# Integrated Experimental Phase Equilibria and Thermodynamic Modelling Research and Implementation in support of progress of process pyrometallurgy towards sustainability

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**Abstract.** Responding to the many sustainability challenges facing the metallurgical industry, we report progress that has been made on the development of predictive tools that can be applied to a wide range of technologies. The aim is to provide accurate, fundamentally-based thermodynamic tools that can be used by industry to improve process efficiencies, metal recoveries and productivities, and reduce energy requirements of pyrometallurgical systems. The program involves an integrated experimental and thermodynamic modelling research on phase equilibria in complex multi-component, multi-phase gas-slag-matte-speiss-metal-solids system with the $Cu_2O$-PbO-ZnO-FeO-$Fe_2O_3$-CaO-$Al_2O_3$-MgO-$SiO_2$-S major and As-Sn-Sb-Bi-Ag-Au-Ni-Co-Cr-Na minor elements. The experiments involve high temperature equilibration in controlled gas atmospheres, rapid quenching and direct measurement of equilibrium phase compositions with quantitative microanalytical techniques, including electron probe X-ray microanalysis and Laser Ablation ICP-MS. The thermodynamic modelling is undertaken using FactSage software package with advanced thermodynamic solution models. The continuing development of analytical and research methodologies has resulted in significant advances in predictive capability. Implementation of the results of fundamental studies involves ongoing collaboration of researchers and industry technologists, and the provision of advanced professional training. An overview of recent progress in research, implementation and applications in industrial practice will be presented in the paper.

## 1 Introduction

Our present society faces major technological challenges in the form of rapid developments in renewable energy sources, such as solar panels, wind turbines, battery energy storage, and in electric vehicles, electrical and electronic devices. The growth in the production of advanced materials used in these devices has led to significantly increased demands in the amounts, number and combinations of different metals, and, consequently, to significantly increased complexity and variability of metallurgical feed streams, in primary metals production and metals recycling. Most metals undergo some form of pyrometallurgical processing, either in primary production or recycling, so it is essential that these industrial processes be modified, or new processes developed, to address these processing problems.

The research carried out at the Pyrometallurgy Innovation Centre (PYROSEARCH) has been developed in close consultation with our industry partners and is a part of a long-term strategic partnership to provide industry and the research community with state-of-the-art predictive tools, and fundamental information that can be used to improve the efficiency of existing operations and to develop new metallurgical process technologies. Using a knowledge-based approach, fundamental information in conjunction with powerful computer-based predictive tools, delivering accurate and reliable descriptions of phase equilibria and thermodynamics in multi-component systems, can be developed. To this end, an integrated experimental and thermodynamic modelling research program is underway to enable the development of a thermodynamic database for the complex multi-component, multi-phase, gas-slag-matte-speiss-metal-solids "$Cu_2O$"-PbO-ZnO-FeO-$Fe_2O_3$-CaO-$SiO_2$-S-$Al_2O_3$-MgO-$Cr_2O_3$-$Na_2O$-(As-Sn-Sb-Bi-Ag-Au-Ni-Co) system. The strategic target of the program is the digitalisation of pyrometallurgical processes [1] – the development and implementation of computerised Virtual Reactor models of individual reactors, accurately describing the outputs of the processes as a function of input and process conditions, supporting the implementation of feed-forward control and computerised systems for the optimisation of integrated process operations.

Our industry partners are major Australian and international metal processing and recycling companies, and technology developers from around the globe. Current projects are focused on the characterisation of the chemical behaviour and thermodynamic properties

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of systems encountered in the pyrometallurgical, primary and secondary copper and lead processing, ironmaking and the recovery and recycling of non-ferrous metals from end-of-life (EoL) devices..

## 2 Research methodology outline

The integrated experimental/thermodynamic modelling approach developed by the PYROSEARCH team is used as the basis for the development of the thermodynamic databases for the multicomponent systems [2]: *thermodynamic parameters are fixed by new proactively obtained experimental data points rather than by fitting into the pre-existing experimental points from literature*. The continuously improved database will be used for systematic assessment and identification of further new experiments to be carried out in order to provide new key data required to accurately determine the binary and ternary model parameters. This systematic iterative procedure will involve i) the identification of priorities for experiments from thermodynamic assessment, ii) the development and application of advanced experimental and analytical techniques to characterise the required sub-systems, and iii) the revision of parameters through thermodynamic re-optimisation of the required low- and corresponding high-order systems. Steps i), ii) and iii) are repeated thus progressively improving predictions and database accuracy. The new special “agile” formalised semi-automated methodology will be developed and implemented enabling rapid re-optimisation in step iii). Further details of the new methodology are provided below.

### 2.1 High temperature phase equilibria determination.

The development of the advanced analytical and experimental techniques for the systems identified as essential for further database improvement is an important component of the research, and a critical one to achieve the high accuracy and precision of the predictive tools. This last point is a critical factor for industry, who need to have confidence in the predictive tools that will guide future decision making for major capital investments in novel process routes. The advances of the experimental methodology will be based on a strong foundation – the approach that has been pioneered, and is being continuously further developed by the PYROSEARCH team, and that has been proven to be effective in determining phase equilibria in complex high temperature metal systems [3]. The basic approach involves: *i) High temperature equilibration* in controlled multi-phase, condensed phase assemblages (e.g. slag, metal) and/or gas atmosphere ($pO_2$, $pSO_2$) conditions, *ii) Rapid quenching* to retain any liquids present at the equilibration temperature as uniform amorphous (glassy) or microcrystalline phases on cooling to room temperature, and *iii) Microanalysis* to accurately determine the chemical compositions of all phases present using Electron Probe X-ray Microanalysis (EPMA) and Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LAICPMS) techniques. In brief, very small synthetic samples (0.2-0.5g) containing pure or pre-sintered oxide, sulphide, arsenide and/or metal powders are equilibrated below the liquidus temperatures in a thin (0.025-0.1mm) metal foil envelope, or on an open metal substrate, or on a primary oxide phase substrate material in an open system with controlled gas atmosphere (e.g. fixed $pO_2$, $pSO_2$) or in a closed system having a controlled condensed phases assemblage. The compositions of the liquid (quenched glass or microcrystalline phases at room temperature) and solid phases are then directly and accurately measured in polished cross-sections of the samples. The extents of solid and liquid solutions in equilibrated phases are directly measured providing essential data for subsequent thermodynamic modelling. A simplified phase diagram with the bulk composition deliberately selected to be in a multiphase phase assemblage when at equilibrium at the equilibration temperature is shown in Figure 1a) and an example of the phase assemblages that can be characterized for the determination of phase equilibria shown in **Fig. 1**b) [3, 4].

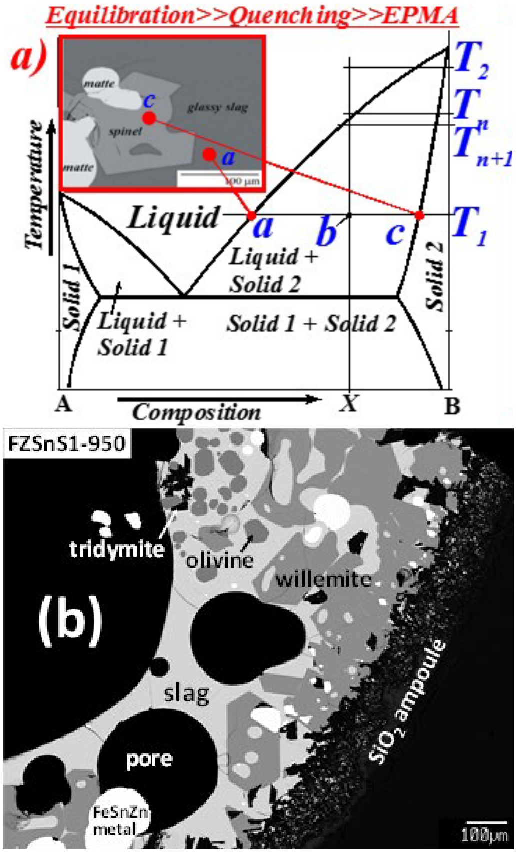

**Fig. 1.** a) Schematic illustration of the experimental technique based on microanalysis [3], b) example of microstructure of gas-slag-metal-willemite-olivine-tridymite equilibrium sample

The database-development-driven selection of priorities for experimental data, significantly expanding the range of systems and conditions to be investigated, and continuously increased requirements for accuracy of experimental data require increasing experimental complexity. The experimental challenges include, but are not limited to, the proof of achievement of equilibria, quenching, gas control, selection of containment / support, high temperatures, liquid immiscibilities, new combinations of phases (e.g. see Figure 2), microanalysis accuracy. Each combination of phases and species will require development of a different detailed experimental design and methodology. The range of advanced approaches that will be applied include, but is not limited to those listed below. Closed system experiments involving sealed silica ampoules will be used for the systems with volatile components; the targeted condensed phase assemblage is defined based on the Gibbs Phase Rule. Substrates used to support the samples are selected from a wide range of materials (including Ir, Re, Pt, Pd, Rh/Pt, Au, Mo, Fe, Co, Ni, Cu, selected ceramics, or primary solid phases), the selection depending on the chemical characteristics of each sub-system and the combination of phases present. For example, Ir metal will be used for: a) systems with metallic Pb, Cu, Ag, Au liquids – because Pt dissolves in these metals whereas Ir does to much less extent; and b) experiments >1700°C – when Pt melts. Similarly, Re will be used for systems with metallic Sn, Sb, Cr at very reducing conditions. Application of the 4-point test to ensure achievement of equilibrium is essential for developments of the individual experimental methodologies; it includes testing the effects of equilibration time, of phase homogeneity, of direction of approach to equilibria, and, importantly, analysing possible reactions and reaction mechanisms.

## 2.2 Thermodynamic modelling

Thermodynamic calculations are performed using the FactSage computer package [5] with advanced thermodynamic solution models. All thermodynamic and phase equilibrium data for the system are evaluated simultaneously to obtain a unique, self-consistent set of model equations and parameters for the Gibbs energies of all phases as functions of temperature and composition accurately describing all values over the complete range of conditions. The binary and ternary parameters are extrapolated into the multi-component ranges of compositions using the predictive power of the currently available sophisticated thermodynamic models used in this study.

### *2.2.1 "Agile" semi-automated thermodynamic database development methodology*

A major issue emerging in the development of multicomponent databases is the exponential increase in chemical interactions to be described with the increasing number of components. Adding a single component, or even incorporating new experimental data into the database, requires the iterative re-optimisation of all low-order and corresponding high-order systems; a significant task when handling a 20 component system that has 190 binary and 1140 ternary sub-systems. If there are no experimental data – there can be no reliable thermodynamic parameters, and consequently no reliable model.

A new "agile" semi-automated thermodynamic database development methodology has been developed to tackle this problem and to be able to efficiently update the databases, a new optimisation methodology will be implemented by the team in this project. The key points in this new methodology are as follows. The sets of target experimental points to be described and corresponding weights will be selected based on the experimental information available. A matrix of first derivatives showing the sensitivity of each target point to each possible model parameter will be calculated using traditional Gibbs energy minimization calculations, which is a relatively slow step. The initial slow Gibbs energy minimisation calculations will then be replaced by a fast analytical approach with linear extrapolation of the existing values through matrix multiplications of the form:

$$\Delta\bar{y} = \mathbf{A}\cdot\Delta\bar{x} \tag{1}$$

where A is the matrix of first-order derivatives (n target values by k model parameters),

$$\Delta\bar{x} = \bar{x} - \bar{x}_0 \tag{2}$$

is the difference between the final set of model parameters and their initial approximation, an

$$\Delta\bar{y} = \bar{y} - \bar{y}_0 \tag{3}$$

is the difference between the final model predictions and model predictions at $\bar{x}_0$ . The optimum values of the model parameters $\bar{x}_{optimal}$ are obtained by solving the relationship:

$$\bar{x}_{optimal} = \bar{x}_0 + \left(\mathbf{A}^T\cdot\mathbf{A}\right)^{-1}\cdot\mathbf{A}^T\cdot\left(\bar{y}_{\text{target}} - \bar{y}_0\right) \tag{4}$$

for the condition

$$\bar{y} \to \bar{y}_{\text{target}} \tag{5}$$

This non-iterative analytical (rather than numerical) optimization approach is orders of magnitude faster than the combination of the thermodynamic calculations using Gibbs energy minimisation and numerical non-linear minimisation.

The first-derivative-based linear extrapolation approach will also enable a) the real-time graphical presentation of predicted and target points as well as b) the real-time systematic tabular presentation of the statistical analysis of agreement between predictions and target values, which makes the optimisation process truly interactive. Also, the new formalised and semi-automated methodology will make it possible to increase the efficiency and flexibility of collaborative work between researchers by organising parallel simultaneous optimisations by several researchers, thus distributing the database development efforts between the research team: once the procedure to optimise the model parameters is formalised and semi-automated, the group of researchers each will contribute to the thermodynamic parameters optimisation by planning and undertaking new experiments, adding corresponding target points and correcting weights, rather than "manually" optimising model parameters. Thus the discrepancies and conflicts within the system will be resolved by the formalised semi-automated system significantly more efficiently and with less oversight. Only periodically will the re-calculations using Gibbs energy minimisations be needed to update the matrix of derivatives. The new methodology will enable researchers undertaking experimental work on a particular sub-system to personally contribute to the thermodynamic optimisation of that system and to select further experimental target points further increasing productivity. Optimisation will be undertaken in iterative cycles, the major discrepancies will be identified at each step, and new experiments will be conducted to resolve discrepancies within time intervals from several days to several weeks rather than months and years using the more traditional approaches.

## 3 Outline of the current research program

Present program is focused on the integrated experimental characterization and thermodynamic database development research of the 19-component system "$Cu_2O$"-PbO-ZnO-CaO-FeO-$Fe_2O_3$-$SiO_2$-S-[$Al_2O_3$-MgO-$Cr_2O_3$]-(As-Bi-Sb-Sn-Ag-Au-Ni-Co). The program is currently extended to also incorporate $Na_2O$.

Effective planning and management of the present research is essential. All the elements are divided into the major elements PbO-ZnO-"$Cu_2O$"-FeO-$Fe_2O_3$-CaO-$SiO_2$-S-$Al_2O_3$-MgO, minor slagging $Cr_2O_3$-$Na_2O$ and other As, Sn, Sb, Bi, Ag, Au, Ni, Co minor elements groups. The transition from the minor to the major group (currently in progress for MgO) is made after all corresponding low order 2-, 3- and 4-metal major elements sub-systems have been sufficiently experimentally characterized. The matrix of conditions is shown in **Table 1**. The research is divided into three streams; 1. Slag / metal (S-free); 2. Slag/matte, metal, sulphates (S-containing); and 3. Speiss/matte/metal (no slag). For each of these streams the work is planned in 4 sub-directions including i) 2- & 3-Me major elements subsystems; ii) 2- & 3-Me minor elements subsystems; iii) 4- and more Me major elements subsystems; and iv). Minor elements slag / matte / metal distributions. The work is progressing simultaneously in all directions following the criteria of maximum value to the sponsors.

An iterative approach is used. A preliminary database is developed and used a) to identify discrepancies, b) to plan experiments, and c) to enable predictions by sponsors. The new experimental data for low and high order systems are continuously obtained and iteratively incorporated into the multicomponent database gradually improving the accuracy of the predictions. The number of systems targeted for investigation and their status is shown in **Fig. 2**.

**Table 1**. Outline of elements included in the program and matrix of conditions.

| | Cu Systems | Pb Systems |
|---|---|---|
| Minor slagging: | "$Cu_2O$"-FeO-$Fe_2O_3$-$SiO_2$-S-CaO-$Al_2O_3$-MgO | PbO-ZnO-"$Cu_2O$"-FeO-$Fe_2O_3$-CaO-$SiO_2$-S-$Al_2O_3$-MgO |
| Minor slagging: | $Cr_2O_3$+ $Na_2O$ | $Cr_2O_3$+ $Na_2O$ |
| Other minor: | As, Zn, Pb, Sn, Sb, Bi, Ag, Au, Ni, Co | As, Sn, Sb, Bi, Ag, Au, Ni, Co |
| Fe Chemistry: FeO-$Fe_2O_3$-$SiO_2$-CaO-$Al_2O_3$-MgO | | |
| *Phases*: gas / slag / matte / metal / speiss / solids (several dozens) | | |
| *Key parameters*: complete range of T, $P_{O2}$, $P_{SO2}$, Fe/$SiO_2$ , Fe/CaO | | |

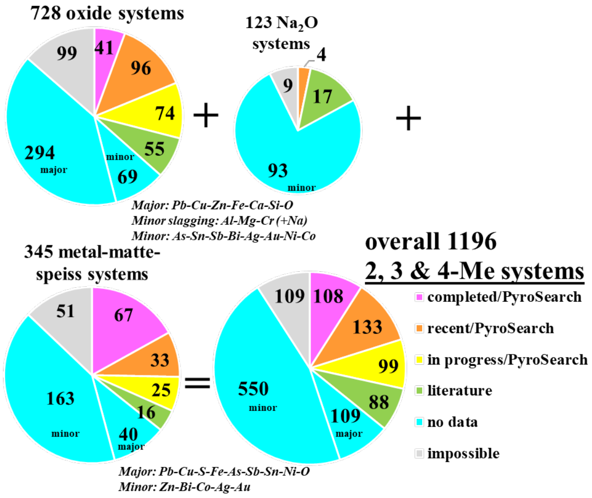

**Fig. 2.** Representation of the number of chemical systems to be characterized to accurately describe the major elements PbO-ZnO-"$Cu_2O$"-FeO-$Fe_2O_3$-CaO-$SiO_2$-S-$Al_2O_3$-MgO, minor slagging $Cr_2O_3$-$Na_2O$ and other As, Sn, Sb, Bi, Ag, Au, Ni, Co minor elements groups.

## 4 Fundamental Research Outcomes

### 4.1 Recent advances in experimental methodology

The experimental research methodology is continuously further developed to enable significant further extension of the range of systems, compositions, temperatures and conditions that can be investigated, and to significantly improve the accuracy of the experiments. Different combinations of elements, phases and conditions require development of special experimental design and methodology. A variety of substrates (primary oxide phases, Pt, Pd, Ir, Re, Pt/Pt, Rh, Au, Mo, W, Fe, Co, Ni, Cu) in open systems and ampoules in closed experiments enable phase combinations to be investigated, including silica-free slags, molten sulphides (mattes), sulphates, speiss and liquid metals. See **Fig. 3** with examples of multi-phase equilibria. Four-point for achievement of equilibrium which includes [6] the effects of equilibration time, of phase homogeneity, of direction of approach to equilibria, and analysing possible reactions and reaction mechanisms. Other areas of improvement include optimization of the operation parameters of electron probe microanalysis (probe diameter, current, voltage, peak and background positions, time spent on peak and background, selection of measured K/L/M lines). This allows peak overlaps (such as Fe-Co, Co-Ni, Ni-Cu, As-Pb, Bi-Pb, Sn-Sb, Ca-Sb, etc.) to be minimized. Optimization of beam conditions enables secondary X-ray fluorescence from adjacent material to be minimized or eliminated, thus avoiding the overestimation of solubilities of certain elements (particularly Fe, Ni, Cu, Zn) in phases that actually do not dissolve these in significant quantities (such as $SiO_2$, Ca silicates, $Al_2O_3$, etc.) [7, 8].

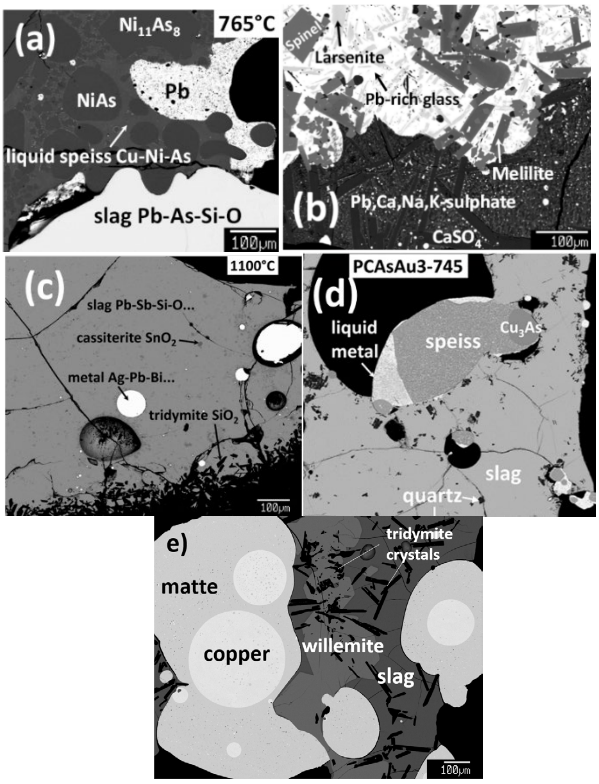

**Fig. 3.** Examples of recent multiphase samples a) oxide slag + Pb metal + speiss (high Cu, As, Ni) + Ni-As solids; b) product of slow cooling of high-Pb slag c) product of anode slime treatment with slag in equilibrium with Ag-rich metal; d) study of Au distribution between slag, Pb metal, liquid Cu-As speiss, and solid $Cu_3As$; e) Zn distribution fayalite slag, Cu metal, Cu-Fe-S matte.

## 4.2 Recent advances in thermodynamic modelling

Recent accurate and detailed experimental measurements have revealed a number of uncertainties associated with the currently used Quasichemical model of the slag phase. A number of systematic theoretical are outlined in the following sections.

### *4.2.1 Correcting the heat capacities of solid and liquid phases.*

Previous (current) databases contain oversimplified descriptions of heat capacities of elements and compounds in which usually a single function of temperature is assigned to all phases of the same composition, i.e. all polymorphs and corresponding liquid (e.g. quartz, tridymite, cristobalite, and liquid/amorphous $SiO_2$). This approach, although providing descriptions for all phases above 25°C (298 K), it does not accurately define the real experimental data on heat capacities of many phases. These simplified descriptions result in step-like changes in heat capacities (and therefore entropies, enthalpies and Gibbs free energies) at melting points of the endmembers and corresponding multicomponent solutions. Most importantly, liquid solutions (slags) calculated from the liquid endmembers typically exhibit heat capacities 20-40% higher than the combination of solid endmembers for the range of temperatures relevant to industrial practice (700-1700 °C). The models therefore do not then accurately represent the physical reality of the system. To compensate for these errors, historically artificial distortions in the interaction parameters between the liquid species had to be introduced thus significantly limiting the predictive power of the database; this is becoming increasingly problematic with the increased solution complexity. Also, little effort was taken to ensure physically relevant descriptions of the heat capacities below the room temperature (down to 0 K) and at very high temperatures (above the melting point of solid endmembers). This often results in a) the erroneous prediction of liquid phase present at very low temperatures, solids at very high temperatures, and liquid miscibility gaps in the ranges of compositions and conditions where they are not actually observed, and b) internally inconsistent values of absolute entropies (which should strictly follow the Third Law of Thermodynamics and converge to 0 $J \cdot mol^{-1} \cdot K^{-1}$ at 0 K for all solid and supercooled liquid phases), and therefore in distorted temperature dependences of many related thermodynamic functions, including the distributions of valuable elements. To address this problem, correction of the $SiO_2$, CaO, $Al_2O_3$ and MgO liquid endmember heat capacities has been carried out to improve the thermodynamic description of common glassy slags down to room temperature (**Fig. 4**).

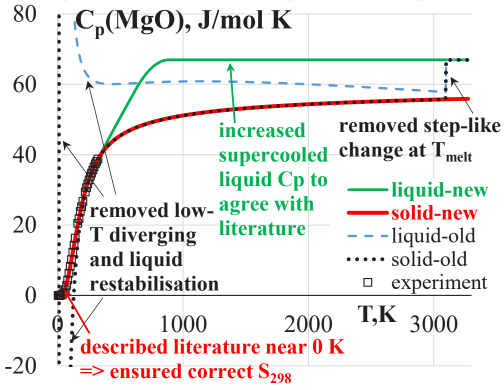

**Fig. 4**. Example of heat capacity vs temperature

### *4.2.2 Gibbs free energies at high temperatures.*

Extensive and accurate experimental results obtained by the PYROSEARCH team at temperatures up to 1750°C have revealed significant uncertainties in the description of Gibbs free energies of high melting temperature pure and binary compounds at higher temperatures (above 1750 °C). Melting temperatures and enthalpies of a number of compounds (CaO, $Ca_2SiO_4$, $Al_2O_3$, MgO) have had to be corrected by the team within previous ARC Linkage Projects. Similarly, it is proposed in the present project to review and correct the melting points and enthalpies of melting of a number of other high-temperature melting compounds, including but not limited to $SnO_2$, $Mg_2SiO_4$, CoO.

### *4.2.3 Revising high-$SiO_2$ liquid*

Accurate EPMA measurements of phase compositions and systematic high-temperature experiments in high-$SiO_2$ areas recently performed by the PYROSEARCH team have demonstrated that the currently used Quasi-chemical thermodynamic model of the $SiO_2$-containing liquids cannot accurately describe the experimental data in the areas of the tridymite/cristobalite liquidus, the monotectic and the miscibility gaps in the Me-Si-O systems (Me = Ca, Mg, $Fe^{2+}$, $Fe^{3+}$, Zn, Cu, Ni, Co, Cr...). The reason for these systematic difficulties has been attributed to the fact that the Modified Quasichemical Formalism (MQM) only accounts for nearest neighbour interactions in the slag, assumed to be 100% ionic liquid. The high-$SiO_2$ liquids, however, are not fully ionic (weak electrolytes), thus resulting in the long-range electrostatic interactions between the uncompensated charged $M^{x+}$ cations and $O^{2-}$ anions, an effect similar to the Debye-Hückel model and clustering well known to be present in the diluted aqueous solutions. Identification and understanding of the underlying reasons for these behaviours provides the opportunity to adjust the models by i) introducing a correction to the Gibbs energy of mixing (**Fig. 5**) of the components in the form of a polynomial sequence so as to more closely simulate the long-distance ionic interactions (Debye-Hückel / clustering) in dilute $MO_x$ solutions in $SiO_2$; that in turn enables ii) the minimisation or removal of the unrealistic entropy (T-dependent) terms with high power on $SiO_2$ that were commonly used in previous optimisations for binary systems and resulted in inaccurate extrapolation to the ternaries, and iii) brings the entropy of mixing of the slag phase much closer to the ideal mixing limit in the experimentally determined immiscible regions. The introduction of these enthalpy and entropy of mixing corrections enabled the tridymite / cristobalite liquidus to be more accurately described in the key binary systems, such as "FeO"-$SiO_2$, CaO-$SiO_2$, MgO-$SiO_2$, $CuO_{0.5}$-$SiO_2$, NiO-$SiO_2$. For example, these improvements enabled the elimination of the 2-5 wt. % (~50-100 °C) uncertainty in the prediction of the tridymite / cristobalite liquidus in the FeO-$Fe_2O_3$-CaO-$SiO_2$, system in reducing and oxidising conditions and thus significantly improve the accuracy of the database. Introducing description of these long-range interactions will potentially improve the description of the minor element distributions in multicomponent systems, and will allow the use of smaller ternary parameters in the $MO_x$-$M'O_y$-$SiO_2$ systems, essentially treating them as near-ideal within the Quasichemical formalism. This approach will be extended to all $SiO_2$-containing subsystems. This will significantly improve the accuracy and predictive capability of the liquid slag model.

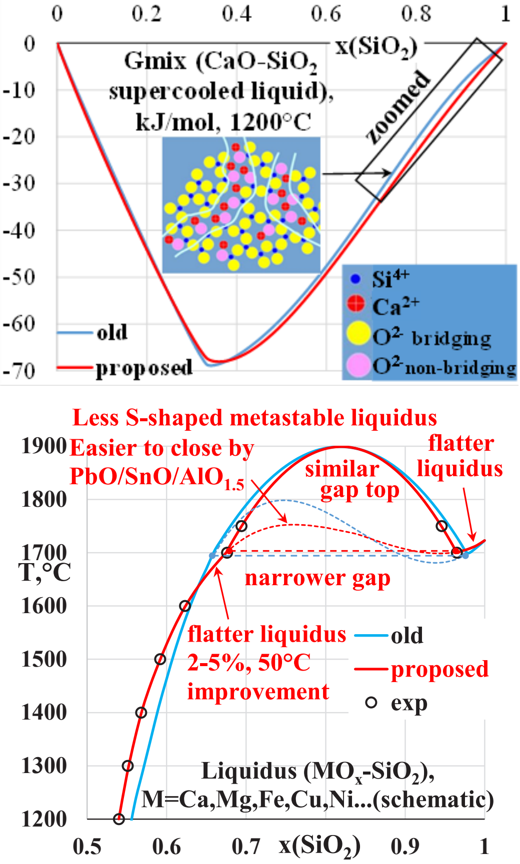

**Fig. 5.** Example of the correction of the high-$SiO_2$ slag model taking into account the different structure of the slags in high and low silica composition ranges.

### *4.2.4 Correcting the slag thermodynamic description around maximum ordering*

The Modified Quasichemical Model (MQM) formalism adopts a one-dimensional solution (Ising model) as an approximate description of the correlation between the entropy of mixing and the strength of the second nearest bonds (the 3D solution of the Ising Model is not available). This 1D approximation works quite well for most systems, but in the cases of strong interactions the limitations of the 1D approximation can become significant, e.g. resulting in a sharp reversal in gradient at the minimum of the enthalpy/entropy of mixing and consequently of the Gibbs free energy of the slag (see **Fig. 5**). For example, this sharp change means it is not possible using the MQM model alone to describe experimental data in the $Ca_2SiO_4$ primary phase field in the $Fe_xO$-CaO-$SiO_2$ system (**Fig. 6**). The following approaches are proposed to rectify this issue: i) introduce a special polynomial sequence describing the enthalpy of mixing to reduce the "sharpness" of the tip at the composition of maximum ordering and ii) limit the configurational entropy of mixing to within ±2 $J \cdot mol^{-1}$ $K^{-1}$ based on the available statistical physics theory. Systematic corrections of the entropies of mixing for all relevant binary systems will be undertaken as part of this project to improve the accuracy of the descriptions and predictions of the database in these multicomponent systems.

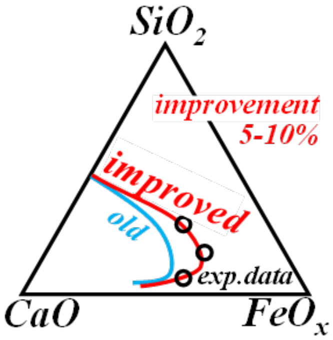

**Fig. 6.** Schematically shown $Ca_2SiO_4$ primary phase field in the CaO-FeO-$Fe_2O_3$ system at constant temperature.

### *4.2.5 Optimised Solution models*

As part of the process of preparing accurate optimised thermodynamic descriptions of the many chemical sub-systems it is necessary to develop appropriate databases for the extensive solutions present in solid, liquid and gas phases. **Table 2** provides a summary of the current PYROSEARCH database. Most solutions are non-ideal in their chemical behaviour so appropriate selection of thermodynamic models is necessary to best describe these individual systems.

## 5 Implementation

### 5.1 Example: WEEE smelting

The NiO-$Al_2O_3$-$SiO_2$ system is relevant for multicomponent slags formed at high-temperature recycling of waste electronic and electrical equipment (WEEE). In this process, recovery of Ni and corrosion of furnace refractory wall by slag can be modelled using multicomponent thermodynamic database designed for complex systems of non-ferrous pyrometallurgy [1]. Accurate experimental data on the phase equilibria in the system are needed. These data are used to optimize the values of interaction parameters in thermodynamic models for slag and solid phases within the database.

Only one paper was found in literature focused on phase equilibria in the NiO-$Al_2O_3$-$SiO_2$ system [9]. That study was based on assessment of binary sub-systems, with experiments in the ternary system limited only to a few joins. Thus, high-temperature phase equilibria study was designed to find equilibrium compositions of slag and solid phases for a wide range of temperatures.

The liquidus projection of the NiO-$Al_2O_3$-$SiO_2$ system has been selected for the experimental study within the 1470-1740 °C temperature range in air atmosphere. Within a given temperature range, the system is not sensitive to oxygen partial pressure, since all components exhibit single oxidation state: $Ni^{2+}$, $Al^{3+}$ and $Si^{4+}$. The experimental results can be applied to the conditions of WEEE recycling, which typically performed in equilibrium with metallic alloy. The substrates made of Pt, PtIr or Ir in a form of wire or foil were used as holding materials during the equilibration.

Experiments covered primary phase fields of NiO (monoxide), $NiAl_2O_4$ (spinel), $Al_2O_3$ (corundum), $Al_6Si_2O_{13}$ (mullite), $SiO_2$ (cristobalite) and $Ni_2SiO_4$ (olivine). A ternary compound close to $Ni_5Al_6SiO_{16}$ stoichiometry [10] has been identified. The most challenging part of the study was the measurement and modelling of tie-lines for the high temperature liquid miscibility gap adjacent to the NiO-$SiO_2$ side. Solubility of $AlO_{1.5}$ in NiO monoxide was determined as a function of temperature between 1530 and 1740 °C. The parameters of thermodynamic models have been optimized to obtain good description of experimental data. The resulting liquidus projection of the NiO-$Al_2O_3$-$SiO_2$ system is provided in **Fig. 7**.

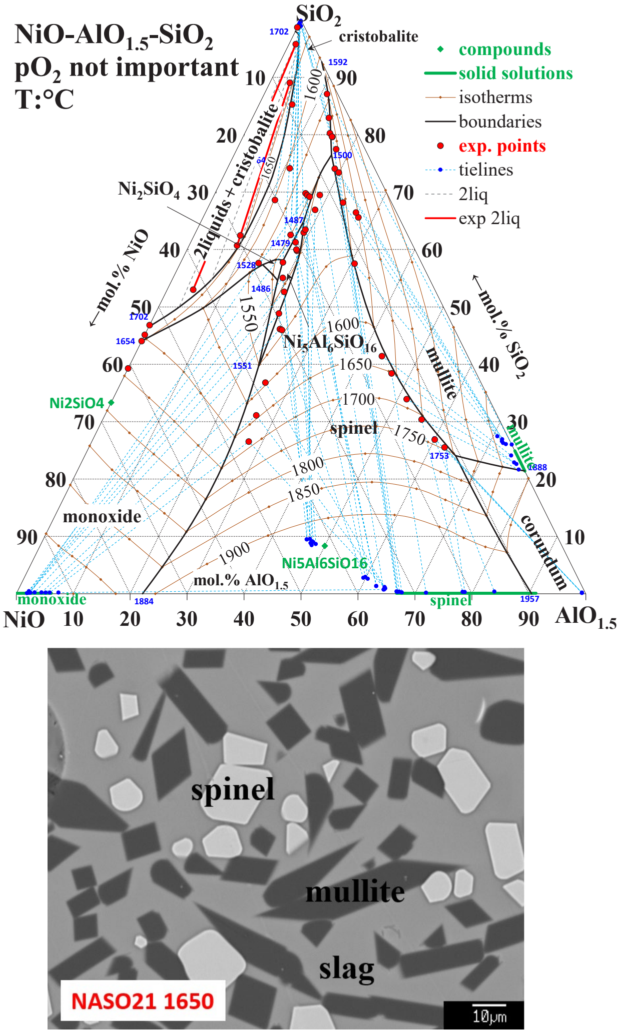

**Fig. 7.** Liquidus projection of the NiO-$Al_2O_3$-$SiO_2$ system Symbols are experiments, solid lines are thermodynamic model calculations. Example of one experimental point is provided on the micrograph.

### 5.2 Laboratory-scale characterization and modelling of complex multi-component systems

To provide the sponsor companies verification of the accuracies of the thermodynamic databases and the predictions using the computer-based tool laboratory-scale experiments are carried out to reproduce the conditions encountered in industrial practice. The systematic investigation involves:

- Reviewing and confirming the industrial process conditions including chemical compositions, temperature, partial pressures including $p(O_2)$, $p(S_2)$, $p(SO_2)$ as appropriate.

- Preparing preliminary model predictions of the system using the revised database.
- Undertaking a series of experiments in the well-controlled laboratory conditions identified during step 1 to accurately reproduce complex industrial chemistry.
- Analysing and comparing specially quenched industrial plant and laboratory samples and thermodynamic predictions.
- If necessary, improving the thermodynamic database through new targeted cycle of low order experiments and thermodynamic optimization.

The aims of this program are to a) increase the accuracy and reliability of the predictions and b) provide confidence in the use of these predictive tools in industrial applications.

**Table 2**. Summary of phases in the current database for the pyrometallurgical processing and the thermodynamic models used to describe these. MQM = Modified Quasichemical Model [11, 12], CEF = Compound Energy Formalism [13, 14], B-W = Bragg-Williams ideal mixing model.

**Slag:** $(Cu^{+1}, Fe^{+2}, Fe^{+3}, Si^{+4}, Al^{+3}, Ca^{+2}, Mg^{+2}, Pb^{+2}, Zn^{+2}, Ni^{+2}, Co^{2+}, Sn^{+2}, Sn^{+4}, Sb^{+3}, As^{+3}, As^{+5}*, Bi^{+3}, Ag^{+1}, Au^{+1}, Cr^{2+}, Cr^{3+}, Na^{+}*)(O^{-2}, S^{-2})$, MQM (*recent/in progress)
**Liquid matte/metal/speiss:** $(Cu^{I}, Cu^{II}, Fe^{II}, Fe^{III}, Pb^{II}, Zn^{II}, Ni^{II}, Sn^{II}, Sb^{III}, As^{III}, Bi^{III}, Ag^{I}, Au^{I}, Cr^{II}, Co^{II}, Ca^{II}, Mg^{II}, Na^{I}*, O^{II}, S^{II})$, MQM
**Liquid salt** (Ca, Mg, Pb, $Na_2$*, Zn)($SO_4$), MQM
**Spinel:** $[Cu^{+2}, Fe^{+2}, Fe^{+3}, Ni^{2+}, Al^{+3}, Mg^{+2}, Zn^{+2}, Cr^{2+}, Cr^{3+}, Co^{2+}, Co^{3+}]^{tetr}[Cu^{+2}, Fe^{+2}, Fe^{+3}, Ni^{2+}, Cr^{3+}, Al^{+3}, Ca^{+2}, Mg^{+2}, Zn^{+2}, Sn^{4+}, Co^{2+}, Co^{3+}, Vacancy^{0}]_2^{oct}O_4$, CEF
**Monoxide:** (FeO, $FeO_{1.5}$, NiO, CoO, $CrO_{1.5}$, $AlO_{1.5}$, CaO, MgO, CuO, ZnO), B-W
**Corundum:** ($FeO_{1.5}$, $AlO_{1.5}$, $CrO_{1.5}$, $SnO_{1.5}$, NiO), B-W
**Mullite:** $(Al^{3+}, Fe^{3+}, Cr^{3+})_2(Al^{3+}, Sn^{4+}, Si^{4+})(O^{-2}, Vacancy^{0})_5$, CEF
**Olivine:** $[Fe^{2+}, Ni^{2+}, Co^{2+}, Cr^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}]^{M2}[Fe^{2+}, Ni^{2+}, Cr^{2+}, Co^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}]^{M1}SiO_4$, CEF
**Melilite:** $[Ca^{2+}, Pb^{2+}]_2[Al^{3+}, Zn^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}][Fe^{3+}, Al^{3+}, Si^{4+}]_2O_7$, CEF
**Pyroxenes (proto-, clino-, ortho-):** $[Fe^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}]^{M2}[Fe^{2+}, Fe^{3+}, Mg^{2+}, Al^{3+}, Ni^{2+}, Zn^{2+}]^{M1}[Fe^{3+}, Al^{3+}, Si^{4+}]^{B}Si^{A}O_6$, CEF
**Dicalcium silicates:** ($Ca_2SiO_4$, $Fe_2SiO_4$, $Mg_2SiO_4$, $Pb_2SiO_4$, $Zn_2SiO_4$, $Ni_2SiO_4$, CaO), B-W
**Wollastonite, pseudowollastonite:** ($CaSiO_3$, $FeSiO_3$, $MgSiO_3$, $ZnSiO_3$, $PbSiO_3$), B-W
**SFCA:** $[CaO, FeO][Fe_2O_3, CaSiO_3, Va][Fe_2O_3,Al_2O_3]_2$, CEF
**Willemite:** $[Zn^{2+}, Fe^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}][Zn^{2+}, Fe^{2+}, Mg^{2+},Ni^{2+}, Cu^{2+}]SiO_4$, CEF
**Feldspar:** $(Ca, Pb, Na*, Va)[Al, Zn][Al, Si]_3O_8$, CEF
**Zincite:** (ZnO, FeO, $Fe_2O_3$, $Al_2O_3$, CaO, MgO, CuO, NiO, $SnO_2$, $Ca_2Fe_6Zn_6O_{17}$), B-W
**Melanotekite:** $Pb_2(Fe,Al)_2Si_2O_9$, B-W
**Larsenite:** $Pb(Zn, Mg, Fe, Ni)SiO_4$, CEF
**Magnetoplumbite:** $(PbO,CaO)[Fe_2O_3,PbFeO_2,PbZnO_2,Al_2O_3][Fe_2O_3,Al_2O_3]_5$, CEF
**Delafossite:** $[Cu^{+}][Al^{3+}, Fe^{3+}, Cr^{3+}, Sn^{3+}]O_2$, B-W
**Fcc and bcc solids alloys:** (Fe, Cu, Ni, Co, Cr, O, S, Pb, Zn, As, Sn, Sb, Bi, Ag, Au), B-W
**Digenite-bornite:** ($Cu_2S$, FeS, PbS, ZnS, $Ni_2S$, $Ag_2S$, $Vacancy_2S$), B-W
**Villamaninite:** $(Cu, Ni, Fe)S_2$, Millerite (NiS, CuS), B-W
**Sphalerite, wurtzite** (Zn, Fe)S
**Pb-Ag-Au-Zn compounds and solutions**
**Pb-Ca-Mg-Bi compounds and solutions**
**MeS_cubic**: (FeS, PbS, CaS, MgS, $Cu_2S$, Vacancy, S), B-W
**$(Cu, Ni)_7As_3$**, B-W;
**$Cu_3As$** (solid speiss): $(Cu^{I}, As^{III}, Ag^{I}, Au^{I}, Fe^{I}, Ni^{II})$, MQMQA
**ORTH** $[Fe, Ni][As, Sb, S]_2$, CEF;
**GAMM** $Cu_3X$ (Cu, Ni, Sb, Sn) MQMQA;
**HEX** MeX_(Fe,Ni,As, Sb, Sn, Cu), MQMQA
**~450 solid Compounds and small solutions:** sulfate, sulfide (FeAsS, $Cu_3AsS_4$), oxide, intermetallic, e.g. $Ca_2Sb$, $Ca_5Sb_3$, ZnSb, $Sn_4Sb_3$
**Ideal gas: >150 species**, including $N_2$, $H_2O$, CO, $CO_2$, $SO_2$, SO, $As_2$, AsS, AsO, Zn, ZnS, ZnO, AgS, Pb, PbS, PbO, Bi, $Bi_2$, BiO, BiS, Sn, SnO, SnS, Ag, AgO, AgS, Sb, $Sb_2$, SbO, SbS and more.

### 5.3 Advanced professional education

As discussed in [15], significant advances in metallurgical industrial practice can be made by implementation of the advanced research outcomes. The successful application of comprehensive thermochemical data and complex predictive models can be only undertaken only by well-educated and trained professional staff. External experts can assist in implementation of the advanced research, but it is down to the industrial R&D staff to make this work and therefore to derive the benefits from the improved performance. Targeted training and education programs are needed to prepare staff to make the most of the advanced characterization and predictive research methods that are available. These programs should be specifically developed for all organization levels from high through middle management, R&D, technical and production staff, to the operators.

There are different ways in which expert research and academic organisation, such as University, can assist industrial operations in education and implementation, these include not only undergraduate education such as, full time and exchange, Master and PhD programs but also on-line expert support, training examples, visits / secondments by industrial R&D staff, contribution to components of the graduate programs, development and delivery of the specialized courses, in-person and distance education, focused projects. The Pyrometallurgy Innovation Centre at the University of Queensland has developed and is delivering systematic targeted implementation and education programs containing most of the above components assisting it's sponsors in increasing value and benefits from the research outcomes. For example, through

- advanced distance education pyrometallurgy course on theoretical and practical foundation of high temperature processing in ferrous, non-ferrous and recycling operations;
- beginner, intermediate and advanced FactSage training courses for sponsors' staff;
- extended visits / secondments of industry R&D staff, (2-6 months) and full time PhD's currently working at sponsor's operations;
- One-on-one projects focused on particular industrial issues undertaken in close collaboration with sponsor companies.

## Concluding statements

In the coming decade, a relatively short time frame in terms of industrial development, significant improvements in the outputs of critical metals will be required to address global issues associated with climate change and decarburization. This will necessitate increases in productivity, efficiency and reduced environmental impact of existing operations, and the development and implementation of new technologies. Improved process outcomes and faster implementation of process improvements can be achieved by taking advantage of advanced predictive tools.

In the case of pyrometallurgical processing, use of the advanced thermodynamic databases can assist in predicting the outcomes of complex multicomponent systems before these processes are undertaken in practice. To take full advantage of these tools industry needs a suitably trained workforce. Both of these factors point towards the need for closer collaboration between industry and Universities, and the further investment in tertiary education and research.

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