade theorem [4], lever rule [4], Schreinmeher’s rule [5] and thermodynamic modelling [6-10].

Quenching technique brings the advantages of static phase equilibrium determination techniques, in particular, a possibility of accurate control and verification of achievement of equilibrium. Confirmation of the achievement of equilibria though is always one of the most important questions in experimental phase equilibria studies. The key tests to ensure the achievement equilibrium include:

1. Changing the equilibration time to confirm that no further changes take place as the time is increased.
2. Confirming the chemical homogeneity of each of the phases.
3. Approaching equilibrium from different directions followed by analysis of the results.
4. Analysing possible reactions taking place during equilibration, application of the available analytical techniques looking for possible signs of incomplete reaction pathways during equilibration. SEM imaging and EPMA analysis of

the trends of the compositions across the phases used in the present series of studies are particularly effective in this analysis.

The continuous and simultaneous application of all four tests is essential; none of the separate tests on their own can be taken as the final prove of the achievement of equilibria.

The approach used in these equilibrium studies should be to consider each experiment as a kinetic process leading towards achieving equilibria; the closer to the equilibrium – the less driving force – the more chances of not achieving equilibria. Possible elementary reactions taking place during the experiment should be listed and traces of intermediate stages should be specifically searched for in each sample. The morphologies of phases, microstructures and compositions of different parts of phases are used for such “forensic” analysis. Important factor to take into account is the rate of specific reactions taking place during equilibration. For example, the rate of the chemical reactions between the gas and condensed phases is generally lower than the rates of reactions between two condensed phases such as liquid/liquid or liquid/solid systems. The diffusion in the liquid phase is significantly faster than in the solid phase. These are just examples, and there are much more of the common characteristics of the systems and reactions at high temperature, and experienced research should continuously learn the kinetics and properties of different parts of the investigated system.

This “4 test approach” with particular attention to the kinetics of the reactions taking place during achievement of equilibria should be applied to all systems, and a number of common measures to minimise the uncertainties should be developed and continuously applied.

Samples with the liquid slag in experiments aimed to establish liquidus conditions are pre-melted at a temperature higher than the final temperature, and then are equilibrated at temperature  $T_1$  below the liquidus (see Figure 1) so that two (or more in higher order systems) condensed phases are formed. The premelt is essential to a) homogenise the sample, and b) promote crystallisation of the new, fresh layers of crystals coexisting in equilibrium with the liquid phase thus eliminating many uncertainties including a possibility that some solids are undissolved or the solid is not in equilibrium with the liquid phase due to the slow diffusion in the solid state.

For solid-state equilibration the metastability should always be assumed unless proven otherwise. For example, if the solid state transformation temperature is measured, the two starting types of samples are pre-sintered with the phase assemblages corresponding to each of the opposite sides of the equilibrium. The series of experiments starting from different directions are then undertaken and the equilibrium condition is bracketed only by the experiments with the phase assemblage changed from the opposite side phase assemblage to the equilibrium during corresponding experiment.

The specific properties of phases and rates of associated reactions are taken into account. For example, relatively viscous liquid can be quenched readily, but would have slow diffusion limiting the rate of achievement of equilibria; the starting bulk composition is then selected to obtain higher proportion of solids, less “distance” for diffusion, ready nuclei (no complete melting). In contrast, fluid liquid can be readily equilibrated, but would have difficulty in

quenching; the proportion of solids in the sample should then be minimised to reduce availability of nuclei and surfaces for crystallisation, and to reduce the “enthalpy” introduced by solids needed to be conducted into the quenching media.

The modern analytical techniques bring advanced capabilities to the characterisation of the samples if it is performed by the expert – researcher in the field. The tendency to delegate the SEM and EPMA analysis to technical staff inexperienced in phase equilibria, metallurgy and high temperature reactions is not bringing full advantages of the technique, and in many cases is an inappropriate approach since none but the expert researcher is in a position to know what to look for in the sample, and be able to identify small but essential details. Only the trained metallurgical expert researchers undertake measurements in the Pyrometallurgy Research Centre.

Common “standard” procedure, or common steps are usually involved in the analysis of the sample:

1. Search and identification of all phases present in the sample and their relation to existing phase equilibria and crystallographic data (common reference compilations like Slag Atlas [3] Phase Diagram for Ceramists [4] and XRD Powder diffraction database [2] can be used).
2. Investigation of macroscopic features in the sample with focus on possible in-homogeneities or any other special features.
3. Search for the best representative local area for the equilibrium measurements. The qualified researcher must do this using knowledge of the kinetics of possible reactions in the investigated system. For example, in solid state gas equilibration experiments only the surface of the sample exposed to the gas atmosphere should be selected (the core of the sample may be treated as a closed system). The outer liquid areas should be looked for in liquid quenching experiments for the best quenched zone. The core of a solid phase should be avoided for analysis – the areas of crystals in direct contact with the liquid phase must be used to establish solid – liquid tie-lines. There are many other examples which cannot be listed within the framework of the paper, but which can relatively easily identified by an expert researcher with experience in the metallurgy field.
4. All analytical and imaging equipment capabilities must be used to avoid uncertainties. For example, EDS are essential to confirm the phases selected for EPMA. Increasing image contrast of the back-scattered electron image to the maximum can help to identify composition inhomogeneity – this should be a common practice for the selection of the points for EPMA. The use of different imaging types (e.g. secondary and back-scattered electron image, topographical image) is essential to ensure all phases are found; back-scattered electron image alone is not sufficient since some phases with different compositions can have the same contrast.
5. Standards always have to be included as un-known samples at the beginning, in the middle and at the end of the EPMA series of measurements.
6. Images of the actual measured areas should be collected; it is important for further analysis to include a) typical, representative images and b) images of some abnormal special features.
7. The adequacy of results must be checked at the time of the EPMA measurements relative to the known preliminary information so that possible reasons for major inconsistencies be investigated during the EPMA session.
8. The overall EPMA session is the major part of investigation of the sample.

These and some other common steps are used in the studies at the Pyrometallurgy Research Centre.



### Further developments and modifications of the experimental technique

Two types of equilibration experiments are particularly common in the investigation of the gas / liquid slag / metal or matte equilibria:

- (a) Open system experiments: the conditions (e.g. partial pressure  $P_{O_2}$ ,  $P_{SO_2}$ ) are controlled by a gas mixture (e.g. CO/CO<sub>2</sub>/SO<sub>2</sub>).
- (b) Closed system experiments: the condensed phases control the conditions (e.g. effective oxygen pressure) in the system – this may be achieved by experiments in an inert atmosphere such as Ar.

Since a) the final results are not sensitive to slow bulk compositional changes in multi-phase systems and b) only small samples are needed for measurements, slag suspension techniques have been developed that rely on the wetting of the support material by the liquid phase [11]. A number of variations of containerless suspension approaches have been developed to date [12]. Examples of the use of interfacial tension to the support of the liquid slag include:

- a) metal drop electromagnetic levitation technique [12, 13], and
- b) primary phase suspension or substrate technique [11-13].

The electromagnetic levitation has proved to be a) more difficult to do and b) more exposed to possible uncertainties (in particular, related to the high temperature gradient between the suspended metal droplet with suspended slag film and surrounding gas phase), however this approach may still be better suited for some complex systems. The primary phase substrate suspension technique has mostly been used at the Pyrometallurgy Research Centre and has been very successful in extending experimental capabilities to the chemical systems and conditions that could be investigated by conventional approaches. Numerous examples of the application of the substrate techniques are now available in literature [14-29]. The primary phase substrate suspension technique has been recently extended by Henao et al [27, 28] to the investigation of the minor elements distribution through the combination of the EPMA technique and selective dissolution approach that enables very low concentrations of some minor elements in some phases to be measured with alternative chemical analysis techniques such as ICP, mass spectrometry and other. Note that the use of microstructural analysis and EPMA measurements in all phases are still undertaken prior to the selective dissolution so that all advantages of the EPMA approach are maintained. The substrate approach has recently been extended to the copper matte – slag equilibration – the small size of the sample enabled the matte phase to be quenched and therefore matte composition to be measured with EPMA [28].

The use of the substrate suspension technique requires to take into account the factor that a relatively small proportion of liquid being equilibrated with a relatively large proportion of solid. For example, the use of the magnetite sintered in air from the iron metallic foil as a substrate may introduce relatively large excess of the “condensed” oxygen into the system due to the oxygen excess beyond the Fe<sub>3</sub>O<sub>4</sub> stoichiometry – magnetite substrates therefore are prepared at low fixed  $P_{O_2}$  to produce magnetite close to the stoichiometric Fe<sub>3</sub>O<sub>4</sub> composition. Additional positive factor for the use of the substrate is the slow diffusion in the solid state relative to the diffusion in the liquid phase – effectively, only small part of the substrate takes part in the equilibration reaction with the liquid, and the extent of the solid stage diffusion is monitored by EPMA.

Given the small amount of the liquid phase, the impurities in the gases (such as O<sub>2</sub> in the high purity Ar) may cause uncertainties and require additional measures to remove contamination.

### Summary

The equilibration / quenching / EPMA approach to phase equilibrium determination has greatly extended the range of metallurgical systems that can be characterised, but only after adequate care is taken it is possible to be reasonably sure of the accurate outcomes. Examples of the application of this experimental approach can be found in a number of publications for various chemical systems, and a summary of earlier publications relevant to different chemical systems is given in Jak et al [29].

## **2.2. Thermodynamic modelling**

### Thermodynamic modelling - brief description

Thermodynamic databases are developed through thermodynamic optimisation that involves selection of proper thermodynamic models for all phases in a system, critical simultaneous evaluation of all available thermodynamic and phase equilibrium data and optimisation of thermodynamic model parameters to obtain one self-consistent set best reproducing the experimental data as functions of temperature and composition.

In the thermodynamic "optimisation" of a system, all available thermodynamic and phase equilibrium data for the system are evaluated simultaneously to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, the thermodynamic properties and the phase diagrams can be back-calculated. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can be identified during the development of the model. These discrepancies can then be resolved through new experimental studies that, if possible, are undertaken in areas essential for further thermodynamic optimisations. Multicomponent data, if available, are used to derive low-order (binary and ternary) model parameters, and if multicomponent data for a system are lacking, the low-order parameters are extrapolated. In this way, the thermodynamic databases are developed and all the data are rendered self-consistent and consistent with thermodynamic principles. FactSage computer system [30] has been used by the author for the thermodynamic modelling. The molten slag phase is modelled by the Modified Quasichemical Model [31-33] in which short-range-ordering is taken into account. Oxide solid solutions are described with a polynomial model or with the Compound Energy Formalism [34], the latter taking into account the crystal structure and physical nature of each solution.

### Special data requirements

Availability of several types of data is an essential requirement to determine unambiguous set of thermodynamic model parameters of chemical systems. These necessary types of data include heats of formation, heat capacities, Gibbs free energies of compounds and of reactions, thermodynamic activities in solution phases, crystal structure information and data on special transition reactions including magnetic transformations and phase equilibria data including solubility limits in complex solutions, liquidus, solidus and other similar information. It is essential factor that the phase equilibrium data cannot guarantee the establishment of the correct unambiguous set of thermodynamic

parameters. The extents of complex solid solutions are essential data in addition to the liquidus temperatures. Availability of the experimental data in multi-component systems is essential to test thermodynamic model predictions extrapolated using only the binary and ternary parameters – the usual important practice in the development of the multi-component thermodynamic models is to repeat several cycles from low order systems to the multi-component and back. The practice of using only low order systems to derive the set of thermodynamic model parameters followed by extrapolation into the multi-component systems without testing the predictions (due to the lack of data) introduces significant uncertainties. The relative accuracy of the available experimental data to the sensitivity of the predicted values to changes of the thermodynamic parameters is essential – if predicted value is not sensitive to the changes of a thermodynamic parameter, then significantly higher accuracy of an experimental value would be needed.

#### *Integrated thermodynamic database development using modelling and experimental studies*

The combination of experimental and thermodynamic modelling studies carried out in parallel is an important factor in planning and undertaking of phase equilibrium studies to ensure high quality research outcomes. The initial thermodynamic modelling enables a) to evaluate existing experimental data and b) to focus new experimental work on areas where discrepancies of data need to be resolved or where new data are required. One of the important uses of the thermodynamic modelling is prediction of phase equilibria and thermodynamic properties of the multi-component systems close to the industrial slags chemistry and conditions. At the same time, agreement of predictions with experimental results in the multi-component compositional area is the real test of the validity of the thermodynamic model. There is usually a lack of experimental information for the multi-component slags and therefore a tendency to claim a multi-component database is developed on the basis of only binary and ternary data thus effectively extrapolating the low order parameters into a multi-component area. The present experimental program, in addition to the work on the binary and ternary systems, specifically focuses on multi-component systems in the composition and oxygen partial pressure ranges close to the important industrial slags. The thermodynamic model then is checked and corrected to agree with those multi-component measurements in the vicinity of the industrial slags. This is an important feature of the present study - the optimisation is performed in a number of cycles from binary and ternary to the multi-component systems and back so that binaries and ternaries are reoptimised to reach agreement also with the extensive data set in the multi-component area. The resulting thermodynamic database therefore is optimised to agree with experimental data for lower order systems and for the multi-component slag systems. Examples of the integrated experimental and thermodynamic modelling approach can be found in previous publications [35-41].

### **2.3. Recent results relevant to the Cu smelting systems**

#### ***2.3.1. Liquidus and Cu solubility in slag***

A series of studies focused on phase equilibria and thermodynamics of the chemical systems important to the Cu pyrometallurgical production have been undertaken over recent years using the integrated experimental and thermodynamic modelling approach [11-24, 27-29, 42-49]. Studies range from a) the work on low order (binary and ternary) systems that are particularly important foundation for thermodynamic modelling to b) the investigations of the multi-component systems close to the industrial slags – the latter are used directly in industrial practice as well as

provide an essential test in the development of the multi-component thermodynamic model. Figure 2 demonstrates recent results of experimental work [45-46] on a series of pseudo-ternary systems “Cu<sub>2</sub>O”-SiO<sub>2</sub>-(CaO, Al<sub>2</sub>O<sub>3</sub>, MgO, “Fe<sub>2</sub>O<sub>3</sub>”) in equilibrium with metallic copper. New experimental data on these low order copper oxide containing systems in equilibrium with metallic copper [45-46] could be obtained only due to the newly developed experimental approach based on the use of EPMA. The set of new experimental data on low order systems in equilibrium with metallic copper is a critical component for the developed new thermodynamic database [47].

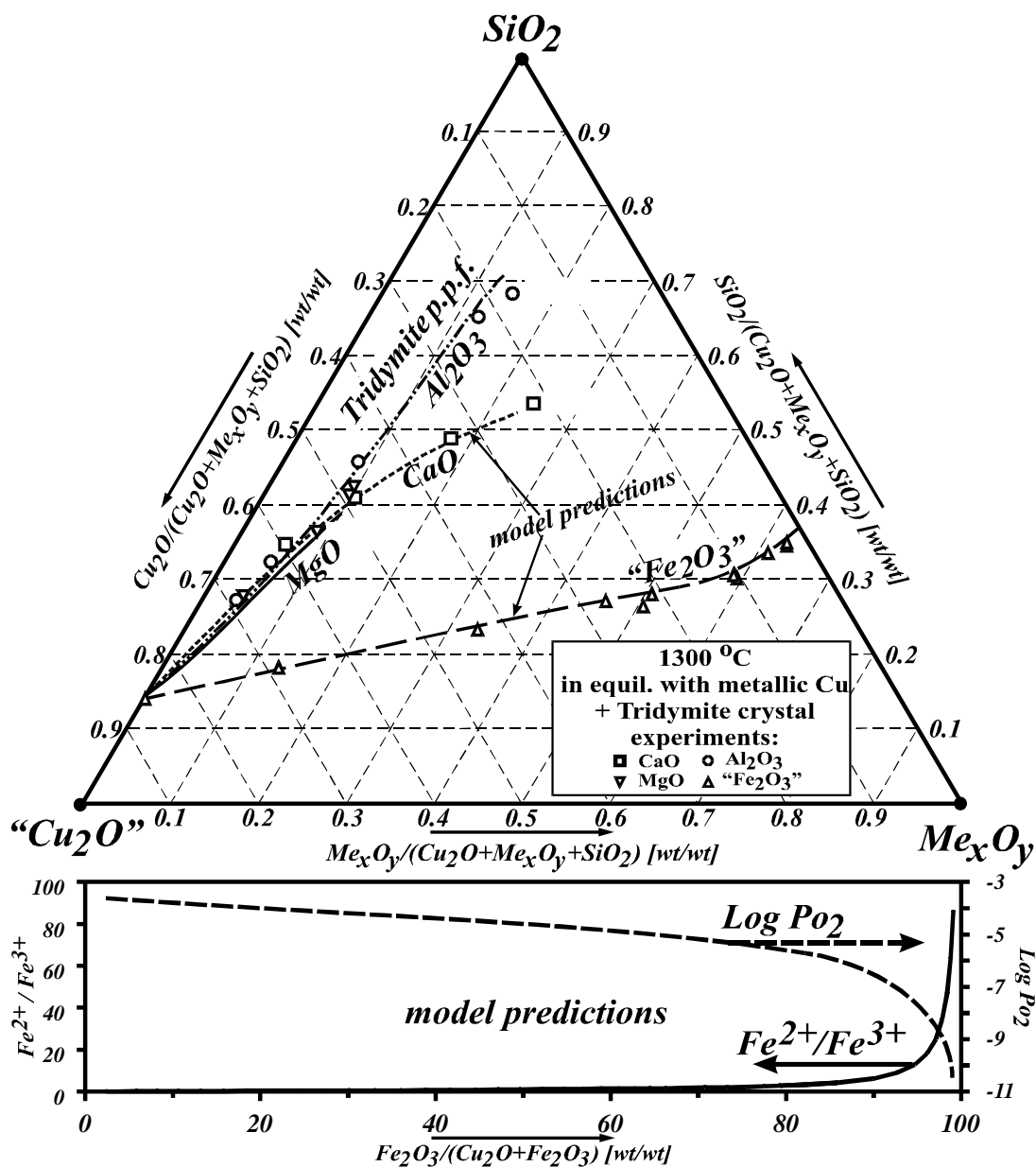


Figure 2. Comparison of predictions using new thermodynamic slag model [47] and experimental data for the 1300°C tridymite liquidus in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-MeO<sub>x</sub>, where Me = Ca, Al, Mg and Fe in equilibrium with metallic Cu [45-46].

Figure 3 provides an example of study on multi-component system “Cu<sub>2</sub>O”-“FeO”-SiO<sub>2</sub>-CaO- MgO-Al<sub>2</sub>O<sub>3</sub> system in equilibrium with metallic Cu at conditions close to the industrial copper cleaning slag [21]. The agreement between experimental data and FactSage predictions with the new thermodynamic database is demonstrated in this figure.

FactSage is then used to investigate the trends – effect of various impurities can be analysed (see Figure 3). Further detailed analysis of a number of important characteristics can now be undertaken quantitatively.

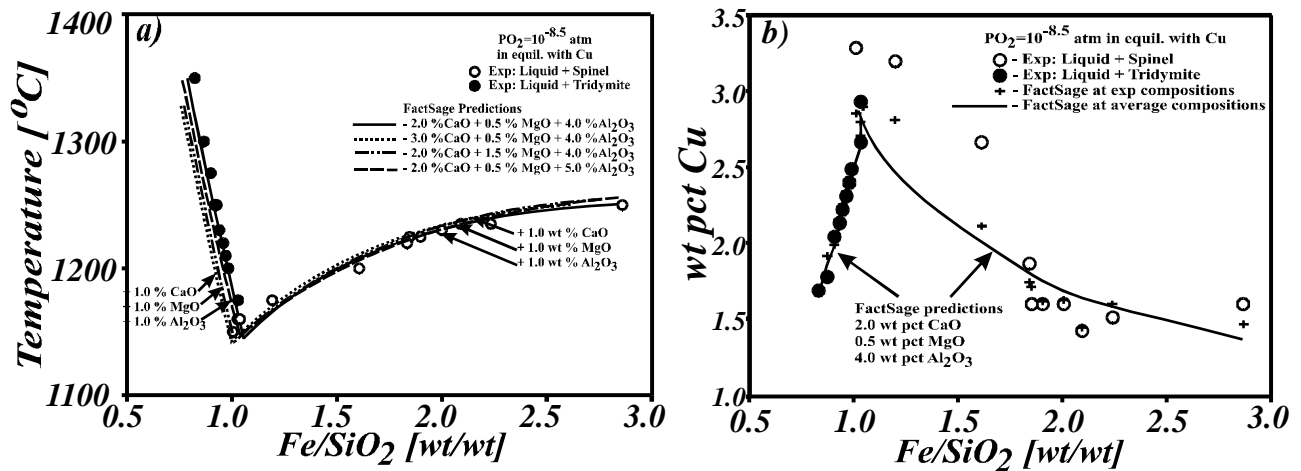


Figure 3. Comparison of using new thermodynamic slag model [47] and experimental data [21] on a) liquidus and b) Cu solubility in slag at  $P_{O_2}=10^{-8.5}$  atm in the “Cu<sub>2</sub>O”-“FeO”-SiO<sub>2</sub>-CaO- MgO-Al<sub>2</sub>O<sub>3</sub> system in equilibrium with metallic Cu.

Figure 4 illustrates the effect of the Fe/SiO<sub>2</sub> and CaO/SiO<sub>2</sub> ratios on the Cu concentration chemically dissolved in slag in equilibrium with metallic copper taken from the experimental study [24] and predicted with thermodynamic model [47]. The increase of both Fe/SiO<sub>2</sub> and CaO/SiO<sub>2</sub> ratios in the sulphur-free slag in equilibrium with metallic copper results in the decrease of the chemical solubility of copper in slag. The comparison of the experimental and predicted trends indicates at the need to further improve the current thermodynamic database – this in particular highlights the importance of both experimental and thermodynamic modelling approaches to be carried out in parallel within integrated research program.

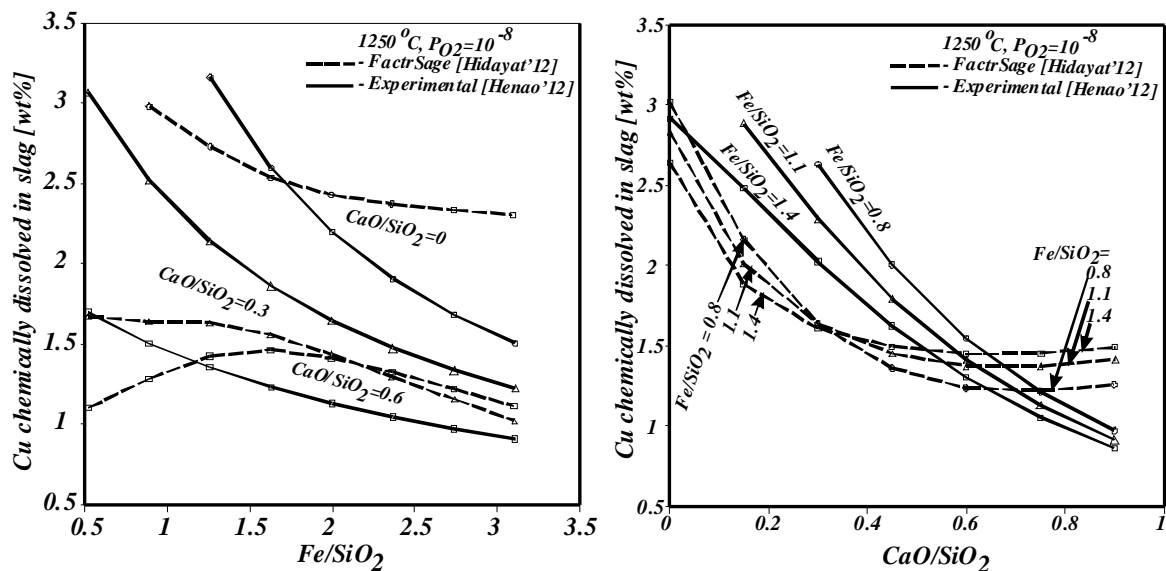


Figure 4. Cu solubility in slag at 1250°C and  $P_{O_2}=10^{-8}$  atm in the “Cu<sub>2</sub>O”-“FeO”-CaO-SiO<sub>2</sub> system in equilibrium with metallic Cu as a function of Fe/SiO<sub>2</sub> and CaO/SiO<sub>2</sub> ratios showing experimental [24] trends and predictions using new FactSage thermodynamic database [47].

### 2.3.2. Effect of S on Cu solubility in silicate slag

The trend of the Cu solubility in the slag in presence of sulphur (e.g. in contact with matte) as a function of slag composition and matte grade is one of the important practical and theoretical issues that has been the subject of attention by many researchers over several decades [50-62]. The concept of the sum of the oxidic and sulphidic copper solubilities in silicate slags related to the so called sinusoidal trend of Cu solubility as a function of matte grade (low Cu solubilities at low matte grades, then maximum at ~30-40 wt % Cu, then low again at ~60-65 wt % Cu, and then increasing at > 70 wt % Cu in matte) has been supported by various researchers including Sehnalek and Imris [50], Yazawa et al [51, 52], Nagamori [53, 54], Takeda [55, 56]. Several other researchers, however, did not observe the maximum of Cu solubility as a function of matte grade [57-61]. Analytical X-ray Photoelectron Spectroscopy study [62] focused on identification of the oxidic and sulphidic copper in the silicate slag confirmed presence of “oxidic copper” but did not produce conclusive evidence of the presence of the sulphidic copper association in the slag. The quasichemical solution model using the thermodynamic computer package FactSage was extended to describe the sulphide capacities and metal sulphides dissolved in molten slags; the model described well the experimental sulphide capacities along with other thermodynamic properties of the molten oxide and sulphide systems [63-67] – this may be taken as an indication of the validity of the model; predicted Cu solubility in the slag as a function of matte grade with this model did not show the maximum [66]. Note that all previous experimental studies had uncertainties associated with the use of relatively large samples equilibrated in crucibles and with physical separation of matte and slag for further bulk analysis of each phase composition.

The present studies with the equilibration / quenching / EPMA technique [24] have resolved the uncertainties of previous techniques performed with the bulk analyses of the slag, metal or matte phase compositions and provide direct EPMA measurements of Cu dissolved in the liquid slag phase (converted to glass on quenching) equilibrated with copper metal or matte. These experimental data in combination with the thermodynamic modelling tools can now be used to more accurately and quantitatively evaluate the effect of sulphur presence on the Cu dissolution in the slag. The Cu solubility in the “FeO”-CaO-SiO<sub>2</sub> slag were experimentally characterised at 1250°C, P<sub>O<sub>2</sub></sub>=10<sup>-8</sup> in equilibrium with liquid copper metal (a<sub>Cu</sub> close to 1) [24] and with the matte at P<sub>O<sub>2</sub></sub>=10<sup>-8</sup> and fixed P<sub>SO<sub>2</sub></sub> [68]. The Cu solubilities in slag in equilibrium with the matte were recalculated to the condition of a<sub>Cu</sub> = 1 for comparison purpose using the assumption that Cu obeys Henrian behaviour at low concentrations and considering reactions  $2Cu_{matte} + \frac{1}{2}O_2 \leftrightarrow Cu_2O$  and

$2Cu_{matte} + \frac{1}{2}S_2 \leftrightarrow Cu_2S$ . For example, for the reaction  $2Cu_{matte} + \frac{1}{2}O_2 \leftrightarrow Cu_2O$  the equilibrium constant  $K_{eq}$  is

$$K_{eq} = \frac{a_{Cu_2O}}{a_{Cu,matte}^2 P_{O_2}^{1/2}} = \frac{\gamma_{Cu_2O} x_{Cu_2O}}{a_{Cu,matte}^2 P_{O_2}^{1/2}} \text{ so that } x_{Cu_2O} = \frac{K_{eq} P_{O_2}^{1/2}}{\gamma_{Cu_2O}} a_{Cu,matte}^2, \text{ where } x_{Cu_2O} \text{ is } Cu_2O \text{ concentration in the slag in}$$

mol fraction,  $P_{O_2}$  is equilibrium oxygen partial pressure,  $\gamma_{Cu_2O}$  is Cu<sub>2</sub>O activity coefficient in slag relative to the pure

liquid standard state, and  $a_{Cu,matte}$  is Cu activity relative to the pure liquid standard state.

The term  $\left(\frac{K_{eq} P_{O_2}^{1/2}}{\gamma_{Cu_2O}}\right)$  (constant for the Henrian region at fixed temperature and  $P_{O_2}$ ) was calculated for each

experimental point using the  $x_{Cu_2O}$  value measured by EPMA in the experimental sample, and the  $a_{Cu,matte}$  value predicted with FactSage for the 1250°C,  $P_{O_2}=10^{-8}$  and fixed  $P_{SO_2}$  of 0.1 and 0.6 for the matte phase composition also measured with EPMA in the quenched sample. The copper solubility was then recalculated for the  $a_{Cu,liquid} = 1$  with the same fixed term  $\left(\frac{K_{eq} P_{O_2}^{1/2}}{\gamma_{Cu_2O}}\right)$  thus obtained from experimental data with assistance of thermodynamic modelling.

Figure 5 presents the plot of the ratio of the Cu solubility in slag in presence of S (recalculated according to the procedure outlined above) to the Cu solubility in slag without sulphur. This value indicated at how the presence of sulphur in the system effects the Cu solubility in the slag phase. The results presented in Figure 5 illustrate the effect of sulphur on the copper solubility - the Cu solubility values in presence of S recalculated to the  $a_{Cu,liquid} = 1$  are higher than the corresponding Cu solubilities in equilibrium with pure liquid Cu without sulphur. The results plotted in Figure 5 indicate that the presence of sulphur in the slag increases solubility of Cu. These data do not provide an indication of the mechanism of this effect, and no final conclusion could be made on the nature of Cu solubility, however the above results clearly demonstrate that the sulphur has a noticeable effect on the Cu solubility in slag.

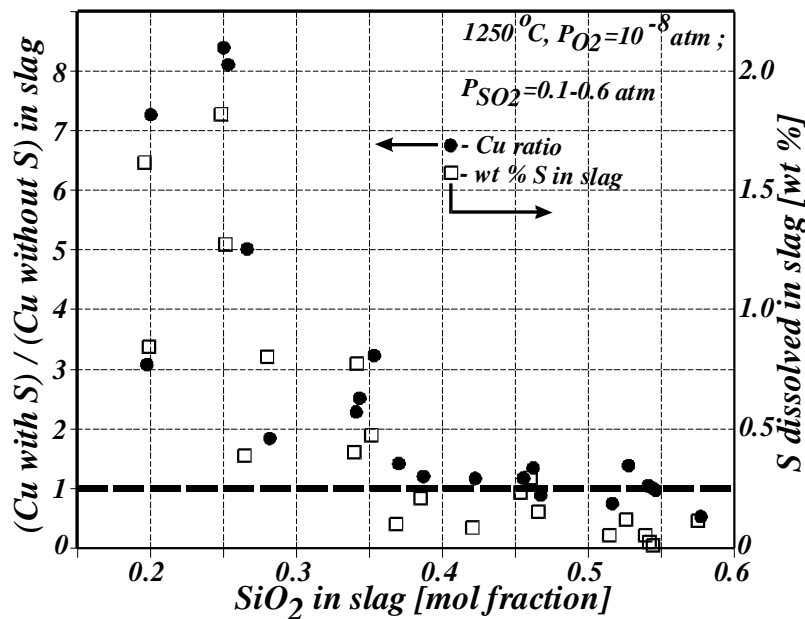


Figure 5. Ratio of Cu dissolved in slag in presence of S (in equilibrium with matte [68]) after recalculation to  $a_{Cu,liquid} = 1$  relative to the Cu dissolved in slag without S (in equilibrium with Cu metal [24]), both at 1250°C,  $P_{O_2}=10^{-8}$  atm as a function of  $SiO_2$  in slag.

This example also demonstrates how new experimental approach in combination with the FactSage thermodynamic model enable advanced, more precise, quantitative characterisation of a system behaviour to be achieved.

The following sections will further demonstrate how new advanced tools can now be used for the analysis of thermochemistry to assist in improvement of industrial operations.

### 3. Industrial Applications

#### 3.1. Cu smelting predominance diagram

The application of the predominance diagrams to illustrate and characterise main processes taking place in pyrometallurgical reactors has been an essential approach widely used by metallurgists, and developed and introduced into the use by many scientists, the contribution of Prof. Yazawa [69] is particularly important in this area, as well as in many other metallurgy fields. Following Yazawa's [69] approach, parts of the predominance diagram related to the main copper pyrometallurgical production steps have been predicted using the new FactSage thermodynamic model of the slag phase [47] along with the model for matte and Cu metal models taken from the FactSage public database [66] (see Figure 6). The set of constant total pressure (sum of the partial pressures of the O- and S-containing gaseous species) solid lines (parallel to the lines p-t for  $P_{total}=1$  atm and A-D for  $P_{total} = 0.3$  atm) is close to the conventional constant  $P_{SO_2}$  lines. The set of constant matte grade dashed lines (parallel to the lines q-p for 40 wt % Cu and B'B for 60 wt % Cu matte) were predicted for the equilibrium with tridymite. The corresponding positions of the 50 wt % and 70 wt % Cu matte grade dotted lines reported by Yazawa [69] are given for comparison.

The phase field boundary r-t corresponding to the equilibrium between gas, white metal and blister, as well as the set of dash-dot lines for fixed sulphur concentrations in the blister are predicted for the Fe-free Cu-O-S system. The main copper production path ABB'BCDE is indicated here for the  $P_{total} = 0.3$  atm which approximately corresponds to the 50 % oxygen enrichment – details are discussed below. Tables 1 and 2 summarise conditions for some lines and some production steps in the “Yazawa” predominance diagram Figure 6.

The new thermodynamic model [47] can now be used to further investigate the behaviour of the system and to predict important trends. For example, the effect of the higher Fe/SiO<sub>2</sub> slag ratio corresponding to the equilibrium with the spinel (magnetite) solid phase on the location of these constant matte grade lines predicted with the new model [47] is illustrated in Figure 6b). The increase of the Fe/SiO<sub>2</sub> in the slag towards equilibrium with spinel results in increase of the  $P_{O_2}$  necessary to achieve the same matte grade at a given total pressure of the O- and S- containing gaseous species.

Table 1. Reactions and corresponding conditions for specific lines in the predominance diagram (Figure 6).

Equilibria	Reactions	Equilibrium constant	Equation for the line
Matte-slag p-q	$FeS(l) + 1/2O_2(g) = FeO(l) + 1/2S_2(g)$	$K_{eq} = \frac{P_{S_2}^{1/2} a_{FeO}}{P_{O_2}^{1/2} a_{FeS}}$	At fixed %Cu in matte: $\log P_{O_2} = \log P_{S_2} + \text{constant.}$
Matte-gas t-p	$1/2S_2 + O_2 = SO_2$	$K_{eq} = \frac{P_{SO_2}}{P_{O_2} P_{S_2}^{1/2}}$	for a constant $P_{SO_2}$ $\log P_{O_2} = \text{Const} - 1/2 \log P_{S_2}$
Matte – blister r-s	$Cu_2S_{liq} = 2Cu_{blister} + xS_{blister} + 1/2(1-x)S_2$	$K_{eq} = \frac{a_{Cu,blister}^2 a_{S,blister}^x P_{S_2}^{(1-x)/2}}{a_{Cu_2S}}$	
Blister –gas C-D	$S_{blister} + O_2 = SO_2$		
Blister –gas D-E	$O_{blister} + CO = CO_2$		



Table 2. Reactions during copper production (Figure 6)

Production step	Reaction
A→B - Smelting:	$2\text{CuFeS}_2(\text{concentrate}) + (4-1\frac{1}{2}y)\text{O}_2(\text{g}) + x\text{SiO}_2(\text{s}) \rightarrow \{\text{Cu}_2\text{S}+y\text{FeS}(\text{l,matte})\} + \{(2-y)\text{FeO}+x\text{SiO}_2(\text{l,slag})\} + (3-y)\text{SO}_2(\text{g})$
B→B' - Slag/matte separation:	$\text{O}_{\text{condensed}} \text{ in matte, sulphates, oxides, slag (e.g. Fe}_2\text{O}_3, \text{Cu}_2\text{O, CuSO}_4)$ $\text{O}_{\text{condensed}} + \text{S}_{\text{matte}} + \text{Fe}_{\text{matte}} + x\text{SiO}_{2(\text{s})} \rightarrow \text{FeO-xSiO}_2(\text{l}) + 3/2\text{SO}_{2(\text{g})}$
B→C - Converting 1. slag blow from matte to white metal	1) $\text{FeS}(\text{l})+1.5\text{O}_2(\text{g})+x\text{SiO}_2(\text{s}) \rightarrow \text{FeO-xSiO}_2(\text{l})+\text{SO}_2(\text{g})$
B→C - Converting 2. blister blow	2) $\text{Cu}_2\text{S}(\text{l})+ \text{O}_2(\text{g}) \rightarrow 2\text{Cu}(\text{l})+ \text{SO}_2(\text{g})$
C→D - Refining: S blow – oxidation (S, removal, gas/liquid)	1) $\text{S}(\text{in Cu})+ \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$
D→E - Refining: O blow – reduction (O removal, gas/liquid)	2) $\text{O}(\text{in Cu})+ \text{CH}_4 \rightarrow \text{CO}/\text{H}_2\text{O}(\text{g})$
Side reaction – oxidation of Cu into slag:	$2\text{Cu}(\text{l, metal/matte})+ 0.5\text{O}_2(\text{g}) \rightarrow \text{Cu}_2\text{O}(\text{slag})$

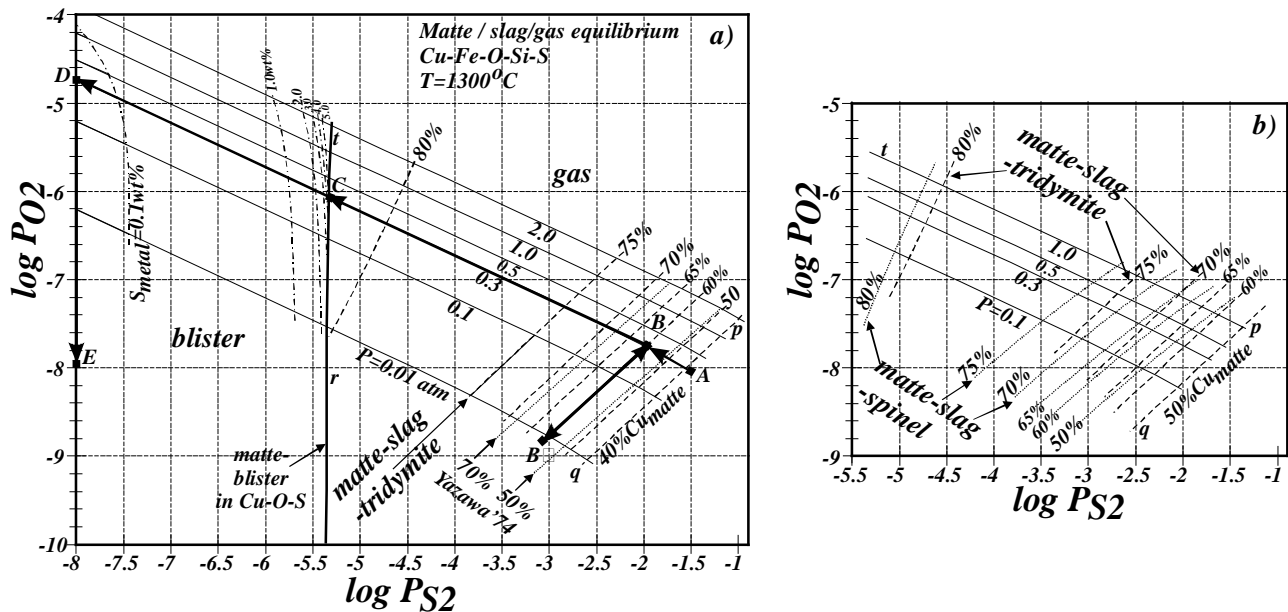


Figure 6. a) S-O predominance diagram for the system Cu-Fe-Si-O-S calculated with FactSage using new slag model [47] for 1300°C, b) Effect of the change in Fe/SiO<sub>2</sub> in slag between the tridymite and spinel liquidus.

Present thermodynamic models can now be used to further investigate complex effects of some of the important operational input parameters on the key smelting process output parameters. The following examples demonstrate such thermochemistry analyses.

The predicted effect of the total pressure, temperature, primary phase (actually Fe/SiO<sub>2</sub> in the slag) and common impurities including CaO, Al<sub>2</sub>O<sub>3</sub> and MgO on the Cu chemically dissolved in slag phase and on the equilibrium P<sub>O2</sub> and Fe/SiO<sub>2</sub> in slag as a function of equilibrium matte grade are illustrated in Figure 7. Note that the maximum total pressure of the O- and S-containing gaseous species of 2 atm is selected for this analysis reflecting possible conditions generated by hydro-static pressure of the matte and slag liquid layers.

Figure 7a) demonstrates that the increase of the total pressure for a given matte grade effects the P<sub>O2</sub> and does not effect the Cu solubility in the slag. The Cu solubility increases with the increase of matte grade. The trend of the Fe/SiO<sub>2</sub> in the slag ion equilibrium with tridymite as well as with the gas and matte phases is shown in the top part of Figure 7a), as well as corresponding top parts of Figures 7b), c) and d).

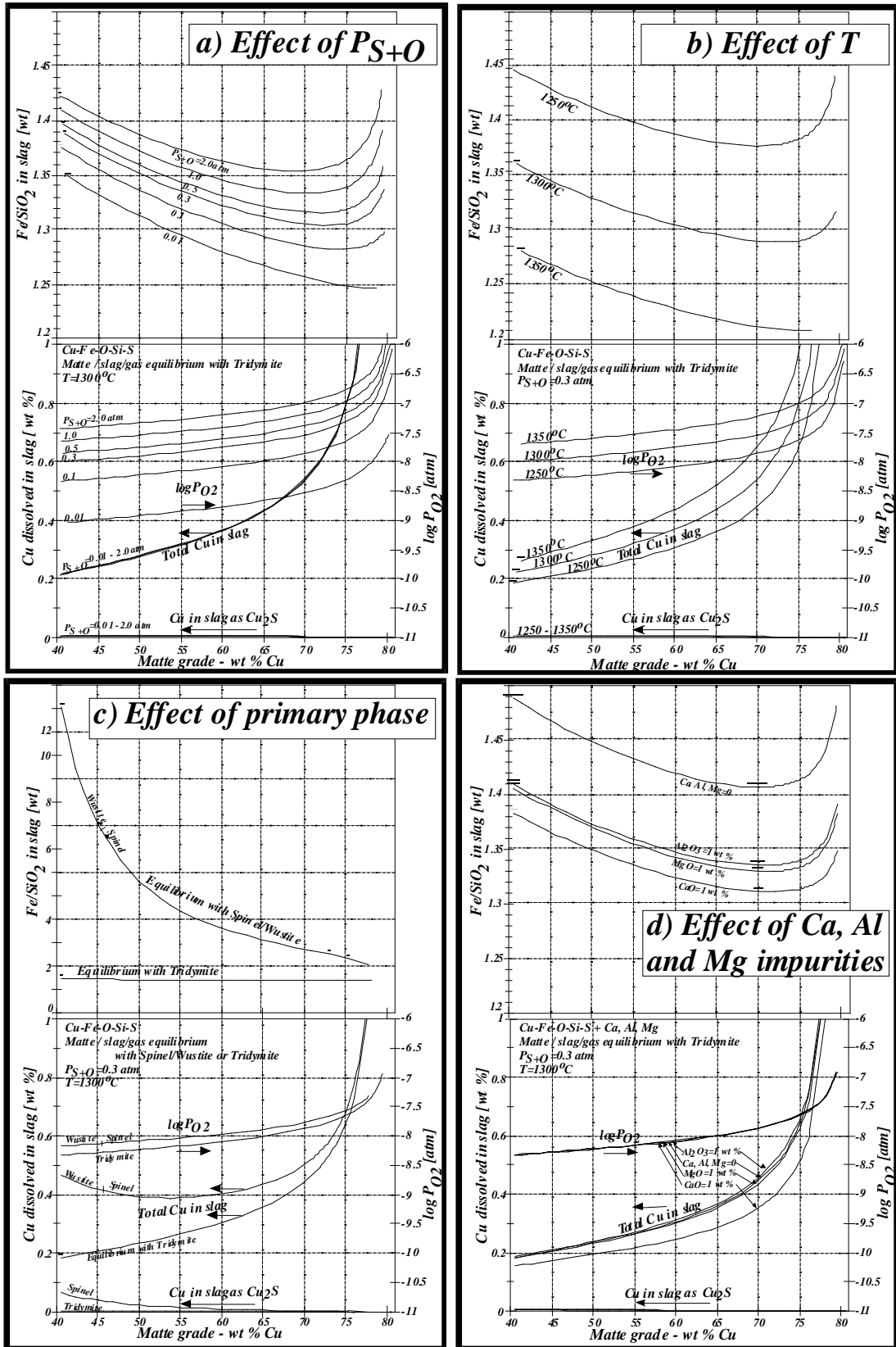


Figure 7. Sensitivity analysis of key smelting process output parameters including chemically dissolved Cu in slag,  $P_{O_2}$  and Fe/SiO<sub>2</sub> in slag in equilibrium with tridymite or spinel, on important input parameters (including a) total pressure = oxygen enrichment, b) temperature, c) primary phase = Fe/SiO<sub>2</sub> in slag and c) CaO, Al<sub>2</sub>O<sub>3</sub> and MgO impurities) for the Cu smelting predicted with FactSage using new slag model [47].

The increase of temperature (see Figure 7b) results in the small increase of the Cu dissolved in slag – this is a cumulative effect of the changing  $P_{O_2}$  and the Fe/SiO<sub>2</sub> in the slag in equilibrium with the tridymite phase.

The effect of the slag chemistry – the Fe/SiO<sub>2</sub> change from the tridymite to spinel equilibria - is predicted to result in the increase of the Cu solubility in slag. This trend may be related to the reaction  $Cu_2S + FeO \leftrightarrow Cu_2O + FeS$

and  $K_{eq} = \frac{a_{Cu_2O} a_{FeS}}{a_{Cu_2S} a_{FeO}}$ , so that  $a_{Cu_2O} = \frac{K_{eq} a_{Cu_2S}}{a_{FeS}} \times a_{FeO}$ , where the first term of the product  $\frac{K_{eq} a_{Cu_2S}}{a_{FeS}}$  is

approximately constant for a given matte grade, and  $a_{FeO}$  increases with Fe/SiO<sub>2</sub> ratio in slag.

The effect of CaO, Al<sub>2</sub>O<sub>3</sub> and MgO impurities are illustrated in Figure 7d), where Al<sub>2</sub>O<sub>3</sub> and MgO are predicted to decrease the Fe/SiO<sub>2</sub> in slag in equilibrium with tridymite, but to have insignificant effect on the Cu solubility in slag. The increase of CaO in slag by 1 wt % is predicted to decrease the Fe/SiO<sub>2</sub> in slag in equilibrium with tridymite and also results in some decrease of the Cu dissolved in slag at a given matte grade.

The effect of Fe/SiO<sub>2</sub> (in the range between the equilibrium with tridymite and with spinel) on the chemically dissolved Cu in slag and on the equilibrium  $P_{O_2}$  predicted with the current thermodynamic databases for given temperatures, matte grades and total pressures are illustrated in Figure 8. In general, the figure demonstrates that the Fe/SiO<sub>2</sub> in the slag in equilibrium with the matte having 55-60 wt % Cu has relatively small effect on the Cu solubility in the slag.

Note that the proportion of Cu dissolved in slag in the form of Cu<sub>2</sub>S is predicted to be negligible.

These predictions of the key input and output operational parameters are given here to illustrate the opportunities for advanced analysis created by the integrated research program that involves a combination of experimental studies and computer thermodynamic modelling.

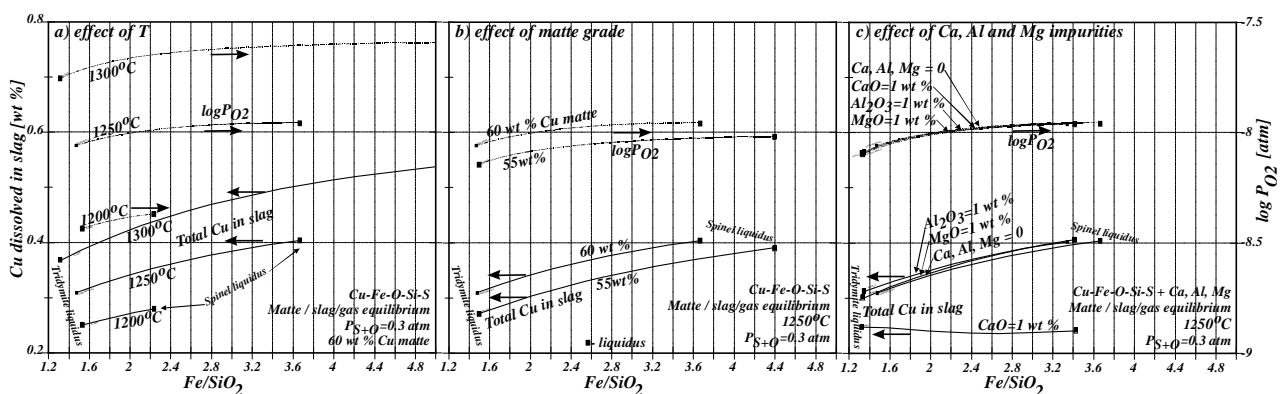


Figure 8. The effects of the Fe/SiO<sub>2</sub> ratio (in the range between equilibrium with tridymite and with spinel) on the chemically dissolved Cu in slag and on the equilibrium  $P_{O_2}$  predicted with the current thermodynamic databases for the matte + slag + gas equilibria at given temperatures, matte grades and total pressures.

### 3.2. Energy predictions – one step reactor model

The use of the advanced experimental and thermodynamic modelling research tools have enabled a high cumulative level of information on the thermochemistry and phase equilibria of the copper smelting systems and a high cumulative level of the understanding of reactions and processes to be achieved. These tools can be used in a different way. For example, they can be involved in identification of priorities of optimisation of the operations – search for the most efficient direction in improvements of the industrial operations can be assisted using thermodynamic modelling. For this purpose a simplified one-step reactor thermodynamic model of the Flash Smelting Furnace was assembled and used for the analysis. Figure 9 illustrates simplified schematic of this one-step-reactor model. Main input and output parameters are given in Table 3. The one-step reactor model takes concentrate with coal and flux as well as air and oxygen blast as an input. A certain proportion of the solid feed is assumed to be physically carried over as a mechanical dust after oxidation in the gas to corresponding sulphates and oxides states. Oxygen efficiency was assumed to be 100% for analysis purposes only (with full understanding this may not be the case, however the fact that no ingress of air due to the negative draft pressure was introduced may offset this). The materials remaining after the mechanical

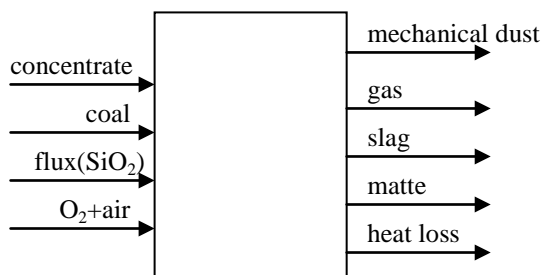


Figure 9. One-step-reactor model.

dust carry over and corresponding reactions of gas with the dust is assumed to reach equilibrium producing gas, matte and slag. The total feed of 100 t/h of chalcopyrite with 50 vol % oxygen enrichment producing 60 wt % Cu matte and  $\text{Fe/SiO}_2 = 1.6$  slag was taken as the base case (some data are taken from the example given by Davenport [70]). Addition of  $\text{SiO}_2$  flux, coal and air were used to adjust output to targeted matte grade,  $\text{Fe/SiO}_2$  in slag and temperature at a given heat loss ( $40000 \text{ MJ/h} = 11.11 \text{ MW}$  per 100 t/h feed rate [70]). Several variants were predicted starting from the base case, then increasing  $\text{Fe/SiO}_2$  in slag, increasing temperature by  $10^\circ\text{C}$ , decreasing heat losses (this may be also viewed as adding enthalpy through air preheat or other measures), and decreasing Cu entrained in slag. Most of the predicted input and output values are listed in Table 3 and are self-explanatory. The concentration of Cu chemically dissolved in slag (row 19) is predicted with the thermodynamic model, and the concentration of Cu physically entrained in slag (row 20) was assumed to be 0.5 wt % for analysis purpose. The total Cu lost into the smelting slag and comparison of Cu losses to the base case are given in rows 21 and 22 respectively. The corresponding Cu production and comparison relative to the base case are given in rows 23 and 24 respectively. The energy saving or consumption due to the Cu lost into slag given in row 26 (no further flotation or other slag cleaning was assumed) are evaluated using the values on total energy for primary Cu production less energy for electro-refining taken from Hayes 2003 [71]. The total coal used, coal per one tonne of Cu produced and corresponding saved coal and saved  $\text{CO}_2$  emissions are given in rows 27 through 30 respectively. Note that the variation in coal use given in row 29 is related to the Cu produced. The

corresponding energy saved was evaluated assuming calorific value of coal used in electric stations to be 24 MJ/kg coal. The number of the 1.5 MW wind mills at 30% capacity equivalent to the energy savings compared to the base case is given in row 32.

Table 3. Flash Smelting Furnace thermodynamic modelling

	Parameter	Changed parameter				
		Base	Fe/SiO <sub>2</sub>	T	Heat losses	Entrained Cu
1	Value of the change	0	+0.4	+10°C	+0.5MW	- 0.1 %
2	Total Feed [t/h]	100.0	100.0	100.0	100.000	100.000
3	Concentrate Feed [t/h]	87.389	89.917	87.317	87.460	87.389
4	O <sub>2</sub> efficiency	1.000	1.000	1.000	1.000	1.000
5	%Mechanical (physical) dust carry over	4.500	4.500	4.500	4.500	4.500
6	Dust added to the fresh feed [t/t]	0.0450	0.0450	0.0450	0.0450	0.0450
7	%O <sub>2</sub> enrichment	50.00	50.00	50.00	50.00	50.00
8	<b>%Cu in matte</b>	<b>60.00</b>	<b>60.00</b>	<b>60.00</b>	<b>60.00</b>	<b>60.00</b>
9	Availability of furnace	0.9	0.9	0.9	0.9	0.9
10	Coal added to the feed [t/t feed]	0.0057	0.0022	0.0065	0.0049	0.0057
11	Enriched air [Nm <sup>3</sup> /h]	33251	33223	33457	32986	33251
12	SiO <sub>2</sub> flux added to the concentrate [t/t conc.]	0.1378	0.1096	0.1378	0.1378	0.1378
13	Fe/SiO <sub>2</sub> in the slag	1.60	<b>2.00</b>	1.60	1.60	1.60
14	T [°C]	1250	1250	<b>1260</b>	1250	1250
15	Heat losses [MW]	-11.11	-11.11	-11.11	<b>-10.61</b>	-11.11
16	logP <sub>O<sub>2</sub></sub>	-7.96	-7.91	-7.89	-7.96	-7.96
17	P <sub>SO<sub>2</sub></sub>	0.40	0.42	0.40	0.41	0.40
18	Generation of slag kg/h	36245	34920	36214	36271	36245
19	% Cu chemically dissolved in slag	0.32	0.35	0.34	0.32	0.32
20	% Cu physically entrained in slag (assumed)	0.50	0.50	0.50	0.50	<b>0.4</b>
21	Cu in slag [t/y]	2350	2350	2386	2352	2065
22	Saved Cu compared to the base [t/y]	0	-64	37	0	-286
23	Total Cu production [t/y]	234380	240859	234183	234540	234666
24	Variation of the Cu production compared to the base case [t/y]	0	6479	-197	160	+266
25	Saved Cu compared to the base [% from production]	0	-0.03	+0.015	0	-0.12
26	Energy variation primary – electrowinning refining [GJ/y]*	0	-7423	4292	-4	-32916
27	Coal used [t/year]	4479	1765	5136	3840	4479
28	Coal used [t/t copper produced]	0.0191	0.0073	0.0219	0.0164	0.0191
29	Variation of coal [t/year] (<0 = saving)	0	-2,839	661	-643	-5
30	Variation of CO <sub>2</sub> [t/year] (<0 = saving)	0	-10,409	2,423	-2,356	-20
31	Variation of energy @ 24 MJ/kg coal [GJ/y] (<0 = saving)	0	-68,130	15,856	-15,421	-131
32	Variations of wind mills [@14191 GJ/y per mill**] (<0 = saving)	0	-5.3	1.4	-1.1	-2.3

\* Total energy for primary Cu [GJ/t] = 116  
 Energy used for electro-refinery of Cu [GJ/t] = 0.81  
 Energy variation (primary – electrowinning refining) [GJ/t] = 115

\*\* Wind mill year production 1.5MW at 30% capacity  
 [GJ/y] = 14191 GJ/y

Results clearly indicate that relatively modest adjustments and optimisation of operational practices can give significant increase of the Cu production and significantly decreased use of energy and CO<sub>2</sub> footprint. This analysis also demonstrates how the selection of priorities in optimisation of the operations can be assisted with advanced theoretical tools. The important advantage of this approach to the modelling of the metallurgical reactors is the fact that the mass and energy balance is predicted together with partitioning of the major and minor elements between phases. Chemical reactions and the final phase compositions predicted using complex thermodynamic models of the multi-component solution phases. The demonstrated approach therefore is superior compared to the common solution of the heat and mass balance based on the use of spreadsheets with fixed partitioning coefficients.

### 3.3. Thermodynamic description of Cu smelting processes

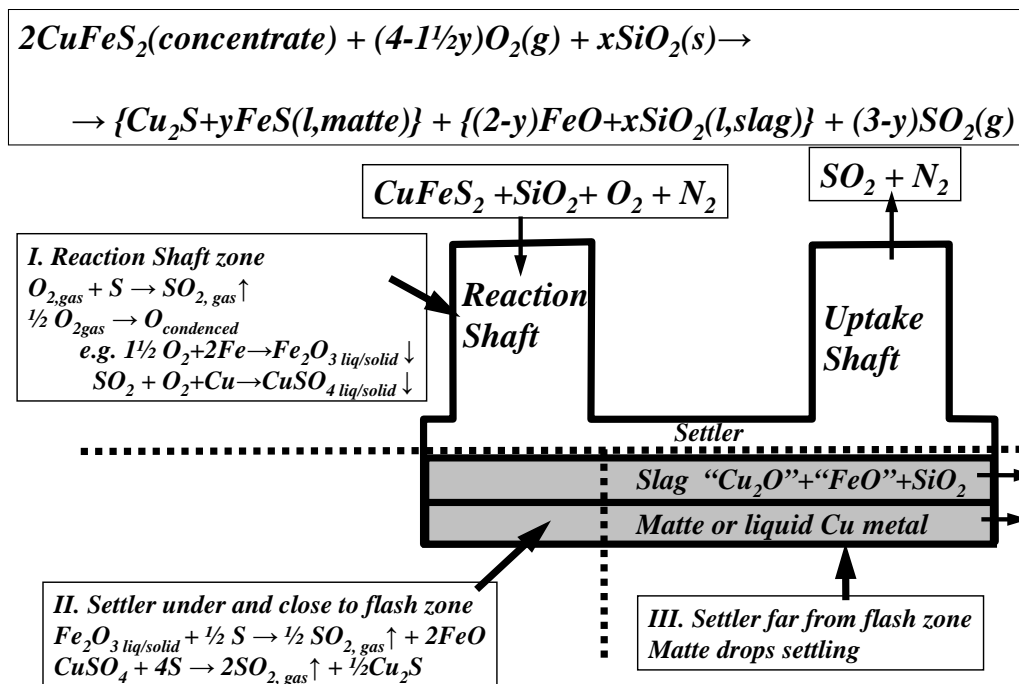


Figure 10. Schematic of the Cu Flash Smelting Furnace.

A one-step reactor approaching equilibrium outlined in the previous section is a common first approximation of some pyrometallurgical processes. Any process, however, represents a combination of areas with different reactions and different conditions in various parts (or locations) of the reactor. The optimisation of any process requires identification of a limiting condition – the “bottle neck” that restricts possible changes of input parameters. This “bottle neck” would appear in one particular location of a reactor with a specific reaction and a condition that can differ from other locations and from the average condition. The one-step reactor approximation assumes the average condition over the whole reactor, and this is clearly an over-simplification. Analysis of the reactions taking place in different locations in the furnace with the purpose to identify the limiting condition (so called “bottle neck”) therefore is believed to be an essential step for any process optimisation, and an example of such an analysis of difference in conditions in various locations in a reactor is given below in this section. Important factor is that this analysis must be accompanied by the experimental and analytical supporting research.

Different reactions taking place in different locations in a Flash Smelting Furnace are illustrated in Figure 10. The flash smelter may be viewed as a three-stage reactor. **I. Reaction shaft:** The oxidation takes place in the Reaction Shaft. Part of the feed (surface of larger particles and whole small particles) is over-oxidised so that the excess of oxygen in the condensed form is produced (e.g. ferric iron  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{CuSO}_4$  etc), at the same time, the core of larger particles may remain un-reacted due to kinetic limitations and stay under-oxidised (e.g.  $\text{FeS}$ ,  $\text{Cu}_2\text{S}$  etc). The over- and under-oxidised particles do not practically react with each other in the reaction shaft due to the low chances of coalescence and relatively slow diffusion of main reactants through the gas phase. **II. Settler under Reaction Shaft:** After most of the material from the reaction shaft (including over- and under-oxidised particles) is plunged into the bath underneath the Reaction Shaft, all particles are forced in direct contact together resulting in establishing condensed

phase interactions, reactions, convective and diffusive mass transfer etc. The condensed oxygen from the over-oxidised particles will react with under-oxidised material including un-reacted sulphides thus producing SO<sub>2</sub> gas. Similar description of some of these reactions and further references can be found in Taskinen [72]. **III. Settler far from Reaction Shaft:** After most of the oxidation / reduction reactions complete in the settler area close to the Reaction Shaft, decantation of the matte droplets from the slag layer may take place in the rest of the settler. Some further particles may still fall down onto the slag from the gas area above the settler, some further reactions may take place between the gas and slag phases and further down in the bath – occurrence and extent of those are expected to be significantly less important than the reactions in and underneath the Reaction Shaft, and the former are yet to be identified; if significant – then four or more stages would have to be introduced into analysis of the Flash Smelter in order to identify specific conditions deviating from the average over the reactor, and therefore particular locations in the reactor that could determine the limit for a possible optimisation of the process (a “bottle neck”).

The improved level of knowledge as well as the advanced level of the research tools now provide new opportunities in detailed and quantitative investigation of the complex reactions taking place in the industrial furnaces; this can greatly assist in the identification of the limits in optimisation of the processes, help to understand the reasons for some operation instability and therefore increase availability and decrease costs of the operations.

#### **4. Conclusions**

Advanced research tools have become available. There is an opportunity now to use these powerful outcomes to improve metallurgical operations. This can only be done through implementation stage. The latter, though, requires high level of expertise and most likely can only be successful if the efforts of technologists with high level of metallurgical expertise are joined together with the experienced researchers in a close collaborative efforts.

The combination of several approaches is believed to be the most efficient and promising approach that should include the following:

- a) continuous laboratory-based fundamental and applied experimental research,
- b) theoretical modelling,
- c) plant tests and experiments, and
- d) systematic implementation program combining collaborative efforts of technologists and researchers.

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