University Research on molten slags, matte, speiss and metal systems for high temperature processing – challenges, opportunities and solutions.

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Keywords: thermodynamic databases, FactSage, integrated research methodology,
high-temperature phase equilibria, industrial support, education

ABSTRACT

Recent decades have seen significant advancements in analytical and experimental techniques, thermodynamic theory, and computational capabilities in high temperature research which are particularly timely to address the challenges of increasingly complex and variable feedstocks in both primary and secondary pyrometallurgical processes, the need to optimise and improve them. Currently a research program is in progress on the development of the 20-component multi-phase thermodynamic database for pyrometallurgical smelting, refining and recycling systems describing thermodynamics and phase equilibria of molten slag, matte, speiss, salts, alloys and associated solids. The integrated experimental and modelling program has been supported for nearly two decades by several consortia of 14 major international companies with over 30 operations around the world, integrates many components, incorporates many in-house developments, and brings together many different groups of professionals of different levels from junior and mid-career to senior from both industry and university sectors. ***The aims of the paper are*** a) to outline the many components and issues of the overall program including analytical, experimental and thermodynamic modelling research as well as implementation of the results in industrial practice, professional education, planning and organisation issues, b) to highlight the opportunities, challenges, and possible solutions, c) to present these to all different groups of professionals involved in the current program and thus, importantly, *d)* ***to facilitate possible future further developments and collaborations in the field of phase equilibria and thermodynamics of complex high-temperature systems***.

INTRODUCTION

1. The purpose of the paper

Significant technological society changes associated with decarbonisation, developments of renewable energy sources, electric vehicles, increasingly complex electrical and electronic devices have led to increasingly complex and variable pyrometallurgical processing streams. To address these challenges, optimise existing processes, and develop new pyrometallurgical technologies knowledge-based approaches are required. Fundamental information and powerful computer-based predictive tools can provide accurate and reliable descriptions of phase equilibria and thermodynamics in multi-phase multi-component systems. The Pyrosearch Laboratory (Pyrosearch) at The University of Queensland (UQ) developed and uses integrated experimental and thermodynamic modelling methodology to create computational tools used by Australian and international metal production and recycling industrial companies. The aim of the overall research program is to support the industry in transition towards higher sustainability and efficiency. The current objectives of the program are to i) develop a 20-component thermodynamic multiphase, multicomponent database for non-ferrous smelting, refining and recycling systems describing molten slag, matte, speiss, salts, alloys and associated solids using the integrated experimental and thermodynamic modelling approach, and ii) implement the research outcomes into industrial practice. The research program has been continuously supported over the last nearly two decades by the consortia of over a dozen of major international metallurgical and recycling companies with over three dozen industrial operations around the world, as well as by Australian and USA government grants. Significant progress has been achieved in fundamental and applied research, and in implementation of research outcomes into industrial practice.

The aims of this paper are to outline the developed research approach, different components integrated into one program, the issues encountered by the authors while working on this program, possible solutions and opportunities, and to present these to different groups of professionals to facilitate possible further developments and collaborations in the field.

The combination of many components in one overall research program is an important basis of the program.

The integrated experimental and modelling approach to develop thermodynamic databases presented by authors in this paper incorporates a *complex combination of many components* of different nature including but not limited to the i) analytical, ii) experimental, iii) thermodynamic modelling, iv) computational science, v) organisational, vi) financial, vii) industrial implementation and viii) educational. This combination is an important basis of the program. Every component itself is complex and challenging, requires specific in-depth discussion and is of interest to a specific professional audience. The next level challenge is to bring together all these components into one integrated research program undertaken by a group of professionals with different but closely related complementary expertise. Each component therefore will be described at a high, generic, relatively simplified and superficial level to allow a) to keep the focus on the combination of them and b) to make it accessible to all different audiences of professionals of different spheres of expertise and levels. References will be given to the more detailed discussions on each component of interest to each specific group of professionals.

The combination of different groups of professionals in one team is another important factor, these include:

- Young undergraduate students – future industrial metallurgists and researchers learning and making their career choices;
- Junior, middle career and senior researchers involved in scientific developments, and assisting in implementation of the research outcomes into industrial practice and in education;
- Senior academics involved in the development of the research programs and in university education;
- University and scientific organisations senior management involved in major organisations decision making;
- Young and middle career industrial research and development (R&D) metallurgists implementing the scientific and research advances into practice and improving metallurgical operations;
- Young and middle career industrial process metallurgists running the industrial processes, identifying and implementing improvements along with the R&D staff;
- Senior industrial executive R&D management leading industrial research and development programs;
- Senior industrial executive management making decisions on the companies' major developments and finance;
- Government officials looking after legislation and policies, as well as government funding.

Each of these groups is important for the sustainable development and operation of strategic and long-term research programs. The authors attempt to bring together all these groups in understanding of a) the overall combination and b) each component in order to facilitate further collaborative research and implementation developments in the field.

2. More on current challenges and opportunities for pyrometallurgy

As indicated above, significant technological changes are taking place in our societies right now and in the coming decades associated with decarbonisation and the developments of renewable energy sources, electric vehicles, and new increasingly complex electrical and electronic devices. The growth in the production of advanced materials used in these sophisticated technological devices has led to significantly increased demands in both volumes and variety of primary metals production and in metals recycling. As metal scarcity grows, primary concentrates are becoming increasingly complex. This is compounded by the rising number and diversity of metals found in recycled technological devices, which significantly increases the complexity and variability of metallurgical feed streams. Both short-term (daily-weekly-monthly) and long-term (multi-year) variations are observed. To address these challenges and minimize environmental impact, modifications to existing and development of new metallurgical technologies are crucial to enhance process efficiency and productivity. Adaptation of pyrometallurgical operations to these challenges requires implementation of a knowledge-based approaches using the fundamental information and powerful predictive computer tools for the accurate and reliable predictions of separation of the multi-component multi-phase process streams directly related to the phase equilibria and thermodynamics in multi-phase multi-component systems.

Significant gaps in knowledge on high temperature properties 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 the need to address a) stricter environmental regulations, b) stronger economic competition, c) better equipment and options in process control and data management, and, importantly, d) increased complexity and variability of the process chemistry. ***The supply*** of the needed fundamental data on the chemistry of the processes is becoming possible since a) new experimental techniques are becoming available due to b) the developments of modern advanced analytical techniques, dramatic improvement of their capabilities and availability, c) new theoretical modelling approaches and d) the significantly increased computer capabilities. This demand / supply combination is the basis for *the renaissance in research on the high temperature chemistry of metallurgical systems.*

3. Phase equilibria and thermodynamics are critical for the high temperature processes modelling and optimisation

As illustrated in FIG 1, the optimisation and improvement of the existing processes and the development of new processes requires good control of the process parameters, that in turn requires adequate characterisation and modelling of all factors influencing the process output as a function of the input parameters. For pyrometallurgical operations the factors that require accurate characterisation for the stable operation include 1. thermodynamics and phase equilibria, 2 physicochemical properties (e.g. viscosity etc), 3. micro-kinetic (20-1000 µm) and 4. macro-kinetic (0.1-10 m) factors, 5. plant data accuracy and 6. plant control accuracy, where the thermodynamics and phase equilibria are particularly critical and important.

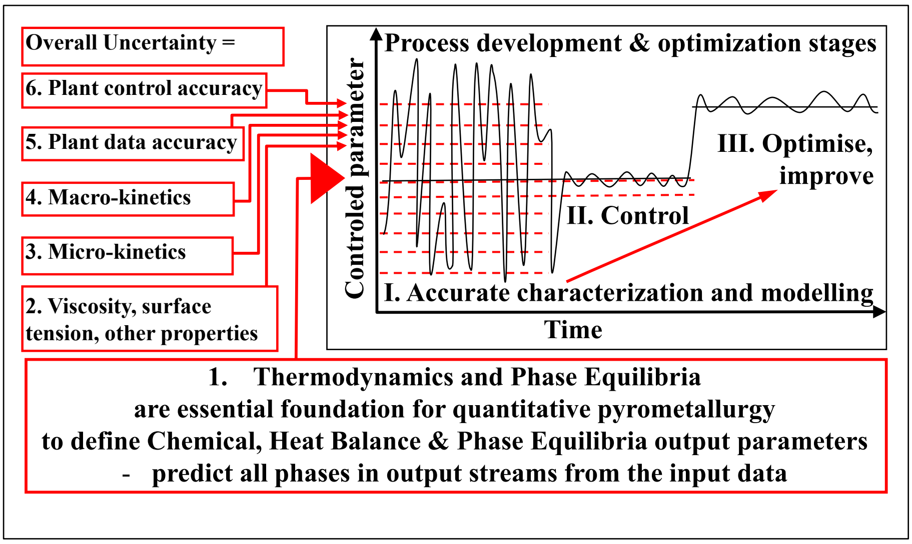

FIG 1 – Some factors influencing process uncertainty and the key stages in achieving process optimisation – characterisation / modelling and control

In any pyrometallurgical process involving molten phases, adequate and simultaneous control of at least three key output parameters is essential (see TABLE 1): 1. ***chemical target*** (product composition), 2. ***heat balance*** (to control process temperature) and 3. ***phase equilibria*** (liquidus temperatures or proportion of solids) (Jak, 2018). These three output parameters are directly controlled by the amounts and compositions of the materials introduced into the reactor. All these input and output parameters are interrelated - each output parameter depends on all input parameters with different sensitivities and is strongly determined by the thermodynamics and phase equilibria of the system. *Reliable models accurately describing thermodynamics and phase equilibria* *of the whole chemical system over a wide range of compositions, temperatures and pressures are therefore critical for the optimisation and control of existing and for the development of future pyrometallurgical processes.*

TABLE 1 – Typical input, target and calibration parameters used in pyrometallurgical processing

Examples of input parameters	Kinetic “calibration” parameters	Target output parameters
Oxygen coefficient (O_2/feed ratio) Duration of blow and rate	Oxygen efficiency	***Chemical*** - e.g. matte grade, Cu or Pb in slag, %S in blister
O_2 enrichment, fuel (coal, oil), dust and reverts, recycling, feed rate, composition (e.g. Cu/S/Fe), mineralogy, electric power	Heat loss	***Heat Balance*** - temperature
SiO_2 and CaO fluxes, slagging impurities levels (e.g. Al_2O_3, CaO, MgO)	Flux utilisation	***Phase equilibria*** - Liquidus, %solids, freeze-lining thickness, e.g. Fe/SiO_2, CaO/SiO_2 in slag

In industrial practice, a range of process models and predictive tools are used depending on the needs, availability of necessary data and other factors (Jak, 2018). For example, simplified thermodynamically-based models with the kinetic “calibration” parameters valid for limited range of conditions specific for a given reactor, e.g. (Nikolic et al., 2018), can be very effective as process advisers for improved process control, preparation of blends, short- and long-term production planning, limited scale-up predictions, staff training, and, importantly, for the development of the feed-forward control. These thermodynamic predictive tools can further be used to develop process predictive tools (virtual reactors) and be incorporated into “Pyro-GPS” systems (similar to the GPS systems) used for optimisation of complex plant flowsheets (see FIG 2).

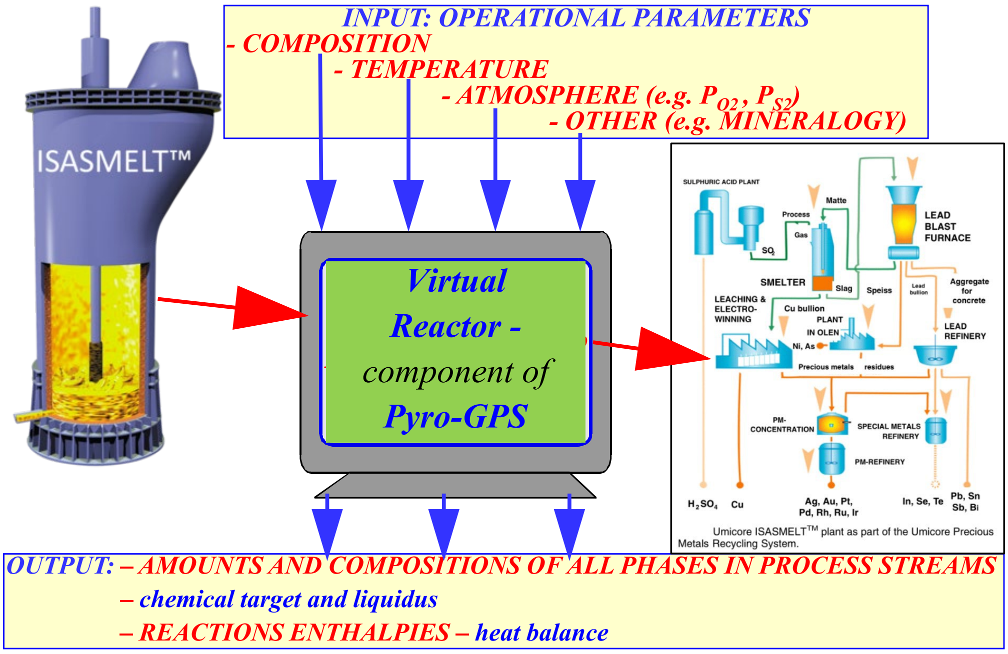

FIG 2 – Illustration of the key role of fundamentally based thermodynamic tools in predicting process outcomes and assisting in process optimisation (Jak, 2018)

The research program on the development of the multi-component multi-phase thermodynamic predictive tool outlined in this paper aims to provide the required strategic foundation for further developments in pyrometallurgy.

4. Research requirements for the development of computer predictive tool for pyrometallurgical thermodynamics and phase equilibria

Pyrometallurgical processing systems generally involve large number of phases with complex properties. The key liquid phases include slag, matte, speiss, salts (e.g. sulphates) and alloys. The majority of the key solid phases are solutions, many with wide ranges of compositions (e.g. spinels, melilites, olivines, pyroxenes, dicalcium silicate). Due to strong atomic-level interactions and intricate internal structures, most of these phases exhibit complex relationships between their thermodynamic properties, composition, and temperature. Accurately predicting the thermodynamic properties of key liquid and solid solution phases encountered in pyrometallurgy necessitates the use of suitable ***theoretical thermodynamic models***. These models must be capable of capturing the complex dependence of thermodynamic functions on composition, temperature and pressure, and performing reliable extrapolations and interpolations beyond the range of available experimental data. Thermodynamic predictions for the multi-component multi-phase systems also require appropriate ***computational capabilities*** - the computer packages capable of performing complex and multiple calculations at practically acceptable speed and incorporating i) adequate thermodynamic models, ii) Gibbs free energy minimisation module, iii) input / output interface and, importantly, iv) the databases containing thermodynamic model parameters on all possible phases including stoichiometric compounds as well as solutions (slags, mattes, salts, speiss, alloys, solids, etc.). Prediction of the thermodynamic properties of the actual phases requires ***experimental data*** to fix model parameters. In summary, the critical research components necessary to predict equilibrium chemical behaviour of the pyrometallurgical processing systems include:

a. appropriate theoretical thermodynamic models,
b. adequate computational capabilities, and
c. sufficient and accurate experimental data.

The following sections will provide some comments relevant to these critical research components.

DEVELOPMENT OF THE TOOLS

5. Thermodynamic computer packages providing required computational capabilities in pyrometallurgy

Several commercial thermodynamic software packages have been developed for predictions in a field of pyrometallurgy. The most widely used are FactSage (Jung and Van Ende, 2020) (www.factsage.com) and Thermo-Calc (Andersson et al., 2002) (www.thermocalc.com). FactSage contains the databases for wide range of molten systems, including oxides, sulphides, molten salts, and metals, which are based on high-quality thermodynamic assessments. Thermo-Calc, in addition to extensive metallic thermodynamic databases, has oxide and molten salts databases, as well as capabilities in modelling physical properties for some molten phases and advanced kinetics for alloys. Other available products are MatCalc (www.matcalc-engineering.com), MTDATA National Physical Laboratory, UK, (Gisby et al., 2017), Pandat (www.computherm.com) and MPE (CSIRO, Australia (Chen et al., 2013; Chen, 2015)). When customised user interface is needed, related software tools are often available for customised applications such as ChemApp (Petersen and Hack, 2007), ChemSheet (Koukkari et al., 2000), ChemAppPy (www.gtt-technologies.de) and SimuSage (Petersen et al., 2007), that are compatible with the FactSage databases. Thermo-Calc users can benefit from developer kits for Python, Matlab, and a collection of subroutines in a form of DLL called TQ-Interface.

6. Thermodynamic computer modelling – brief outline, experimental data needs and thermodynamic database development

A number of key points related to the thermodynamic modelling are listed below.

- The Gibbs energies of stoichiometric compounds including pure end members are calculated from the entropy at 298K (S_{298}), the enthalpy at 298K (ΔH_{298}) and heat capacities (Cp(T)) – these are generally considered as the most accurate and self-consistent data – important foundation of the solution models in thermodynamic databases (see FIG 3).

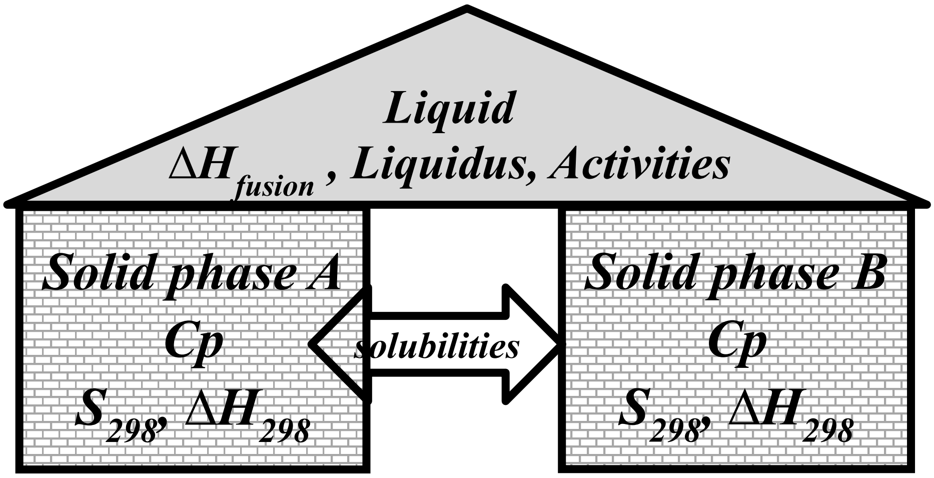

FIG 3 – Thermodynamic database structure

- A two-component thermodynamic solution model consists of i) the expression for end-members (S_{298}, ΔH_{298} and Cp(T)) and ii) adequate solution model expression related to the internal atomic-scale structure of the solution phase that determines an ideal entropy of mixing and iii) binary excess parameters describing deviations from the corresponding ideal behaviour as a function of composition, temperature and pressure determined by the trends of internal interactions between the two components at atomic scale. The solution model expression must be sophisticated enough to adequately describe complex Gibbs free energy of mixing determined by the internal structure of the phase, e.g. M-shaped entropy of mixing in the solutions with strong internal atomic-scale interactions and ordering in phases such as silicate slag (molten oxide solution) (Pelton and Blander, 1986). For example, a) the Modified Quasichemical Model (Pelton et al., 2000; Pelton and Chartrand, 2001; Pelton et al., 2001) is used for the liquid slag and matte phases, b) the Compound Energy Formalism (or sublattice model) (Chartrand and Pelton, 2001; Hillert, 2001) is used for the solid solutions with complex crystal structure, and c) the Bragg-Williams random mixing model is used for solutions with weak or positive deviation from ideal in the present study within the FactSage computer package (Bale et al., 2016) or custom tools developed using ChemApp (Petersen and Hack, 2007).
- A three-component thermodynamic solution model incorporates mathematical expressions for the extrapolation of the Gibbs energy of binary systems into ternary space, as well as mathematical formalism for the ternary excess thermodynamic parameters. The latter describes the effect of the third component on the binary interactions of the given two components. Generally, only binary and ternary thermodynamic parameters in the solution models of slag and other condensed phases are used since the effect of the next order

interactions is negligible or does not exist at all. The extrapolation of the Gibbs energy of binary systems into ternary and higher order composition space is different for different components and is specific to a particular ternary system (Chartrand and Pelton, 2000; Pelton, 2001). The Gibbs free energies of the solutions with the number of components higher than three are generally described by binary and ternary parameters.

- Condensed phases in pyrometallurgy such as slag, matte, salts, speiss, solid oxide solutions are complex, non-ideal solutions, with strong interactions, so that the binary and ternary thermodynamic parameters for accurate description of solution properties cannot be derived without experimental data. Experiments over the whole range of conditions with adequate accuracy are necessary for the description of the thermodynamic properties of the multi-component solutions – so the ***critical conditions for the accurate multi-component multi-phase model are A. sufficiently abundant and B. sufficiently accurate experimental data of all types***, including
    i) Heat capacities (Cp) as a function of temperature, S_{298}, ΔH_{298} for all stoichiometric compounds and all end-members of the solutions, calorimetric data;
    ii) Gibbs free energies of phases G_i and of reactions ΔG_R, thermodynamic activities;
    iii) Phase equilibria (liquidus / melting points, miscibility gaps, solid solubilities, distribution coefficients), and
    iv) Structural information (such as, solid solutions, crystal structures, site occupancies, etc).

  The lack of experimental data severely limits the development of accurate model parameters. This requirement can be summarised and will be further referred to in the paper by the slogan: "***No experiment, no model parameter***".
- Thermodynamic databases of multi-component multi-phase systems are developed through thermodynamic "optimisations" when all available thermodynamic and phase equilibrium experimental data for the system are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as Cp(T), S_{298}, ΔH_{298}, G_i, ΔG_R and 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. These discrepancies can then be resolved through new experimental studies. The gaps in experimental data can in identified so that further experimental investigations are undertaken in areas essential for further thermodynamic optimisations.
- The self-consistent thermodynamic databases developed in this way are used for interpolations and extrapolations in a thermodynamically correct manner and for predictions of equilibrium phase compositions and phase assemblages in multi-component, multi-phase systems.

7. Thermodynamic solution models used in the present program

Balance between predictive capability, complexity and accuracy of model predictions and available experimental data

The balance between predictive capability of a model, model complexity and accuracy of model predictions, extrapolations and interpolations depends on the available experimental data. Generally, the simpler the model (the less parameters it has) – the more predictive power it has, but at the same time the lesser capacity to describe complex trends and therefore the lesser accuracy the model has. The more complex model is – the more parameters generally it has – the more chances those parameters are not accurate enough when extrapolated, therefore significant additional experimental data are needed to determine parameters of more complex models. It is common that abundant and accurate experimental data set cannot be described with too simple and predictive model, therefore A. sufficiently abundant and B. accurate experimental data set requires more sophisticated model to be described, and therefore can fix parameters for such more sophisticated thermodynamic model, which in turn eventually results in more accurate and reliable description and predictions of the thermodynamics and phase equilibria of the multi-component systems. This can be re-formulated in an alternative way – the accurate and reliable sophisticated models with good predictive power require A. sufficiently abundant and B. sufficiently accurate experimental data set – supporting the statement indicated above “no experiments – no model parameter”.

Brief outline of the thermodynamic models used in the present program

For the complex molten solutions with strong interactions and short range ordering at atomic scale, and corresponding complex trends in Gibbs free energy of mixing several approaches were developed, these are: 1) introduction of associates at the composition of maximum ordering within the single sublattice; 2) two-sublattice ionic models with complex ions corresponding to the composition of short-range ordering; and 3) quasichemical models in which the entropy of mixing takes into account the effect of short-range ordering. The Modified Quasichemical Model (MQM) available in FactSage (Bale et al., 2016) used for the molten oxides (slags), sulphides and salts solutions in the present study incorporates many important additional complex functionalities, such as: 1) flexibility in the choice of pair (quadruplet) fractions or site fractions for the polynomial expansion for the Gibbs energy of quasichemical reactions (Pelton et al., 2000); 2) freedom in the choice of coordination numbers, allowing the control in position and shape of short-range ordering for different systems sharing the same component (Pelton et al., 2000); 3) combining quasichemical and Bragg-Williams random mixing contributions to the excess Gibbs energy (Pelton and Chartrand, 2001); 4) the opportunity to introduce associate species in cases when binary quasichemical interaction cannot describe the observed phenomenon, i.e. charge compensation effect; 5) different interpolation methods of binary model parameters into multicomponent space (Pelton and Chartrand, 2001; Decterov, 2018); 6) possible quadruplet formalism for ionic liquids with several cations and anions (Pelton et al., 2001). All these modifications constitute a framework, which allows the description of the complex trends in the real solutions using MQF, which, in combination with sufficiently abundant and accurate experimental data, can achieve high levels of accuracy in multi-component compositional space.

For complex solid solutions such as spinels, melilites, pyroxenes, olivines and many other, the Compound Energy Formalism (CEF) (Hillert, 2001) is a widely accepted modelling method (Frisk and Selleby, 2001). The main two features of CEF are the assumption of distinct sublattices within the crystal structure, and the random mixing within each sublattice. The main model parameters are in the Gibbs energy functions of all solution endmembers, as well as excess parameters for the interaction of atoms (species) within the same sublattice. As in the case of MQF, different models can be developed within CEF. Large flexibility of CEF comes from the option of using more than two sublattices, which MQF does not allow. The same components, including charged ions, can be present on several sublattices. This approach creates many “virtual” endmembers, necessitating the development of careful strategies to reduce the number of adjustable parameters through linear combinations and reciprocal reactions (Hillert et al., 2009). In multicomponent solutions, the introduction of a new solution component results in the dramatic increase in undefined endmembers, which makes expansion of solutions, such as Spinel, extremely challenging. In certain applications, such as non-stoichiometric solid speiss solutions, Modified Quasichemical Formalism (MQF) with single sublattice demonstrated similar results to CEF with less parameters (Shishin and Jak, 2018). The MQF-based models for solid solutions are now being tested in ternary and multicomponent systems.

As indicated above, the Bragg-Williams random mixing model is used for simple solutions in the present study.

Further more detailed discussions on thermodynamic models are given in (Shishin et al., 2024).

8. Overall experimental data requirements for constructing multi-component multi-phase thermodynamic database

As discussed earlier, a sufficiently abundant and accurate set of experimental data is crucial for a reliable thermodynamic description of pyrometallurgical systems. Some additional, more detailed points regarding data requirements are given below:

- All potential phases across the ***entire composition and temperature range*** need characterization. This ensures the model's versatility for use by a diverse range of professionals to predict behaviour i) at various stages throughout a pyrometallurgical process and ii) within different reactor zones. Imagine a GPS system – if a specific area is not mapped, the route guidance might be inaccurate if your journey takes you through that unmapped region.
- At a minimum, ***all binary systems*** should be investigated. For simple binary systems with no intermediate compounds around 10-20 liquidus data points may be sufficient. However, complex and important binary systems containing multiple binary compounds and solid solutions may require 40-50 experiments to determine both the liquid slag's binary thermodynamic parameters and the solids' thermodynamic properties. As an example, the simple Sb_2O_3-SiO_2 binary system (no intermediate compounds) only required 10 experimental points, while the more complex PbO-SiO_2 system (with 4 intermediate compounds at the liquidus and more at lower temperatures) needed 40 experiments (Wen et al., 2023).
- All ternary systems have to be investigated at least to a minimum level of ~ 20-30 liquidus points for a simple ternary and up to 200-300 experiments for a complex and important ternary with binary and ternary compounds and solid solutions to determine ternary thermodynamic parameters for the liquid slag as well as thermodynamic properties of solids. For example, the simple PbO-Cu_2O-ZnO ternary system required only 12 experimental points (Wen et al., 2023) whereas a complex PbO-"Fe_2O_3"-SiO_2 ternary system required 146 experiments (Shevchenko and Jak, 2019c).
- Selected 4-component subsystems should be experimentally investigated to validate the extrapolation of ternary thermodynamic parameters.
- To ensure reliable and accurate model predictions for industrially relevant conditions, selected 4-component and higher-order subsystems should be experimentally characterised.
- The current 20-component, multi-phase gas-slag-matte-speiss-metal-solids systems with the PbO-ZnO-"Cu_2O"-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 include:
    - $22!/(20!\cdot 2!) = 231$ binaries and $22!/(19!\cdot 3!) = 1540$ ternaries in the 22-component PbO-ZnO-"Cu_2O"-FeO-Fe_2O_3-CaO-Al_2O_3-MgO-SiO_2-As_2O_3-As_2O_5-SnO-SnO_2-Sb_2O_3-Bi_2O_3-Ag_2O-Au_2O-NiO-CoO-CrO-Cr_2O_3-Na_2O oxide system, and
    - $15!/(13!\cdot 2!) = 105$ binaries and $15!/(12!\cdot 3!) = 455$ ternaries in the 15-component Pb-Zn-Cu-Fe-S-As-Sn-Sb-Bi-Ag-Au-Ni-Co-Cr-Na metal/matte/speiss system.
- Complete experimental characterisation of all these binaries and ternaries would require many years of work of a laboratory such as Pyrosearch (these numbers do not even include 4- and higher order sub-systems nor combined slag-matte-metal systems). *Careful planning of the experimental work therefore is a critical factor* to ensure the continuing practical impact from this research program is delivered – this is discussed in the following sections.

9. Requirements for the overall experimental research program

As indicated above – adequate experimental characterisation of the current 20-component gas-slag-sulphate-matte-speiss-metal-solids systems is a very big task requiring significant efforts over extended period of time. Such significant research program, to be realistic, sustainable and practically executable requires a systematic planned gradual approach that would meet

a) the financial and organisational criteria - would attract i) continuing financial support with continuously returned value to the industrial and government sponsors and ii) high-expertise continuous research expert team, and
b) the scientific or technical criteria.

These criteria are discussed as follows:

- Experimental and analytical methods should be available to generate A. sufficient and B. accurate data – this is the 1st necessary criterion,
- Intermediate, not fully optimised but, at the same time, accurate and reliable enough for some practical calculations thermodynamic database should be made available to the sponsors to provide immediate value to sponsors to justify continuing financial support – the *iterative approach* adopted in this program provides a practical solution of *bringing continuing value to sponsors* and thus maintaining the continuing financial support of the program,
- *Continuous support by research team of the implementation* of the intermediate results into the industrial practice is a critical factor to ensure this study is bringing the value to sponsors and thus maintaining the continuing financial support of the program,
- Criteria to produce the minimum number of experiments sufficient for model development is important given the large number of the overall experiments needed,
- Integration of experimental and modelling is critical to ensure i) efficient progress of both experimental and modelling components, ii) high accuracy of both experiments and models are achieved, and iii) minimum but sufficient number of experiments is undertaken to develop the model of the required accuracy,
- Effective planning of experimental and modelling components is critical for the program with the large number of sub-systems being investigated, large number of experiments performed, large number of research staff involved and with the large number of sponsors and users of the database,
- Adequate computational method and computer tool for the experimental and modelling data management and manipulation in the process of the continuing iterative re-optimisation of the thermodynamic parameters is critical given the large number of experiments and large number of sub-systems continuously studied and re-optimised,
- Expert research team with adequate combined skills capable of running different components of the overall research program is a critical necessary factor.

As a summary – the following components are identified as critical combination to respond to the challenges:

1. financial and organisational criteria:

    1.1 iterative approach in the thermodynamic database development,
    1.2 ongoing implementation into industrial practice,
    1.3 effective planning, and
    1.4 minimum sufficient experimental data for the thermodynamic model development

2. scientific or technical criteria:

    2.1 Experimental data A. sufficiently abundant and B. sufficiently accurate data for the thermodynamic model development,
    2.2 Integration of experimental and modelling studies,
    2.3 Adequate experimental and modelling data for computational management / manipulation during re-optimisation, and
    2.4 Expert research team with necessary combined skills.

The following chapters will provide further comments by the authors on the above critical components.

METHODOLOGY

10. Integration of experiments and thermodynamic modelling is critical

The integrated experimental/thermodynamic modelling approach has been implemented at Pyrosearch and has enabled the rapid and efficient development of complex thermodynamic databases for the multicomponent systems: thermodynamic parameters are fixed by the new targeted experimental data points rather than by fitting into the pre-existing from literature and other sources experimental data. The continuously improved database is used for systematic assessment of completed experiments and identification of further new experiments that need to be carried out to accurately determine the binary and ternary model parameters. This systematic iterative procedure involves 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 performing experiments, and iii) the ongoing revision of thermodynamic parameters through re-optimisation of the required low- and corresponding high-order systems. Steps i), ii) and iii) are repeated progressively improving predictions and database accuracy. The interval between planning and completing experiments in case of the Pyrosearch program is reduced to few days or weeks, and all tasks planning and undertaking of experiments and thermodynamic optimisations, are undertaken in many cases by the same researcher.

The integration of experimental and modelling components of the research ensures modelling is used i) to analyse the agreement between different types of data, ii) to identify discrepancies in previous and, importantly, recent experimental results, and iii) to suggest required further experiments if needed or to conclude the work on a given sub-system, as well as iv) to plan further experiments as need (bulk composition, proportion of solids, equilibration path). Experiments in turn are critical to continuously test and gradually improve model accuracy. It is critical that the interval between request for and execution of experiments is minimum to allow dynamic model development and dynamic continuous planning of further experiments. The model-focused and model-based experiments planning ensures minimum but sufficient number of experiments are undertaken for a given system and at the same time ensures consistency and accuracy of experiments as well as of the model are tested during the research program progress.

11. Experimental phase equilibria methodology – critical for the high temperature phase equilibria and thermodynamics

As discussed above, the thermodynamic model development requires different types of experimental data, phase equilibria are one of them but a critical type that is described in the present paper. The requirement for A. the sufficiently abundant and B. the sufficiently accurate high-temperature phase equilibria measurements poses significant experimental difficulties due to a number of issues including but not limited to the highly reactive/corrosive properties of liquid phases in these systems, issues with containment, the high vapour pressures of some metal species, changing composition during equilibration due to interaction with substrate, establishing gas/slag/matte/metal equilibria, evaporation etc. Previous experimental techniques cannot provide wide enough range of applicability and the accuracy required for thermodynamic database development at high temperatures, particularly for systems containing complex solutions and multicomponent systems.

The equilibration/quenching/microanalysis methodology developed by Pyrosearch (Jak et al., 1995; Jak, 2012) has overcome all of these limitations and it is now the preferred approach to phase equilibria determination in these complex systems (FIG 4). The methodology involves equilibration of small synthetic samples (typically less than 0.5g prepared by mixing pure powders and pelletising) at accurately controlled temperature and gas atmosphere conditions. The sample is then rapidly quenched to low temperature thus retaining the phase assemblage and phase compositions present at the equilibration temperature. The microstructures in the samples prepared using standard metallographic techniques are analysed with optical and scanning electron microscopy (SEM). The phase compositions present in the samples are measured using advanced microanalytical techniques including: i) electron probe X-ray microanalysis (EPMA), and ii) laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). The compositions and process conditions are deliberately selected so that multi-phase materials are formed in the equilibrated samples. Any change to the sample bulk composition only changes the proportions of the phases, not their compositions that are measured with microanalysis after the experiment. The methodology then has the important advantage that the results do not depend on the small bulk composition changes (within certain limits) that may take place during equilibration. Recent developments in experimental techniques now allow the phase equilibrium measurements and elemental distributions between phases to be obtained in slags/sulphates/mattes/speisses/metal alloys /solid solutions in closed and open systems over a wide and continuously extended range of conditions thus meeting the conditions of being A. sufficiently abundant and B. sufficiently accurate. Contamination from crucible materials is avoided by using synthetic substrates of the primary phase material. A range of metal substrates (Pt, Pd, Ir, Re, Rh/Pt, Au, Mo, W, Fe, Co, Ni, Cu) have also been used for specific systems and process conditions. Successful equilibrium experiments have been carried at temperatures up to 1740°C and now being extended to higher temperatures. In all cases, proof of equilibrium is established through the "4-point" test that includes the following: 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; and 4. Analysing possible reactions taking place during equilibration using 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 are particularly effective in this analysis.

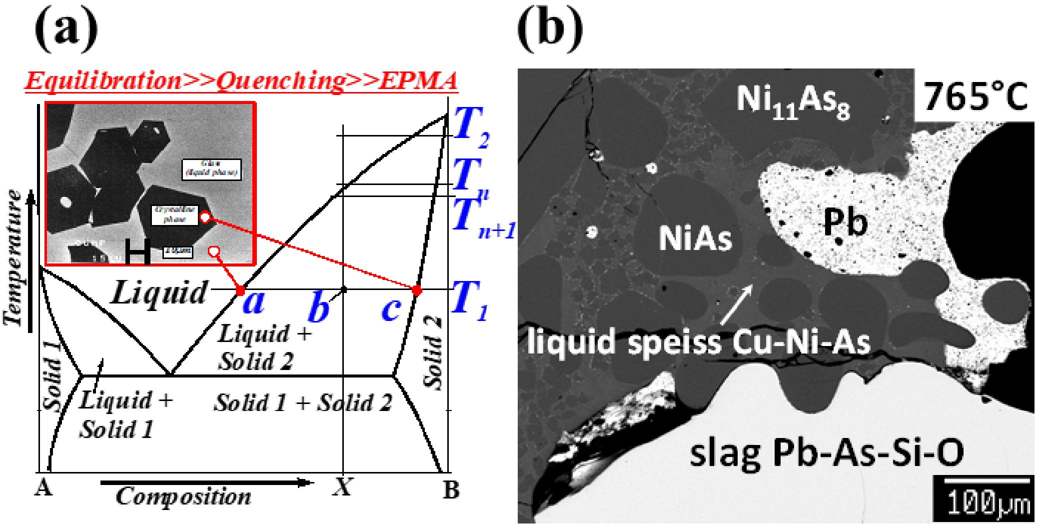

FIG 4 – a) Illustration of the Pyrosearch approach to high temperature phase equilibria determination using equilibration-rapid quenching-microanalysis, enabling accurate measurement of phase compositions in multi-phase systems under defined process conditions, b) An example of a complex multiphase, multicomponent system at equilibrium (Jak, 2018).

Overviews of the latest advances in the integrated experimental and modelling research approach to the thermodynamic database development for these pyrometallurgical systems are provided in (Shevchenko et al., 2024). The use of these microanalysis techniques has provided breakthrough capabilities in phase equilibrium studies for pyrometallurgical applications, greatly extending the range of elements, bulk compositions and conditions that can be characterised and the accuracy achieved. Development and application of this experimental approach is the critical foundation of the overall research program.

12. Microanalytical techniques further developments

The availability of suitable analytical techniques is an important pre-requisite for obtaining A) sufficiently abundant and B) sufficiently accurate experimental data. The implementation of Electron Probe Microanalysis (EPMA) and Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) microanalytical techniques in the high-temperature phase equilibria has significantly expanded the range of measurable conditions and improved the accuracy of experimental data for phase equilibria studies. Therefore, the continuous development and refinement of these microanalytical methods is a crucial component of this research program. As an example of such advancements, the authors' experience with adapting and further improving these techniques is detailed below.

EPMA

The EPMA method involves the use of the electron microscope to both image the prepared cross sections of the samples and simultaneously measure the compositions of the individual phases present. The impact of the electron beam on the samples results in the emission of X-rays characteristic of each of the elements present. Wavelength Dispersive Spectrometry (WDS) is used to select the wave lengths for particular elements for analysis. The measurement of intensities of the X-rays reflects the concentrations of the element present under the electron beam. Final analysis is obtained following corrections based on the overall matrix composition, for example, the ZAF correction where Z stands for the average atomic number, A – for absorption, and F – for fluorescence. The technique allows quantitative measurement of chemical compositions of both crystalline and amorphous phases on objects down to ~1 µm diameter. The region of interest is selected and navigated by scanning electron microscopy. EPMA also allows microanalysis of microcrystalline materials with non-zero diameter beam. Notwithstanding its superior spatial resolution, EPMA has often been perceived as reliable only for major elements with concentrations >1 wt.%. Recent advances in the EPMA instrumentation such as the field-emission electron gun, large-size diffraction crystals, and automation of aggregated intensity from multiple spectrometers (Donovan et al., 2016) have made it feasible to use EPMA to measure at least the more abundant trace elements (> 100 ppm) on a regular basis.

Over the years, authors have developed a number of further custom improvements to this methodology for specific metallurgical applications.

One of the custom improvements are the analytical protocols to measure minor/trace elements in chemically complex phases (Chen et al., 2021). These protocols address major issues associated with trace element analysis by EPMA such as Minimal Detection Limit (MDL), spectral interferences, beam damage and background correction to ensure the accuracy of the measurement.

The standard ZAF correction procedure was further improved. Systematic uncertainties of the standard ZAF correction were identified in many binary and ternary systems by measurement of the secondary standards – stoichiometric compounds existing within the system of interest, e.g. $PbSiO_3$, Zn_2SiO_4, Fe_2SiO_4, $Ca_2Fe_2O_5$, etc. The authors routinely synthesize and use stoichiometric compounds as secondary standards to monitor analytical uncertainties associated with the standard ZAF matrix correction parameters supplied with the commercial instruments. Improvement in analysis accuracy is achieved by applying further polynomial corrections to the measurement results (Shevchenko and Jak, 2017; Shevchenko and Jak, 2018; Shevchenko and Jak, 2019a; Shevchenko and Jak, 2019b; Shevchenko and Jak, 2021; Cheng et al., 2021; Khartcyzov et al., 2023). These corrections are specific for the same machine and standard procedures used, and allow back-correction of the data obtained in previous years before this ZAF correction bias was known. Alternative matrix correction parameters such as updated Mass Absorption Coefficients (MACs) are also tested and applied where appropriate (Abdeyazdan et al., 2024).

Another potential issue affecting the analysis accuracy in multiphase systems is the Boundary Secondary Fluorescence effect (BSF) – the element of interest was measured at a higher level than the true value when analysing a phase close to a boundary with another phase that contains a significantly higher level of the same element (Llovet et al., 2012). It was observed for transition elements (Cr, Mn, Fe, Co, Ni, Cu, Zn) in light element-rich phases (SiO_2, CaO, Al_2O_3) (Hidayat et al., 2012a; Hidayat et al., 2012b; Xia et al., 2016; Hamuyuni et al., 2016; Shevchenko and Jak, 2018), or when two neighbouring transition element-rich phases are adjacent to each other, such as over-estimated % Fe in metallic Cu surrounded by FeO-rich slag. The authors developed methods to first experimentally estimate the effect using cold-pressed minerals/materials then to apply correction to the unknown measurement results (Shevchenko and Jak, 2019d); in addition to that, authors demonstrated the effect could be minimized by measuring low energy < 5 keV characteristic lines (L lines of some of the transition metals, e.g. Cu, Zn) of element of interest (Shevchenko and Jak, 2021; Khartcyzov et al., 2023).

Focused Ion Beam – Scanning Electron Microscope (FIB-SEM)

An alternative approach to eliminate the secondary fluorescence effect at boundaries in quantitative X-ray microanalysis has recently been developed by the authors (Chen et al., 2024a). Utilizing FIB-SEM dual-beam system, the phase/features of interest with less than 10um size is physically extracted from the matrix and remount onto a suitable non-reactive substrate for subsequent EPMA analysis.

LA-ICP-MS

Originally developed for earth science research, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) has recently been adapted for use on the metallurgical systems for the quantitative analysis of trace/minor elements in solid materials (Avarmaa et al., 2015). This technique employs a focused laser beam to ablate a small portion of the sample, which is then ionized in an inductively coupled plasma and subjected to mass spectrometry for elemental identification and quantification. LA-ICP-MS offers significant advantages over EPMA, notably superior detection limits (down to ppb), enabling precise measurement of trace elements within targeted phases. Previous studies by the authors have showcased LA-ICP-MS's efficacy in accurately measuring trace elements in slag phases, contributing novel fundamental data and resolving discrepancies in literature regarding minor element distributions in non-ferrous melt smelting and converting processes. However, several challenges have constrained the utility of LA-ICP-MS in metallurgy research. Primarily, its analytical precision heavily depends on the availability of matrix-matched standards, which are presently limited for sulphides and metals. Additionally, existing glass standards (e.g. NIST SRMs) lack certain elements crucial for metallurgical applications, notably the platinum group elements. Consequently, authors have dedicated ongoing efforts focused on developing in-house standards. The authors pioneered the creation of silicate glass standards encompassing all six platinum group elements, utilizing an innovative high-temperature and high-pressure apparatus. Furthermore, the authors engineered copper alloy standards doped with various minor elements, specifically tailored for trace element analysis in copper metal via LA-ICP-MS (Chen et al., 2023). Significant improvement in analysis accuracy has been demonstrated (Chen et al., 2024b). In comparison to EPMA, LA-ICP-MS also suffers from inferior spatial resolution (> 15 μm), posing challenges for measuring small features, particularly solids. To overcome this limitation, the authors are actively investigating new laser systems, such as femto-second laser systems, with the potential to enable analysis of features smaller than 5 μm. The downside to the use of LA-ICP-MS is that the material used for analysis is physically removed from the sample – the same area cannot be reanalysed as is the case with non-destructive EPMA analysis.

Speciation of multi-valent elements (e.g. Fe^{2+}/Fe^{3+})

The quantitative determination of multi-valent elements, particularly Fe^{2+}/Fe^{3+} in the slag phase, has long been crucial for thermodynamic modelling in pyrometallurgy. Traditional analysis methods involve wet-chemical titration, necessitating large quantities (over 1 gram) of homogeneous slag material. Mossbauer Spectroscopy offers an alternative approach, requiring less material (~200mg), but accurate quantification often entails complex spectra deconvolution and fitting, leading to potential ambiguities depending on the fitting methods utilized. Microanalysis techniques such as X-ray Absorption Near Edge Spectroscopy (commonly employing a synchrotron beam line) and the

"Flank Method" (utilizing EPMA) have been developed to quantitatively measure Fe^{2+}/Fe^{3+} in specific geological materials, demonstrating good accuracy with the use of matrix-matching standards (Borfecchia et al., 2012; Hoefer and Brey, 2007). Currently, the authors are actively exploring these options for Fe^{2+}/Fe^{3+} measurement in slag and other oxide phases.

Further development of the microanalytical techniques is required i) to extend the ranges of compositions that can be investigated and ii) to further improve the accuracy of the measurements to meet for thermodynamic database development requirement for A. sufficiently abundant and B. sufficiently accurate data. More details are given in (Chen et al., 2024b).

13. Application of microanalytical techniques – new opportunities for high-temperature industrial R&D

As discussed above – implementation of the advanced thermodynamic modelling tools into industrial pyrometallurgical process control requires significantly more advanced characterisation of the actual processes to incorporate adequate calibration parameters to account for kinetic and other factors. The microanalytical techniques (EPMA, LA-ICP-MS) that became available relatively recently provide the capabilities to characterising heterogeneous processes responding to the new demands and created fresh possibilities to improve the characterisation of the industrial systems and thereby make further improvements to industrial practice and support implementation of the advanced models. Most of pyrometallurgical processes involve heterogeneous reactions taking place at microscopic scale at and around the phase interfaces. The microanalytical techniques EPMA and LA-ICP-MS enable advanced microstructural characterisation and accurate composition measurements minimum elemental detection limit down to ~300 ppm at spatial resolutions of approximately 0.5 to ~1-3 micron and down to ppb at spatial resolution of approximately 20 to 80 micron respectively. Microanalysis of industrial quenched samples provides an exceptional opportunity to characterise processes taking place in the reactors. Detailed analysis of the composition trends as microscopy scale of 10-30 micron from the phase boundaries and at larger scale across the quenched samples provides important information on the kinetic reactions taking place in the industrial process and therefore a basis for the incorporation of thermodynamic models to describe real industrial processes.

The examples of applications of microstructural analysis of industrial samples include i) phase equilibria (melting etc) ii) reactions extents (e.g. Cu losses) iii) specific troubleshooting (e.g. freeze-lining, refractories, deposits).

The recent examples include the measurement of distribution of Co, Ni, Zn, Pb, Bi, Sn, As, Te, Se, Ga, In, and Ge in complex copper converting slags (Chen et al., 2021), analysis of iron sinter micro-structure and their link to breakage characteristics (Cheng et al., 2022), understanding the mechanism of refractory degradation in copper smelting (Fallah Mehrjardi et al., 2016), freeze-lining formation in non-ferrous applications (Fallah-Mehrjardi et al., 2014b; Fallah-Mehrjardi et al., 2014a), investigation of reasons for the corrosion of steel walls in lead smelting (Watt et al., 2018), distribution of arsenic in industrial samples of nickel sulphide converting (Hidayat et al., 2017), conditions for the formation of spinels in nickel smelting and their effect on matte droplet settlement (Sineva et al., 2023).

14. Experimental data requirements and the importance of planning experiments

Effective planning of experimental and modelling components is a critical component for the program with large number of systems being investigated, large number of experiments performed, large number of research staff involved and with the large number of sponsors and users of the database. The following section presents further details on the planning derived by the authors from experience.

In case of the current Pyrosearch experience following up of the principle “no experiments – no model parameters” , the experimental component of the work takes approximately 75 % of resources and is a foundation of the overall program. The planning starts from the evaluation of the approximate number of possible experiments to be undertaken for a coming year for a given level of funding - each lead researcher in the team evaluates capabilities depending on experience as well as on the complexity of the system and commits to a particular number of successful experiments per week – this gives an approximate indication of a number of possible experiments and corresponding timing.

In order to prioritise the work to deliver more valuable outcomes, all elements in the overall multi-component system under investigation are divided into *major* elements (Me^{major}), *minor slagging* elements ($Me^{minor\_slagging}$) and *minor other* elements ($Me^{minor\ other}$). The current program includes systematic phase equilibria studies of all low order 2- and 3- metal sub-systems from the major elements list, selected key multicomponent 4- and higher number of metals sub-systems from the major elements and slagging minor elements lists, all low order 2-metal sub-systems $Me^{minor\ other}$-Me^{major}, $Me^{minor\ slagging\ or\ other}$-$Me^{minor\ slagging}$ and 3-metal sub-systems $Me^{minor\ slagging\ or\ other}$-$Me_1^{major}$-$Me_2^{major}$, $Me^{minor\ other}$-Me^{major}-$Me^{minor\_slagging}$, and minor elements distributions of elements between key phases (e.g. slag-metal, slag-matte, matte-metal). Transition from minor to major element list is done gradually after the all necessary major elements sub-systems have been characterised. For example, the current 20-component system at Pyrosearch has Me^{major} = Cu, Pb, Zn, Fe, Ca, Si, Al, Mg, S, O; $Me^{minor\_slagging}$ =Cr, Na and Me^{minor} = As, Sn, Sb, Bi, Ag, Au, Ni, Co. Nickel Ni is included as a major element in matte/speiss/metal and selected oxide solid solution phases.

The following *key directions* are identified for the purpose of systematic planning: i) slag-solids (S-free) phase equilibria (with and without metal phase), ii) slag-matte or -sulphate (S-containing) equilibria (with and without metal phase), iii) matte-speiss-metal equilibria and iv) and minor elements distributions of elements between key phases (e.g. slag-metal, slag-matte, matte-metal). The gaseous species equilibria are not currently in focus of the Pyrosearch program. Two types of experiments are performed – closed experiments undertaken in sealed ampoules for the slag / matte / metal, slag / metal and matte / metal systems; and open or semi-open experiments with the P_{O2} and P_{SO2} in the gas / slag / matte and gas / slag / metal systems controlled by the $CO/CO_2/SO_2$ gas mixtures.

The techniques developed during this program for the first time enable the systematic accurate measurements of this kind to be undertaken, and these measurements provide an important foundation for the development of the thermodynamic database as well as for the overall quantitative description of the high-temperature thermochemistry. The total number of experiments needed to completely and quantitatively characterise the whole chemical system as functions of key operational parameters is very large and is increasing exponentially with further addition of new elements. The experimental needs therefore are carefully, critically and continuously reviewed.

The current criteria for priorities in selecting systems for further improvement are 1. importance for industrial sponsors, 2. incorporation of all directions and elements, 3. resolution of identified discrepancies in database predictions, 4. finalising incomplete diagrams, 5. prioritising possible, easy and high-success rate experiments, and 6. higher thermodynamic model parameters sensitivity / importance relative to the experimental accuracy. Selection of experiments to be undertaken is facilitated by analysis of the sensitivity of the predicted values to the thermodynamic parameters relative to the achievable accuracy of experiments.

The issues indicated by the sponsors during the meetings are regularly summarised in a specific table, continuously reviewed and extended. In addition, to assess the accuracies of the databases at particular conditions relevant to the industrial practices, *systematic targeted programs on the laboratory-scale characterisation and modelling* of complex thermochemistry *of the key industrial processes of sponsors* are undertaken. This involves identifying / reconfirming chemistry of the main process streams and conditions, accurately characterising / reproducing complex industrial chemistry by undertaking series of experiments in the well-controlled laboratory conditions and analysing specially quenched industrial plant samples. The results are then used to analyse systematic uncertainties of the predictions against accurate and reliable data obtained in laboratory study and then to identify the needs and the ways for improvements of the models through the new targeted cycle of low order experiments and thermodynamic optimisations.

The integration of experimental and thermodynamic modelling studies helps to optimise the experimental program – to focus on what's needed and to minimise the overall number of experiments undertaken for the required accuracy of the thermodynamic predictions.

The actual program for the coming year is then developed based on the selected priorities and on the indication of a number of possible experiments indicated by the leading researchers.

The current focus of the research program of Pyrosearch is the 20-component development of the database for the system with the "Cu_2O"-PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2-Al_2O_3-MgO-S major, Cr and Na slagging and As, Bi, Sn, Sb, Au, Ag, Ni, Co other minor elements containing gas, slag, sulphate, matte, speiss and metal alloy molten solution phases, 26 major oxide, sulphide and metallic solution phases such as spinel, melilites, olivines, pyroxenes and other, 79 solid solutions with limited ranges of solubility and over 380 oxide stoichiometric compounds.

In order to prepare an accurate description for all compositions and process conditions with the 10 major elements following the criteria outlined above, the numbers of subsystems to be experimentally characterised is illustrated in FIG 5. The application of the priorities outlined above for the current list of major and minor elements, total 176 of binary and 694 ternary oxide sub-systems and several hundred more for the sulphates and matte/speiss/metal sub-systems are considered for experimental and further thermodynamic modelling characterisation.

15. Current experimental phase equilibria data status

Since early 1990's to date the Pyrosearch team has conducted ~20,000 experiments in 389 subsystems (122 completed, 175 studied at advanced level, and 92 in progress at initial level). Data from 107 systems are available in the literature, 133 systems are impossible to experimentally investigate using the current methodologies or they do not exist practically (e.g. Cu_2O-Fe_2O_3, FeO-SnO_2, Fe_2O_3-SnO). There are no measured phase equilibrium data on 288 major + 546 minor sub-systems. Pyrosearch team is currently undertaking approximately 1100-1300 successful experiments per year in over >100 sub-systems.

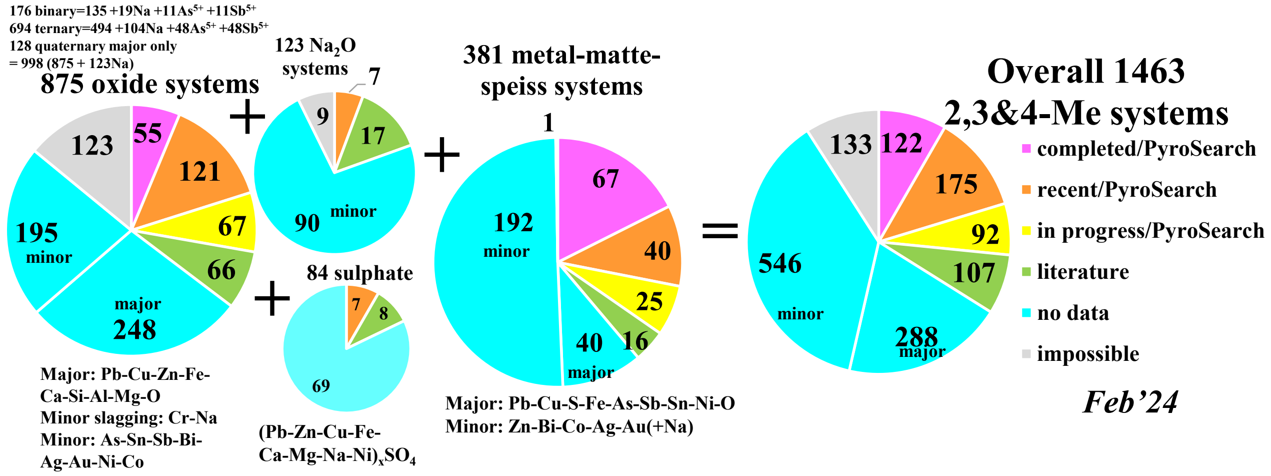

FIG 5 – Summary of chemical systems in 20-component system with "Cu_2O"-PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2-Al_2O_3-MgO-S major, Cr and Na slagging and As, Bi, Sn, Sb, Au, Ag, Ni, Co, other minor elements and current status of database development

16. Advanced thermodynamic optimisation methodology requirements and outline

Continuing re-optimisation of thermodynamic models using such significant number of experiments, management of the thermodynamic parameters and of experimental data is an important issue.

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 to a 20-component system results in the significant increase of the number of the sub-systems that require experimental and thermodynamic modelling characterisation from 171 to 190 binary and from 969 to 1140 ternary sub-systems. All types of experimental data from Cp's, enthalpies and entropies of endmembers and stoichiometric compounds to the multi-component phase equilibria data have to be described by the model simultaneously. Thus, any improvement in a given experimental value require fast and significant re-optimisation. Incorporating a new experimental data on a given binary sub-system into the database requires the iterative re-optimisation of all corresponding ~20 ternary and ~120 quaternary sub-systems – the so-called "pyramid effect". Experimental – thermodynamic modelling integration requires fast and frequent iterative re-optimisations, that in turn need continuous accumulation of optimisation results at each given stage for the use during the next iteration.

A semi-automated thermodynamic database development methodology has been developed and implemented to tackle these issues. The key points in this methodology are as follows. The sets of target experimental points to be described and corresponding weights are selected based on the experimental information available (note – not all available experimental data are included, and at the same time so called "virtual" target points are included where no experiments are available). A matrix of first derivatives showing the sensitivity of each target point to each possible model parameter are calculated using traditional Gibbs energy minimization calculations, which is a relatively slow step. Using the revised approach, the initial slow Gibbs energy minimisation calculations, are replaced by a fast analytical approach with linear extrapolation of the existing values through matrix multiplications of the form $\Delta\bar{y} = \boldsymbol{A} \cdot \Delta\bar{x}$, where A is the matrix of first-order derivatives (n target values by k model parameters), $\Delta\bar{x} = \bar{x} - \bar{x}_0$ is the difference between the final set of model parameters and their initial approximation and $\Delta\bar{y} = \bar{y} - \bar{y}_0$ 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 then obtained by solving the relationship: $\bar{x}_{optimal} = \bar{x}_0 + \left(\mathbf{A}^T \cdot \mathbf{A}\right)^{-1} \cdot \mathbf{A}^T \cdot \left(\bar{y}_{\text{target}} - \bar{y}_0\right)$ for the condition $\bar{y} \to \bar{y}_{\text{target}}$. 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 enables immediate re-optimisation of model parameters for any single target or weight change. It also enables a) the real-time graphical presentation of predicted and target points as well as b) the real-time systematic tabular statistical analysis presentation of agreement between predictions and target values, which makes the optimisation process truly interactive. More details are given in (Nekhoroshev et al., 2024).

The accuracy of the database is analysed using a systematic set of graphical representations together with compact pivot tables across different primary phases/subsystems, including such information as average, min, max, temperature RMS + composition RMS, where RMS (root mean squares) are defined as a square root of average squared differences between target and predicted values.

The new formalised and semi-automated methodology makes 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 intellectual efforts* between the research team members. Once formalised and semi-automated, the procedure can be used to optimise the model parameters by enabling each member of a group of researchers to 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 are resolved by the formalised semi-automated system significantly more efficiently and with less oversight. Only periodically the re-calculations using Gibbs energy minimisations are needed to update the matrix of derivatives. The new methodology enables 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 is undertaken in iterative cycles, the major discrepancies are identified at each step, and new experiments are conducted to resolve discrepancies within time intervals from several days to several weeks rather than months and years using the more traditional approaches.

17. Outline of the thermodynamic database

The current 20-component database in focus includes the "Cu_2O"-PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2-Al_2O_3-MgO-S major, Cr and Na slagging and As, Bi, Sn, Sb, Au, Ag, Ni, Co other minor elements in the gas, slag, sulphate, matte, speiss and metal alloy molten solution phases and many solid solution and stoichiometric phases. The database theoretically consists of 1540 binary and ternary oxide, 455 binary and ternary metal-matte-speiss, and several thousand quaternary systems as well as the systems including oxygen and sulphur together (oxygen in matte, sulphur in slag). Excluding systems of low importance (e.g. containing several minor elements together), there are currently considered 998 oxide binary, ternary and selected 4-component sub-systems (including 123 Na_2O-containing systems recently added), 381 metal-matte-speiss systems, 84 sulphate systems with the total of 1463 2-, 3-, and selected 4-metal component systems. The database includes over 450 stoichiometric compounds, >100 gaseous species, around 130 solution phases (among which there are 29 large solutions) with more than 3000 excess parameters. Most of compound and gaseous species have self-consistent C_P functions over a wide range of temperatures, starting from 0K and optimized S298 and ΔH298 values,. The largest liquid solutions in the system are Slag and Liquid Metal/Matte/Speiss, the latter being modelled as one thermodynamic solution with miscibility gaps. The Slag phase has 50 endmembers made up of 25 free metal cations (including Fe^{2+} and Fe^{3+}, Sn^{2+} and Sn^{4+}, As^{3+} and As^{5+}, Sb^{3+} and potentially Sb^{5+}, Cr^{2+} and Cr^{3+}, and two associates ($NaAl^{4+}$, $NaFe^{4+}$) multiplied by [O^{2-},S^{2-}] anions. There are 276 binary and 2024 ternary oxide systems in slag phase with around 990 excess parameters. Liquid Metal/Matte/Speiss solution consists of 20 endmembers on a single sublattice with over 730 interactions between them. A new liquid solution, Salt, has recently been introduced into the database, describing the interactions between molten sulphates, oxides, and arsenates. Currently, there are 8 cations in the first sublattice and 3 anions in the second sublattice, making up 24 different end members with 33 interactions among them in the Salt solution model.

Most extensive solid solutions in the database are Spinel with 162 endmembers and 611 interaction parameters (some of them are identical for different combinations of elements in sublattices, though), Monoxide (12 endmembers, 74 interaction parameters), Melilite (63 endmembers, 23 interaction parameters), ortho- and clino-pyroxenes (36 and 75 endmembers, respectfully).TABLE 2 provides a summary of the current Pyrosearch database.

TABLE 2 – Summary of phases in the current Pyrosearch database for the pyrometallurgical processing and the thermodynamic models used to describe these. MQM = Modified Quasichemical Model (Pelton et al., 2000; Pelton and Chartrand, 2001), CEF = Compound Energy Formalism (Hillert, 2001; Hidayat et al., 2015), B-W = Bragg-Williams ideal mixing model

Slag: $(Cu^{+1}, Fe^{+2}, Fe^{+3}, Si^{+4}, Al^{+3}, Ca^{+2}, Mg^{+2}, Pb^{+2}, Zn^{+2}, Ni^{+2}, Co^{2+}, Sn^{+2}, Sn^{+4}, Sb^{+3}, As^{+3}, As^{+5}, Bi^{+3}, Ag^{+1}, Au^{+1}, Cr^{2+}, Cr^{3+}, Na^{+}, AlNa^{+4}, FeNa^{+4})(O^{-2}, S^{-2})$, MQM

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, Zn, Fe, Cu, Ni)(SO_4, O, AsO_4, SiO_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, SnO_2, Na_2O), B-W

Corundum: ($FeO_{1.5}$, $AlO_{1.5}$, $CrO_{1.5}$, $SnO_{1.5}$), B-W

Mullite: $(Al^{3+}, Fe^{3+}, Cr^{3+})_2(Al^{3+}, Sn^{4+}, Sn^{2+}, Si^{4+})(O^{-2}, Vacancy^{0})_5$, 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: $[Ca^{2+}, Pb^{2+}, Na^{+}]_2[Al^{3+}, Zn^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}][Fe^{3+}, Al^{3+}, Si^{4+}]_2O_7$, 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, Co_2SiO_4, Sn_2SiO_4, CaO, $Ca_{1.5}AlO_3$, $Ca_{1.5}AsO_4$), 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)$_7$As$_3$, 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.

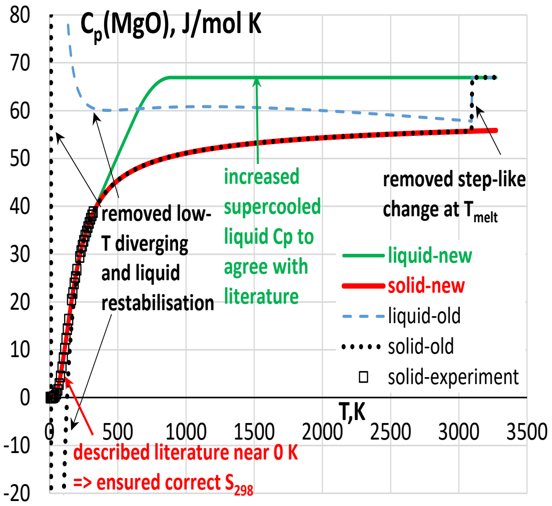

FIG 6 – Example of heat capacity vs temperature

18. Current status of the thermodynamic database development

Recent accurate and abundant experimental measurements by Pyrosearch have provided sufficient data to identify and then rectify many significant systematic uncertainties in the previous thermodynamic database. These systematic uncertainties include thermodynamic descriptions of all liquid end-members as well as in the description of the silicate slag systems with the Modified Quasichemical model. The whole database therefore had to be fully revised starting from the properties of pure liquid endmembers such as SiO_2, CaO, MgO, etc., key sub-systems such as CaO-SiO_2, FeO-Fe_2O_3-SiO_2 etc, and all other binary, ternary and higher order sub-systems. The thermodynamic optimisation methodology developed at Pyrosearch had been critical to enable this significant task to be completed.

Brief outline of the major developments is given below.

Correcting the heat capacities of liquid end-members and of solid phases.

Previous databases contained 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 does not accurately define the real experimental data on heat capacities of most phases. These over-simplified descriptions resulted in the step-like changes in heat capacities (and therefore entropies, enthalpies and Gibbs free energies) at melting points of the endmembers and corresponding uncertainties in the multicomponent solutions. Most importantly, the heat capacities of liquid solutions (slags) calculated from these liquid endmembers were typically 20-40% higher than the real values for the range of temperatures relevant to industrial practices (700-1700 °C). To compensate for these systematic uncertainties, artificial distortions to the interaction parameters between the liquid species were previously introduced thus significantly limiting the predictive power of the database; this becomes increasingly problematic with the increased solution complexity. These uncertainties have recently been corrected as one of the components of the major database revision, as shown in FIG 6. Also, heat capacities of all solid phases were revised to obtain physically relevant descriptions below the room temperature down to 0 K and at very high temperatures (above the melting point of solid endmembers) thus eliminating a number of erroneous predictions 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.

Gibbs free energies of solids 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 of pure and binary compounds at higher temperatures (above 1750°C). The melting temperatures and enthalpies of several compounds (CaO, Ca_2SiO_4, Al_2O_3, MgO, SnO_2, Mg_2SiO_4, NiO, etc.) were corrected significantly. This correction, after overall major revision of the database, resulted in significant improvement of the description of phase equilibria in the temperature range important for industrial operations. For example, the melting temperature of SnO_2 in air was corrected from 1625°C to 2059°C (Shevchenko et al., 2021; Shevchenko et al., 2024) that resulted in the improvement of the predictions of the cassiterite SnO_2 liquidus of 50-150°C for the range of temperatures relevant to industrial practice (700-1700°C).

Revising high-SiO_2 liquid

Accurate EPMA measurements of phase compositions and systematic high-temperature experiments in the 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 a number of 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 dilute aqueous solutions. Identification and understanding of the underlying reasons for these behaviours provided the opportunity to adjust the models by i) introducing a correction to the Gibbs energy of mixing (FIG 7) 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 temperature-dependent, excess entropy terms with high power on SiO_2 that were commonly used in previous optimisations for the binary systems and resulted in inaccurate extrapolation to the ternaries, and iii) making 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 significant improvement of the accuracy of the database. Introducing description of these long-range interactions also improved the description of the minor element distributions in multicomponent systems; it also allowed 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 was extended to all SiO_2-containing subsystems. This significantly improved the accuracy and predictive capability of the liquid slag model.

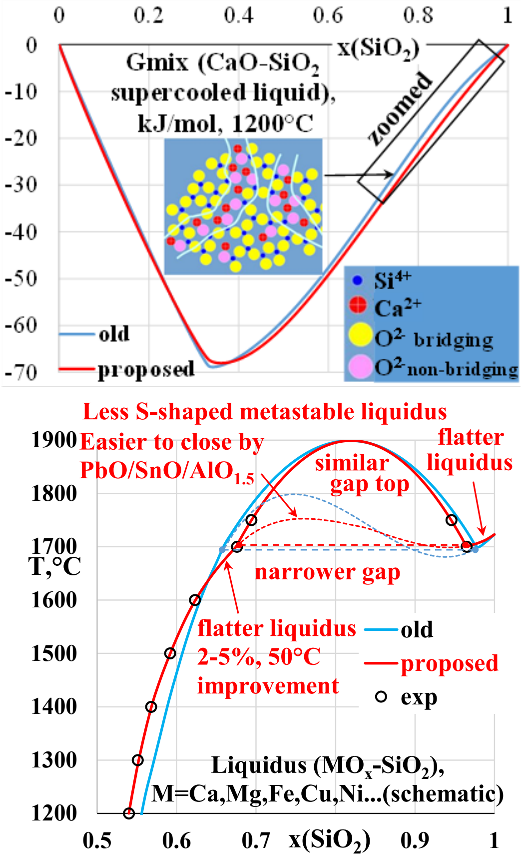

FIG 7 – Example of the correction of the high-SiO_2 slag model taking into account the different structure of the slags in high and low silica composition ranges

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 7). For example, this sharp change means it was 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 8). The following approach was developed and implemented 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 $\underline{+}2$ $J \cdot mol^{-1}$ K^{-1} based on the available statistical physics theory. Systematic corrections of the entropies of mixing for all relevant binary systems have been undertaken to improve the accuracy of the descriptions and predictions of the database (e.g. FIG 8).

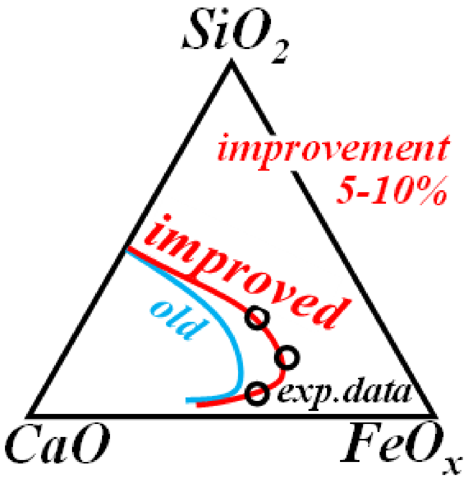

FIG 8 – Schematically shown Ca_2SiO_4 primary phase field in the CaO-FeO-Fe_2O_3 system at constant temperature.

Major revision of the whole thermodynamic database

Major revision of the whole (20 component) oxide database has been carried out - a significant milestone that took substantial team efforts over several years; it included re-optimisation of ~250 subsystems using ~ 12,000 experimental phase equilibria points (including approximately ~10,000 experimental points by Pyrosearch) and significant number of other experimental thermodynamic data (Cp's etc), introduction of the new values for ~2500 thermodynamic parameters for 87 liquid and solid solution phases and ~700 stoichiometric solids. The new completely revised thermodynamic database forms an important basis for further developments.

Further more detailed discussions on thermodynamic optimisations are given in (Shishin et al., 2024).

DEVELOPING THE TEAM

19. Multi-skilled team – critical factor for the strategic research program

Necessary components of the overall program of development of the thermodynamic database include application of the advanced theoretical models, development and application of appropriate sophisticated computational methodology, experimental methodology and analytical techniques as well as implementation of research results into industrial practice. Such program therefore requires a team with i) high level expertise ii) in different areas and iii) of different levels (i.e. senior, intermediate and junior research academics, PhD students, qualified research assistants. The Pyrosearch current structure incorporates i) 5 Theme leaders (advanced experts in high temperature experimentation, laboratory equipment and methods, analytical methods, thermodynamic optimisations and process modelling, and computational thermodynamics), ii) 6 Research Fellows; iii) 7-8 PhD and Master students; iv) 6 well-trained continuing research assistants, v) 7 casual undergraduate research assistants – current University metallurgy undergraduate students, and a few visitors. This is not a usual University group (many University groups have the majority of the research undertaken by PhD students). A strong continuing senior research academics core with the high level of expertise in different interrelated areas is the important factor. It is therefore critical to address the issues of continuity of the senior research academics within existing University system.

20. Industry support is critical for continuing research program

The long term strategic research program requires continuing financial support, and industry therefore is a critical component providing long term stability. *Continuous* implementation of the intermediate results into industrial practice is therefore a critical factor to ensure this study is *continuously* bringing the value to sponsors and thus helps to maintain the *continuing* financial support of the program. In the present research program this is achieved by i) iterative, regular and frequent transfer of the intermediate thermodynamic database to sponsors and ii) proactive implementation activity undertaken by the Pyrosearch staff.

The continuing focus on the industrial impact in turn guarantees the research is continuously directed at the practically important, priority industrial needs.

The overall research program in case of Pyrosearch is organised through three consortia of industrial sponsors with common interests – Cu, Pb and Fe and slag recycling, where industry contributions are complemented by competitive government funds. The size of the overall program is beyond a capacity of a single industrial sponsor to support it. Pyrosearch important functions in this regard therefore are i) to bring various industrial companies together into consortia and with common interests and ii) obtain additional government and University support thus providing value to each individual industrial company.

21. Implementation of research outcomes into industrial practice is an important factor

The collaboration between the industry partners and Pyrosearch has enabled the development of a set of powerful predictive tools based on extensive experimental fundamental information, which can be used to analyse a broad range of industrial systems independent of the technologies used. The collaborative program does not stop there – the important next step is implementation of these advanced tools and information into industrial practice. The tools can be used by companies to improve process efficiencies and productivities, optimise the utilisation of existing plant, predict changes to plant practice to adjust for changes in process feed compositions, design new processes or operations. It has been recognized and acknowledged that the successful implementation of the advanced tools and information into industrial practice requires adequate professional education and training in their use. This has been achieved through a variety of ways in collaboration with sponsor companies.

Upskilling of engineering professionals is achieved through providing

- Dedicated courses in chemical thermodynamic theory, pyrometallurgy fundamentals and the application of FactSage tools to industrial problems, delivered by distance and in person.
- Extended visits, placements and secondments of engineers with the research team.
- Undertaking Research Masters and PhD studies at Pyrosearch.
- Undertaking one-on-one projects with the research team on industrial problems.

Significant progress has been achieved in this direction. For example, over the last few years over 160 engineers successfully completed an on-line Pyrometallurgy course, 182 completed in-person and on-line FactSage course, 7 metallurgical engineers visited Pyrosearch for training or collaborative projects, 10 Master and PhD students from other local sponsor Universities did collaborative research in-person at Pyrosearch, 4 full time Pyrosearch UQ PhD students are now working in sponsor companies, 56 one-on-one focused industrial research projects were undertaken by Pyrosearch staff in collaboration with the sponsor's metallurgists.

The active collaborations between industry and the research team provide important opportunities to obtain high value from the capabilities of the predictive tools. Testing the tools against industrial practice provides i) confidence in their potential for extended use in an industrial context – a critical factor in technology transfer, and ii) guidance in further research directions.

22. Metallurgical research-focused academics roles

Universities are viewed traditionally as institutions where knowledge is stored and passed on through teaching to the undergraduate and postgraduate students. Much less understood are other important roles played by the University academics; those with specialist knowledge in the metallurgical engineering can actively support the metallurgical industry in a number of other ways, by

- Undertaking knowledge generation through fundamental and applied research,
- Developing and maintaining collaborative research links with industry,
- Attracting additional financial support for research from Government sources,
- Developing research infrastructure within institutions, facilities that can be utilised to support industry related research,
- Facilitating communication and support relationships between the metallurgy industry and senior university management,
- Promoting the important role of the metallurgical industry to young people and the broader community.

In addition, by insuring the sustainability of strong research teams with specialist knowledge and expertise, University academics can

- Develop and maintain industry consortia for research and education of common interest to sponsors,
- Actively assist in the optimisation of existing and development of new metallurgical processes,
- Ensure the successful implementation of research outcomes into industrial practice,
- Ensure the availability of expert capabilities and advanced technological for application to individual confidential R&D support,
- Facilitate active technological exchange and links between sponsors metallurgists and between sponsor-nominated Universities,
- Minimise the adverse impacts of periodic economic cycles on the retention of knowledge and expertise for the metallurgical industry.

23. Metallurgical undergraduate education – critical for future progress

Despite of the importance of metallurgical industry, the number of undergraduate students selecting studies in metallurgical engineering and the number of university programs offering educational opportunities in metallurgical engineering have been in decline for many years – this is a worldwide trend. There appear to be a number of contributing factors to this trend:

- Unfavourable public perceptions of the industry and lack of information on the role of metallurgy in our society,

- The lack of industry engagement and support in promoting studies and careers in the field,
- The funding formulae used by Government to support Universities, which are in the main based on the number of enrolments rather than industry or societal needs,
- University and Journal Ranking systems do not favour small specialist fields.

The lack of professionals in the field poses a significant threat to successfully implementing process improvements in existing operations and hinders the major changes needed for future economies. The public and students are increasingly aware of the impacts of climate change and the necessity of transforming our industrial practices to address these challenges. This shift in attitude presents an opportunity to reframe the narrative and public perception of the industry, shifting it from negative to positive. The dramatic shift towards electrification across all sectors – renewable energy, transportation, and electronic devices – has heightened awareness of the critical metals needed to enable these transitions. Additionally, there is a growing need for material conservation and increased metal recycling to minimize environmental impact, reduce energy consumption, and achieve circularity in the use of valuable, non-renewable resources. These are powerful messages the industry can leverage to explain how lead metallurgy plays a vital role in facilitating the recycling of critical, strategic, and precious metals.

Increasing public awareness of the key role of metallurgy is necessary but is not necessarily sufficient to attract students and graduates. The industry needs to be proactive in improving workplace environments and practices so that they are attractive to prospective students and engineers. Students are looking for opportunities where they feel they can make a positive contribution to the environment and are able to use the latest technologies to achieve this. Industry can take positive steps in attracting undergraduates in their early years at university when they have an opportunity to redirect their careers into the discipline, through for example, providing on-site experiences in the form of vacation work, plant visits and internships, financial support scholarships, professional development and social activities.

The allocation of university funding is for the most part determined by class size rather than strategic needs of industry or the country. Small classes for specialist courses are more likely to be removed from the curriculum, small programs are closed in the name of efficient use of limited financial resources. This is the pattern around the world – the only way to change the current trend and provide educational resources is for industry to be more proactive. Industry leaders need to inform university management and governments of the importance of the discipline and actively engage with and provide support to those institutions providing programs in metallurgical engineering.

We strongly believe there are opportunities to increase the number of metallurgy graduates if Industry, Universities and Governments are proactive and work collaboratively together to solve this problem to their mutual benefits.

24. University teaching- and research-focused academics potential important central role in triple academia-industry-government helix

The role of University academics in the research, education and implementation of the scientific advancements into industrial practice thus making real impact to the society is critical. University academics are in the centre of and are inherently connected to all stake-holders. University academics:

i) by definition, are actual experts in a particular field,
ii) have active links and knowledge of industry through research a) at the applied R&D level as well as b) at the industrial R&D management,
iii) are in direct contact with the University management,
iv) are in direct continuing contact and aware of the issues of the changing next generations of specialists, and at the same time
v) educate and directly influence the next generation of specialists, and
vi) are in contact with the government policies and bodies through the research funding applications and schemes.

There is a great potential for more engagement of the University academics into the policy development and decision making of the industry R&D and University management as well as government bodies.

EXTENDING THE METHODOLOGY

25. Thermodynamics and other physicochemical properties

An additional advantage of the use of structurally-based thermodynamic models, such as, the quasichemical formalism (QCF), is that they also provide important fundamental information about the behaviour of atoms within the materials. This information can be used to describe the physicochemical properties of the materials, for example, the viscosities of fluids (Kondratiev and Jak, 2005; Jak, 2009). Thermodynamic models are also critical to describe the viscosities of heterogeneous partly crystallised systems by predicting the proportion of solids and the composition of the remaining liquid phase (Kondratiev and Jak, 2001; Kondratiev et al., 2002; Jak et al., 2003). Extending the thermodynamic computer database predictive capabilities to other slag physicochemical properties is an important development (Thibodeau et al., 2016a; Thibodeau et al., 2016b; Kang and Chartrand, 2016; Smith et al., 2020; Kang, 2015).

26. Future needs in the high-temperature molten phases area

As outlined in the paper above, thermodynamic modelling a) is the central and critical component in the mathematical description and further optimisation of the high-temperature industrial processes, b) has the required methodologies for the development of the accurate description of thermodynamic properties and of phase equilibria, c) has already progressed to the useful level of adequate prediction of high temperature processes, and at the same time d) has great further potential p close the gaps in knowledge. It is therefore an opinion of the authors that more efforts and resources should be invested into further experimental work and thermodynamic modelling, similar to the continuing program undertaken by Pyrosearch. International collaboration of various groups can facilitate faster overall progress.

Further potential exists in the wider use of the first principles (ab-initio) and molecular dynamic simulations in phenomenological modelling of the type presented by authors. Currently, these models do not allow accurate representation of complex solutions at high temperatures. However, they allow to find important reference points for the thermodynamic model, such as enthalpies of formation at 0 K and sometimes heat capacities as functions of T for individual pure compounds and endmembers, including those which were not studied experimentally due to their metastability. These theoretical predictions could become a valuable complement to the experimental techniques described above.

The incorporation of the thermodynamic modelling into description of the industrial processes with kinetics playing significant role is another challenge. Relatively long times (in some cases up to several seconds) are currently required for a thermodynamic calculation at a single condition in a multi-component multi-phase system. Kinetics modelling usually would require multiple thermodynamic calculations making the overall modelling critically slow for practical use. This issue may be and should be gradually solved using significantly more powerful computer capabilities as well as special computational approaches. Linear extrapolation using 1st derivatives outlined above in the thermodynamic optimisation section can be a useful approach in relation to this issue.

The incorporation of thermodynamic modelling into predictions and optimisations of complex multi-unit industrial flowsheets is another great opportunity and at the same significant challenge. Similarly to the kinetic modelling, the relatively long time (in some cases up to several seconds) required for a thermodynamic calculation at a single condition in a multi-component multi-phase system is a barrier for the implementation of thermodynamic modelling into flow-sheet packages such as ASPEN, SYSCAD, METSIM where multiple calculations are needed for numerical minimisation methods for flowsheets with recycling streams. Similar to the kinetic modelling, incorporation of thermodynamic models into the flowsheet modelling can be facilitated with the significantly more powerful computer capabilities as well as special computational approaches. Again, linear extrapolation using first derivatives outlined above in the thermodynamic optimisation section can be a useful approach in relation to this issue.

CONCLUDING STATEMENTS

The key messages to all groups of professionals is that the metallurgical and recycling industry needs complex computerised optimisation tools similar to the GPS systems now used widely. The development of such GPS-like systems in pyrometallurgy is now possible although the task is challenging. To achieve that - the following components are essential, the availability of: i) sufficiently abundant and sufficiently accurate experimental data (that in turn require analytical capabilities), ii) appropriate theoretical thermodynamic models and iii) adequate computational capabilities. The development and implementation of the advanced fundamental information and advanced predictive tools requires long-term efforts of multi-skilled expert teams. To support such teams, the industry financial support and engagement as well as industrial implementation are essential. We believe that historically we are at the start of new digitalisation Pyro-GPS period. The tasks are significant, and the opportunities are significant. The risks not to progress in the direction of digitalisation are also significant.

The messages

i) to young researchers and metallurgists – the metallurgy field is important to the society,
ii) to industry R&D – more advanced information and tools are becoming available bringing more opportunities,
iii) to industry management – there are significant opportunities for improving efficiencies and profitability of the operations, pro-active research support is important, educated metallurgists are needed to convert opportunities into profits,
iv) to University management, government, broader community –metallurgy is important, and the risks not to act now and to miss those opportunities are high; it is important to maintain and expand metallurgy research and education, and
vi) to metallurgy research academics – you can play a central role in the academia-industry-government triple helix.

Collaborative work of many specialists, many industrial companies and many research groups is critical – we are all part of the solution and we all can contribute to the solution.

ACKNOWLEDGEMENTS

The Pyrosearch team acknowledges the financial and technical support from:

- *Pb research industrial consortia* including Aurubis (Germany), Boliden (Sweden), Kazzinc Ltd, Glencore (Kazakhstan), Nyrstar (Australia), Peñoles (Mexico) and Umicore (Belgium);
- *Cu research industrial consortia* including Anglo American Platinum (South Africa), Aurubis (Germany), BHP Billiton Olympic Dam (Australia), Boliden (Sweden), Glencore Technology (Australia), Metso Outotec Oy (Finland), Peñoles (Mexico), RHI Magnesita (Austria), Rio Tinto Kennecott (USA) and Umicore (Belgium);

- *Fe and slag recycling research industrial consortia* including Aurubis AG (Germany), BHP Fe ore (Australia), Rio Tinto ore (Australia), SWERIM (Sweden) and Umicore (Belgium); and
- Australian Research Council (ARC) Linkage program,
- US Defence program “Materials Recovery Technology for Defense Supply Resiliency” and Gopher (USA).

Special acknowledgement to Maurits Van Camp (formerly from Umicore) for his immense input in this program – his legacy stays in this continuing program, in the significant impact it makes to the research and industry communities, and the overall society and in our memories.

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