Challenges and limitations in development of large thermodynamic databases for multiple molten phases using the Modified Quasichemical Formalism

D. Shishin[1]*, M. Shevchenko*[2]*, E. Nekhoroshev*[3] *and E. Jak*[3]

1. Research Fellow, PYROSEARCH, University of Queensland, Brisbane, QLD, 4072. Email: d.shishin@uq.edu.au
2. Research Fellow, PYROSEARCH, University of Queensland, Brisbane, QLD, 4072. Email: m.shevchenko@uq.edu.au
3. Postdoctoral Research Fellow, PYROSEARCH, University of Queensland, Brisbane, QLD, 4072. Email: e.nekhoroshev@uq.edu.au
4. Professor, Centre Director, PYROSEARCH, University of Queensland, Brisbane, QLD, 4072. Email: e.jak@uq.edu.au

Keywords: thermodynamic modelling, FactSage, Quasichemical model, Slag, matte, speiss, metal

ABSTRACT

In the field of pyrometallurgy, the presence of multiple molten phases with distinct chemical compositions, such as slags, mattes, speiss liquids, metals, and molten salts, is a well-known phenomenon. These phases exhibit strongly non-ideal solution behaviour and are mutually miscible to varying degrees. To describe these complex molten liquids, the Modified Quasichemical Model (MQM) has proven effective and has been applied to numerous binary, ternary, and several higher-order multicomponent systems related to pyrometallurgy. In recent decades, the complexity of high-temperature processes has escalated due to increased impurity concentrations in primary ores, the incorporation of recycled consumer products, and the integration of metallurgical plants through by-product and waste exchanges. To address these issues, PYROSEARCH laboratory has been developing large 20-component thermodynamic database using a generalised Calphad methodology integrated with experimental investigations. Over the past decade, strategic decisions were made balancing the ability to generate experimental data, prediction power, accuracy, stability of calculations, as well as computational time, which are discussed in the paper. Examples provided for issues of >3 liquid immiscibility, non-ionic behaviour and exaggerated “sharp” enthalpies of mixing in silicate slags, dealing with multiple oxidation states, as well as comparative analysis of pair and quadruplet approximation in MQM.

INTRODUCTION

Pyrometallurgical production of metals employs selective separation of metals and nonmetals using their preference to one of the liquid phases, a gas phase, or rarely a solid phase. Commonly distinguished liquid types are molten salts, slags (oxide-based liquids), mattes (sulphide-based liquids), metallic liquids and speiss. Speiss liquids are formed between transition metals Fe, Co, Ni, Cu and Zn on the one side, and metalloids As, Sb, (Sn) on the other side. Molten salts are based on pairing between alkali and alkali-earth metals on the one side, and halogens, sulphates, phosphates, or carbonates on the other side. Molten salts are less common in primary pyrometallurgical production of metals from ores but applied in many electrometallurgical applications. They are also becoming increasingly important due to higher rates of recycling of e-waste, attempts to process tailings, incineration of waste, as well as in new emerging technologies for energy storage and generation.

In terms of the bond polarity these types of liquids can be ordered as follows:

Salts > Slags > Mattes > Speiss > Metals

Molten salts, slags, and most mattes at stochiometric metal-to-sulphur compositions exhibit an ionic behaviour. Covalent bonds are observed within the anions of molten salts, i.e. SO_4^{2-} or CO_3^{2-}, and in slags with high proportion of silica or boron oxide. Incomplete dissociation into ions, with the portion of preserved covalent bonds is expected for matte and speiss. Also, when matte (Sundström et al., 2008) and speiss solutions deviate towards excess metal in terms of stoichiometry, metallic type of bonds give important contribution to the observed physico-chemical properties.

The division of liquid into types is relative, they all are mutually miscible to a certain extent, and bond types change with changing composition. The basis for distinction is the ability to form miscibility gaps and the formation of distinct layers. Separation of the liquid layers through skimming or taping is at the foundation of many pyrometallurgical processes. Examples are shown in TABLE 1. The microstructures of samples, containing all five types of liquids are shown in FIG 1. These come from lead production. Molten sulphate salt is not typical for lead smelting and appears due to the introduction of zinc tailings in primary lead production. Speiss forms due to introduction of recycled materials.

TABLE 1 – Examples of pyrometallurgical processes bases on separation of liquid (molten) phases

Process	**Target production**	**Common design of furnaces**	**Liquid (molten) phases to be separated**
Smelting from primary ores	Cu, Ni	Flash furnace, top-submerged lance, side and bottom-blown furnaces	Slag, matte
E-scrap smelting	Cu, Pb, Ni, Au, Ag, …	Top-submerged lance, top blown rotary furnace	Slag, metal
Smelting	Pb	Same as above	(Salt), slag, metal
Fuming	Zn	Side and bottom-blown, plasma, electric arc	Slag, metal (or speiss)
Converting	Cu, Ni	Peirce-Smith, side and bottom-blown	Slag, matte
Fire refining	Cu	Cylindrical anode furnace, tilting furnace	Slag, metal
Slag reduction	Pb	Lead blast furnace	Slag, matte, metal
Drossing	Pb	Kettles	(Liquid speiss), matte, metal
Doré process	Au, Ag	Bottom-blown oxygen cupel	Slag, metal
Smelting	Fe	Blast furnace	Slag, metal
Iron recycling	Fe	Electric arc furnace	Slag, metal
Steel production	Fe	Basic oxygen furnace	Slag, metal
Electrolysis (Hall-Héroult)	Al	Electrolytic cell	Salt, metal

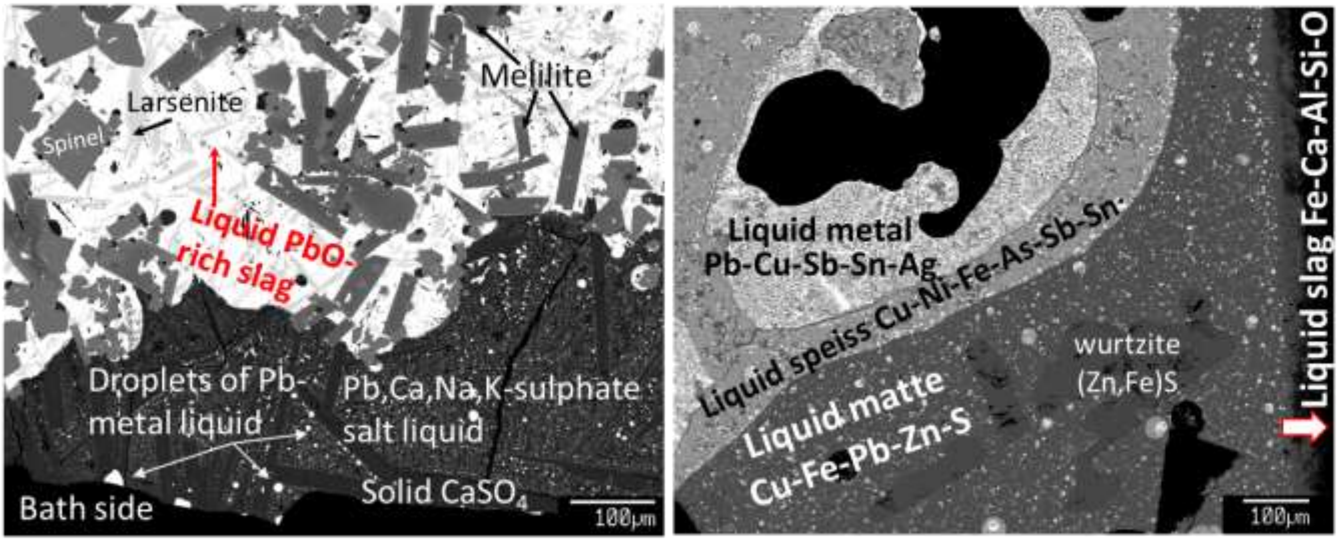

FIG 1 – Example of images obtained using backscattered electron microscopy of samples containing co-existing liquids with miscibility gaps. Left: liquid salt/slag/metal/solids equilibrium at conditions of lead sulphide smelting. Right: liquid slag/matte/speiss/metal/solids equilibrium at conditions of lead drossing. Slag phase is present, but not shown because it is too dark at the selected contrast.

Modern metallurgical production plants deal with rising impurity levels in primary ores. The recycled materials and wastes are also introduced in the process. The exchange of the by-products is used to increase the overall recovery, create new marketable products, and reduce the environmental impact. These changes make the chemistry more complex. Any step-changes in existing operations can be performed more efficiently using predictive computational tools. But these tools should be applicable for a wide range of conditions in terms of composition, temperature, oxidation/reduction potential. They cannot be developed exclusively on the data from existing operations. Calculations of thermodynamic equilibrium based on Gibbs energy minimisations can provide such predictions. When combined with kinetic factors observed in real process, they may significantly reduce the need for costly pilot tests and trials (Castillo-Sanchez et al., 2023). Powerful thermodynamic software has been developed over the last decades. For practical predictions, thermodynamic software requires mathematical models describing the Gibbs energy of all potentially existing phases within the chemical system, as a function of temperature, pressure, and composition.

Most mathematical models, including thermodynamic models, contain adjustable parameters. A combination of thermodynamic models together with the set of optimized adjustable parameters is often referred to as a thermodynamic database. High-quality models potentially have predictive power in complex systems with small number of adjustable parameters. But high-quality thermodynamic database is a product which must provide high accuracy. It is achieved by generating sufficiently abundant data used to fix the values of model parameters. The data used to optimise model parameters should be accurate and represent thermodynamic equilibrium. To achieve the accuracy and reduce the number of potential uncertainties, experimental studies are typically performed in less complex systems, which often means systems of smaller number of components. But the final goal is multi-component calculations. The aim of this publication is to demonstrate challenges we encountered during the development of thermodynamic models of liquid phases for the 20-component system directly relevant to non-ferrous pyrometallurgy applications. The first challenge was that the development had to be conducted in steps, with elements added in time:

Cu-Fe-O-S-Si (2014) + Ca-Al-Mg (2015) +
Pb-Zn-As-Sb-Bi-Sn-Ag-Au (2017) + Cr (2019) + Ni-Co (2020) + Na (2023) (1)

The decisions made in early stages of the project largely determined the direction of development of the models. As the size of the database grew, the larger resources required to introduce.

METHODOLOGY

Development of large multicomponent solution databases require the appropriate and strategic selection of the thermodynamic models and a method of obtaining model parameters while maintaining accuracy, predictive power, and self-consistency. The models should be structurally based, so that model parameters are more than empirical mathematical expressions. For instance, they can correlate to the energy of interactions between the atoms in the phase.

Modified Quasichemical Formalism

The Modified Quasichemical Model (MQM) (Pelton et al., 2000; Pelton and Chartrand, 2001; Chartrand and Pelton, 2001; Pelton et al., 2001), a collaborative effort between CRCT (Montreal, Canada) and GTT (Germany), has demonstrated its ability to describe the thermodynamics of many chemical systems, binary, ternary and of more components. Over the years, the model has undergone several improvements, as detailed in recent publications (Jung and Van Ende, 2020). These enhancements now offer greater flexibility in choosing constituents, formulating expressions for excess Gibbs energy, and interpolating binary parameters into ternary and higher-order systems. Notably, other established models, such as the Bragg-Williams ideal solution and the associate solution model can be reproduced within the MQM framework. These advancements warrant consideration of renaming MQM to the Modified Quasichemical Formalism (MQF) (Chartrand et al., 2024), highlighting its ability to accommodate various models within its structure, as shown in FIG 2. Present publication will outline recent experience in model selection options within the MQF.

In many liquid solutions, strong attractive interactions between certain constituents at the atomic level result in the significantly higher than random probability of finding them next to each other. This phenomenon, known as Short Range Ordering (SRO), alters the probability distribution, leading to a deviation from ideal entropy of mixing (Pelton and Kang, 2007). The main purpose of the MQF is to take into account this deviation. By definition, the ideal Bragg-Williams model neglects the SRO effect. The Associate solution model, which is an alternative way to treat SRO, assumes that strongly interacting constituents are bonded to each other. As a result, it cannot reproduce the random mixing entropy once the molecular associate is introduced (Pelton and Kang, 2007). The full implementation of MQF is only available in FactSage© software (Bale et al., 2016). Thermocalc© software relies on the Ionic Two-Sublattice Model (ITSM) (Sundman, 1991). Unlike MQF, ITSM enables charged and uncharged ions within the same solution, allowing the description of metallic and ionic solutions within the same model.

Ideas how to further improve the flexibility of MQF include the introduction of multiple compositions of Short Range Ordering (Wang and Chartrand, 2021) and variable geometric interpolation technique, beyond the choice Kohler-, Toop- and Muggianu- types (Wang et al., 2023). But these ideas have not been implemented in thermodynamic databases developed by the authors.

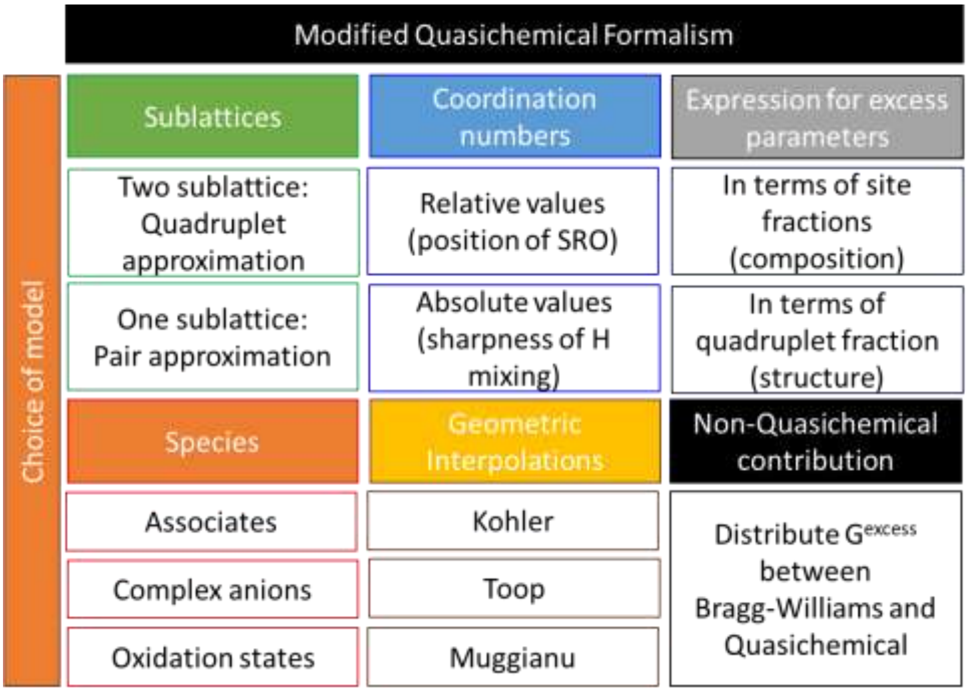

FIG 2. Choice of model options within the Modified Quasichemical Formalism

Extended Calphad Approach

Thermodynamic software requires expressions for the Gibbs energies of complex solution phases in the form of $G = f(T, P, x_1..x_n)$. where T is temperature, P is total pressure, and $x_1 \ldots x_n$ are compositional variables. The adjustable parameters, contained in these expressions, must be derived from experimental data, or in rare cases, from the first-principal methods. Enthalpy of formation, entropy, and heat capacity expressions ($\Delta H_f°$, $S°$, C_P) of solution components, as well as energy parameters for the interactions between them are all examples of model parameters. CALPHAD principles have become a standard for the thermodynamic description of a chemical system (Jung and Van Ende, 2020). The principles for a given system are as follows: a single set of model parameters for all potentially stable phases within the system should be obtained, which provides good description of all types of available experimental data, such as phase equilibria, activity measurements, the distribution of elements among phases, calorimetry, and crystallography (Shishin et al., 2013).

Mathematical models of complex systems, in general, can include the simultaneous contributions of four and more factors. In contrast, in the thermodynamics of multicomponent liquids, decreasing probability of complex interactions among more than three atoms warrants the use of only binary and ternary interaction parameters (Gorsse and Senkov, 2018). This imposes a temptation to study and access only binary and ternary systems, relying on model extrapolation into multicomponent systems. While this may be applicable to metallic liquids, our experience showed that the values of ternary parameters in oxide systems must be verified inside several related quaternary, or even higher order systems. Extrapolations often did not provide the results which were accurate enough.

The experimental methodology had to be improved to produce high quantity of experimental data in 4- , 5- components systems.

Thus, Calphad principles must be further extended when developing a large self-consistent multicomponent thermodynamic database. A larger single set of parameters need to be used, and it should describe all data in all related systems. When performing predictions in multicomponent systems, it is necessary that model parameters are defined (fixed) for all the binary, and eventually, for all ternary sub-systems and all solutions. For the database of 20-components, the theoretical number is 20!/2!/(20-2)! = 190 binary subsystems and 20!/3!/(20-3)! = 1140 ternary subsystems. Such huge numbers, especially for ternary systems, show the advantage of the model with high predictive power. Thermodynamic calculations using the current version of the database are used to determine the conditions of experiments, and compositional areas are selected to improve the confidence of a given parameter. This helps to increase the number of successful experiments and reduce the need to mesh-type planning of experiments. In cases, when experiments cannot be performed due to challenging chemical nature, e.g. Au-O liquids not existing at ambient conditions, the values of parameters must be obtained indirectly, from the data of the multicomponent systems. High number of experiments and parameters means the process of development is inevitably iterative, requiring re-optimization of previously assessed systems. Thus, the integrated experimental and modelling approach, is critical for the development of large thermodynamic databases.

Solid phases

At present, there are 95 solid solutions and 630 solid compounds with fixed stoichiometry in the database developed in PYROSEARCH. Models for liquids cannot be developed independently from solid phases. Phase equilibrium between the liquid and solid phase is one of the most important sources of thermodynamic information, and typically can be measured more accurately, compared to activity or calorimetric information for molten solutions. For notoriously large and complex solid solutions, such as spinel, the models are typically developed within the Compound Energy Formalism (CEF) (Hillert, 2001), which assumes the distinct crystal sublattices, and random mixing within each sublattice. The main model parameters are the Gibbs energy functions of all solution end-members, as well as excess parameters for the interaction of atoms within the same sublattice. As in the case of MQF, different models can be developed within CEF. In CEF, more than two sublattices can be used, which MQF does not allow. This feature is used for pyroxenes, melilite, feldspar. The same components, even charged ions, can be present on several sublattices. This approach creates many “virtual” end-members, necessitating the development of careful strategies to reduce the number of adjustable parameters though linear combinations and reciprocal reactions (Hillert et al., 2009). Still, for solutions like monoxide in the Fe-O system, simpler Bragg-Williams approach was preferred to describe the entropy of mixing (Hidayat et al., 2015). For non-stoichiometric solid speiss solutions, MQF with single sublattice demonstrated similar results as CEF with less parameters (Shishin and Jak, 2018) and more reasonable extrapolation of mixing properties outside of stoichiometry. This may be potentially beneficial for ternary and multicomponent systems.

OVERVIEW OF RESULTS AND ISSUES

Let us consider the selection of the models for important molten phases observed within the non-ferrous pyrometallurgy using the matrix in FIG 2. The summary is provided in TABLE 2, and the following sections discuss in more detail the selected models, their advantages and disadvantages.

TABLE 2 – Selection of sublattice and species within the MQF, chosen for the molten phases within the 20-component system (1) targeted for non-ferrous pyrometallurgy

Solution name	Selected model	Advantages	Limitations
Slag	$(Cu^{+1}, Fe^{+2}, Fe^{+3}, Si^{+4}, Al^{+3}, Ca^{+2}, Mg^{+2}, Pb^{+2}, Zn^{+2}, Ni^{+2}, Co^{2+}, Sn^{+2}, Sn^{4+}, Sb^{+3}, As^{+3}, Bi^{+3}, Ag^{+1}, Au^{+1}, Cr^{2+}, Cr^{3+}, Na^{+}, NaFe^{4+}, NaAl^{4+})$ (O^{-2}, S^{-2})	Takes into account Second Nearest Neighbour SRO between basic and acidic components Compared to purely associate models, less ill-defined parameters Associate still can be introduced for particularly difficult systems (i.e. $NaFe^{4+}$) Separate from liquid matte/metal/speiss and salt overcomes 3-phase immiscibility limit in FactSage	Cannot describe deviation from MeO_x and MeS_x stoichiometry, where x = 0.5, 1.0, 1.5, 2.0 Does not contain Cu^{2+}, Cr^{6+}, Pb^{4+} Assumption of fully ionic liquid does not work near pure SiO_2
Liquid matte/ metal/ speiss	$(Cu^{I}, Cu^{II}, Fe^{II}, Fe^{III}, Pb^{II}, Zn^{II}, Ni^{II}, Sn^{II}, Sb^{III}, As^{III}, Bi^{III}, Ag^{I}, Au^{I}, Cr^{II}, Co^{II}, Ca^{II}, Mg^{II}, Na^{I}, O^{II}, S^{II})$	Possible to describe complete stoichiometry range (even for oxides) Easy to add new component no ill-defined end-members Easy to introduce Bragg-Williams parameters from literature	Cannot describe Second Nearest-Neighbour SRO Lack of flexibility of ternary parameters and geometric interpolations Separate from slag, creates conflicts with oxide liquids
Salt	$(Ca^{+2}, Mg^{+2}, Pb^{+2}, Zn^{+2}, Na^{+1}, Cu^{2+}, Fe^{3+})(SO_4^{-2}, O^{-2})$	Relatively easy to expand using existing molten salt assessments	Separate from slag, which is not the case for some systems

Slag

The slag solution was the original reason for the development of the modified Quasichemical Model (Pelton and Blander, 1986; Wu et al., 1993a; Wu et al., 1993b; Jak et al., 1997a; Jak et al., 1997b). Many binary and ternary oxide systems were reasonably-well described at the time.

Sublattices

One sublattice model was chosen with O^{2-} being the only anion. Since the end-members of the solution were pure oxides, no deviation towards excess metal, or towards oxygen was allowed. For the systems containing Fe-O and Cr-O, species with several oxidation states were introduced (Decterov and Pelton, 1996), i.e. Fe^{2+} and Fe^{3+}, Cr^{2+} and Cr^{3+}, which partially solved the oxygen/metal non-stoichiometry within these sub-subsystems for a limited range of composition. Wide liquid-liquid miscibility gaps between metallic liquid and oxide liquids for most metal-oxygen systems justified the practicality of the model. This eventually grew into FToxid public database of FactSage (Bale et al., 2016), which is currently on of the largest self-consistent oxide database (Jung and Van Ende, 2020). The PYROSEARCH database (Jak et al., 2019) uses the same approach. It is not as big in terms of number of elements, but is continuously re-assessed iteratively, supported by new experimental results. For instance, new data have been generated even for foundational system of Ca-Fe-O-Si in 2022, resulting in major revision. At this point, the properties of all oxide end-members, and all excess parameters in FToxid and the database of the PYROSEARCH database are different.

Alternatives for slags have been developed by Hillert, Sundman and Selleby (Selleby and Sundman, 1996; Selleby, 1997; Hillert et al., 1990), who used Ionic Two-Sublattice Model (ITSM), which become the foundation of TCOX thermodynamic database of Thermocalc. Yet another approach was used by (Jantzen et al., 2021) who started the development of the independent GTOx database in 2000s, citing the need to "give a second opinion to our customers who have licensed the FToxid database… and a better description for … high Na_2O- and K_2O- , and vanadium-containing systems". They used an associate model. For comparison, the models for the slag within the Ca-Fe-Si-O system, which is foundational for many non-ferrous pyrometallurgical processes, are given below:

MQF (FToxid and PYROSEARCH database): $(Fe^{+2}, Fe^{+3}, Si^{+4}, Ca^{+2})(O^{-2})$,

Ionic Two-Sublattice Model (TCOx): $(Fe^{+2}, Si^{+4}, Ca^{+2})_P(O^{-2}, SiO_4^{-4}, FeO_{1.5}, SiO_2, \text{Vacancy}^{-Q})_Q$,

Associate model (GTOx): $(Ca_2O_2, Fe_2O_2, Fe_2O_3, Fe_3O_4/1.5, Si_2O_4, CaSiO_3, Ca_2SiO_4/1.5, FeSiO_3, Fe_2SiO_4/1.5, CaFe_2O_4/1.5, CaFeSi_2O_6/2)$

All these models have been further expanded to include more metals. The TCOx model can describe metallic liquid and slag using the same solution. The current model for slag in UQPY is provided in TABLE 2.

Selection of species: oxidation states

TABLE 2 shows the selection of "Species" for the PYROSEARCH slag model. A decision was made in 2013 to only include Cu^{+1}, but not Cu^{+2} in the slag model for non-ferrous applications. It was demonstrated (Shishin and Decterov, 2012) that the formation of Cu^{+2} is significant at $p(O_2)$ above 10^{-3} atm for temperature > 1100°C, as shown in FIG 3. These highly oxidizing conditions are not encountered for most process steps in the pyrometallurgy of Cu, Ni, Pb, Zn, Fe, Sn or others. The decision significantly reduced the number parameters between Cu^{+2} and other components of the slag, which are difficult to define. Very little reliable experimental data existed for these high $p(O_2)$ conditions. The same logic applies to Pb^{+4}, Cr^{+6}, which are even less stable at high temperatures, and are not expected in liquid slags, but are introduced as solid compounds, when necessary. Some applications, such as using molten copper oxide for high temperature for solar energy storage and oxygen production (Jafarian et al., 2017) do require correct predictions of Cu^{+2}/Cu^{+1} in liquid oxide. These are covered by the Liquid matte/metal/speiss solution model (Shishin et al., 2013), which is discussed further. Some evidence exists that the formation of accretions close to the uptake shaft of the copper Flash Smelting furnaces may involve liquid slag phase equilibria within the Cu-Fe-O-Si system at oxygen partial pressures exceeding 10^{-2} atm. If confirmed, the accurate description would require the introduction of Cu^{+2}. This in turn, would shift the stoichiometry of slags equilibrated with metallic copper further away from Cu^0, contrary to diagram in FIG 3. Introduction of both Cu^0 and Cu^{+2} is not possible within the selected formalism, since charges and uncharged species together are not allowed. Even if was possible, that would create more calculation conflicts with Liquid matte/metal/speiss solution model. The partial solution could be the possibility to turn on and off the Cu^{+2} species in FactSage software, but this makes phase selection complicated for metallurgical engineers.

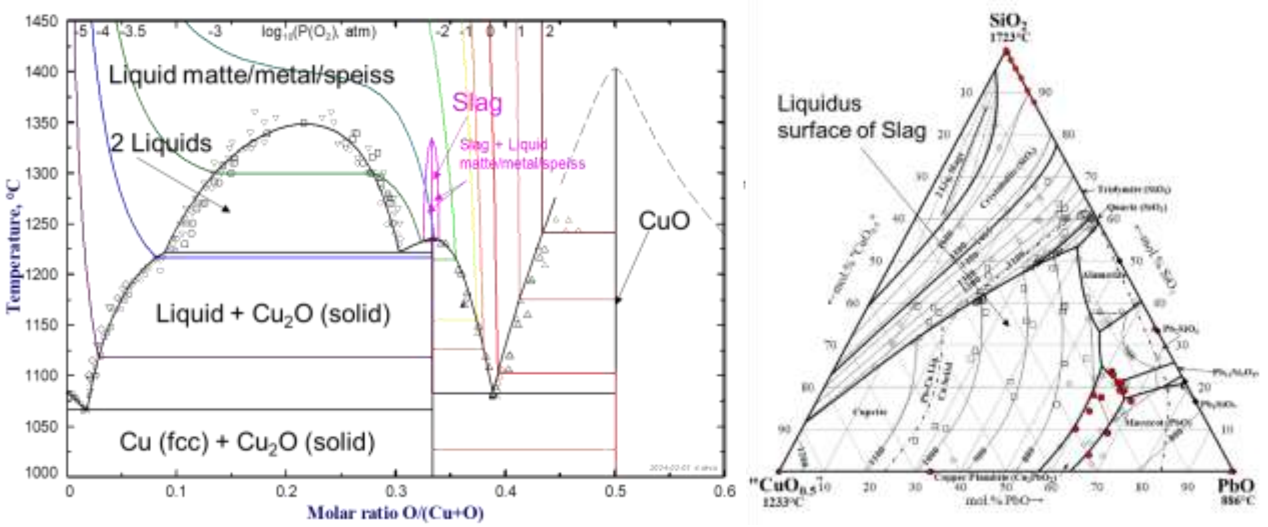

FIG 3. Left: Phase diagram of the Cu-O system (Shishin and Decterov, 2012). The compositional domain of Slag solution is much smaller than Liquid/matte/metal solution. Right: Example of Slag liquidus projection in the Cu-Pb-Si-O system (Wen et al., 2023) demonstrates the practicality of this approach for the description of multicomponent systems in non-ferrous pyrometallurgy.

Selection of species: associates

The presence of Na_2O in slags which also contain Al_2O_3 and SiO_2 result in the so called “charge compensation” effect. Cations of Al^{+3} in the presence of Na^{+1}, assume the position of Si^{+4} and act as a network former (Decterov, 2018). This strong ternary effect cannot be satisfactory modelled without the introduction of $NaAl^{+4}$ associate in the MQF (Lambotte and Chartrand, 2013). The introduction did not require specific changes to the formalism, and good results were achieved for systems exhibiting strong “charge compensation”. Still, model parameters for the $NaAl^{+4}$ species are not well-defined. Thermodynamic properties of virtual liquid $NaAlO_2$ cannot be obtained from the Na_2O-Al_2O_3 data. They can be better fixed, when considering binary and ternary data within the Na_2O-Al_2O_3-SiO_2 simultaneously, but even so, the excess Gibbs energy parameters between $NaAl^{+4}$ and cations other than Si^{+4} are ill-defined. Predictions in multicomponent systems become less reliable and can result in spurious miscibility gaps, such as one observed by (Nekhoroshev, 2019) in the CaO-Na_2O-Al_2O_3-SiO_2 system. The decision to introduce $NaAl^{+4}$, (and $NaFe^{+4}$ for the same reasons), created a challenge**.** Significant resources are required to “scan” the multicomponent systems for possible problems, generate experimental data and make sure the parameters involving these associates are fixed. This direction of work has not fully started yet, since Na^{+1} was the last element to be introduced in in the chemical system (1).

Further evolution of the Slag model within the MQF was largely driven by the need to describe the solubility of sulphur (Kang and Pelton, 2009), giving the rise of the two-sublattice model. The anion S^{-2} was introduced on the second sublattice as shown in TABLE 2, and used the mathematical expressions originally developed for molten salts. In addition to sulphide capacity, the resulting model could be used to predict phase equilibria involving sulphides (mattes) and oxysulfides (Jo et al., 2013), but limited to fixed sulphur-to-metal and oxygen-to-metal stoichiometry. For instance, within the Fe-O-S-Si system, no deviation of stoichiometry is possible near the composition of FeS, but the model was capable of describing miscibility between slag and matte. This approach is suitable to understand the formation of steel inclusions in the slag, but proved not applicable for slag/matte equilibria in copper, lead and nickel smelting. In the PYROSEARCH database, mattes are described using a separate solution. Metal/sulphur non-stoichiometry in mattes is a significant factor for accurate predictions for non-ferrous processes. The introduction of sulphur-containing quadruplets, such as $Cu^{+1}Fe^{2+}O^{-2}S^{-2}$, allowed quantitative modelling solubility of copper in slags (Shishin et al., 2018b), as well as slag/matte equilibria involving Pb, Ni and other metals (Hidayat et al., 2020; Shishin et al., 2020b; Sineva et al., 2023). Still, the selected model does not allow the description of complete miscibility between slag and matte, which is observed in Cu-free Fe-O-S-Si and Ca-Fe-O-S systems. As in the case of Cu^{2+}, the selection of the model was driven by multicomponent practical predictions, at the expense of lower order systems with small practical value. Example of alternative approach, describing slag, matte and metal with using single solution is available $(Fe^{+2}, Ca^{+2})_P(O^{-2}, S^{-2}, S^0, FeO_{1.5}, Vacancy^{-Q})_Q$ (Dilner and Selleby, 2017) in TCOx database of Thermocalc. Large compositional areas of the system in question were not experimentally studied and the agreement with existing experimental data is semi-quantitative. The FToxid Slag was further expanded towards F^-, SO_4^{-2}, PO_4^{-3}, CO_3^{-2}, and other anions, with limited concentrations. Certain challenges in modelling oxyfluoride systems required formalism improvements (Lambotte and Chartrand, 2011), which later were generalised (Wang and Chartrand, 2021). The two-sublattice Modified Quasichemical Model in Quadruplet Approximation assumes the ionic nature of oxides and salts. It uses the Gibbs energy functions for solution end-members, i.e. Cu_2O, Cu_2S, FeO and FeS, to express the magnitude of First Nearest Neighbour SRO, while Second Nearest Neighbour SRO is taken into account by excess parameters.

Coordination numbers

The absolute values of coordination numbers were originally selected to provide the entropy of mixing to be zero at the composition of maximum short-range ordering for the system with infinitely negative enthalpy of mixing. The numerical values were calculated by (Pelton and Blander, 1984), and these values are still used for the coordination numbers of most species in present-day Slag solution: 0.68872188 for +1 cations, 1.37744375 for +2 cations, 2.06616563 for +3 cations, and 2.75488750 for +4 cations. The absolute values are not as important as the ratios of coordination numbers. Possibly due to the low importance, these absolute values are the only model parameters that have been preserved since the early versions of the model. The ratios of coordination numbers determine the composition of maximum short-range ordering. In later publication (Pelton et al., 2000), it was recommended that for the systems with small negative or positive values of enthalpy of mixing, the coordination numbers should be closer to their physical values. In the case of Cu^{+1}, this recommendation was originally not applied, so it was assigned the “default” value for +1 cations. This worked relative well but required the introduction of the positive Bragg-Williams parameters to describe the tridymite liquidus related to the Cu_2O-SiO_2 system (Hidayat and Jak, 2014; Hidayat et al., 2017a). The latest systematic experimental work in the high-SiO_2 region studying the miscibility gas in slags for the systems like Cu-Fe-O-Si (Wen et al., 2021), Cu-Pb-O-Si, Cu-Zn-O-Si demonstrated (Wen et al., 2023) the need for correction. Example is shown in FIG 3 (Right) and labelled as 2 Liq. Slags. After the coordination number for Cu^{+1} was doubled, it was possible to improve the description of the miscibility gaps.

Sharp enthalpy and non-Quasichemical contribution

A large dataset of new experimental data have been obtained for the foundational system Ca-Fe-O-Si, including all subsystems, in 2020-2024 (Cheng et al., 2021; Cheng et al., 2019). With higher accuracy, and large density of experimental points, it was quite difficult to achieve the desirable agreement by using the similar set of model parameters, as in the earlier assessment (Hidayat et al., 2016b; Hidayat et al., 2017b; Hidayat et al., 2016a). The major re-vision was initiated, which included the update in the properties of all liquid oxide end-members. Properties of many solid compounds also required updates. The principles are described in the parallel presentation (Shevchenko et al., 2024). Furthermore, it became clear the liquidus of Ca_2SiO_4 in the Ca-Fe-O-Si and other systems could not be described even after the changes in thermodynamic properties of solids. The reasons for that were difficult to isolate, but in the end it turned out that for the slag phase, the Gibbs energy of mixing was too “sharp” at the composition of Ca2SiO4. The phenomenon of sharp enthalpy of mixing was previously discussed for the metallic systems (Pelton and Kang, 2007), but not applied in slags. The solution was proposed by the present authors to combine the Bragg-Williams and Quasichemical contributions in slags, when required. After the Gibbs energy of mixing was corrected by the combination of the Quasichemical and Bragg-Williams parameters for the CaO-SiO_2 system, as shown in FIG 4, better description in the area of Ca_2SiO_4 was obtained for the several systems containing CaO-SiO_2, such as ZnO-CaO-SiO_2, Al_2O_3-CaO-SiO_2 and MgO-CaO-SiO_2. These results are not yet published.

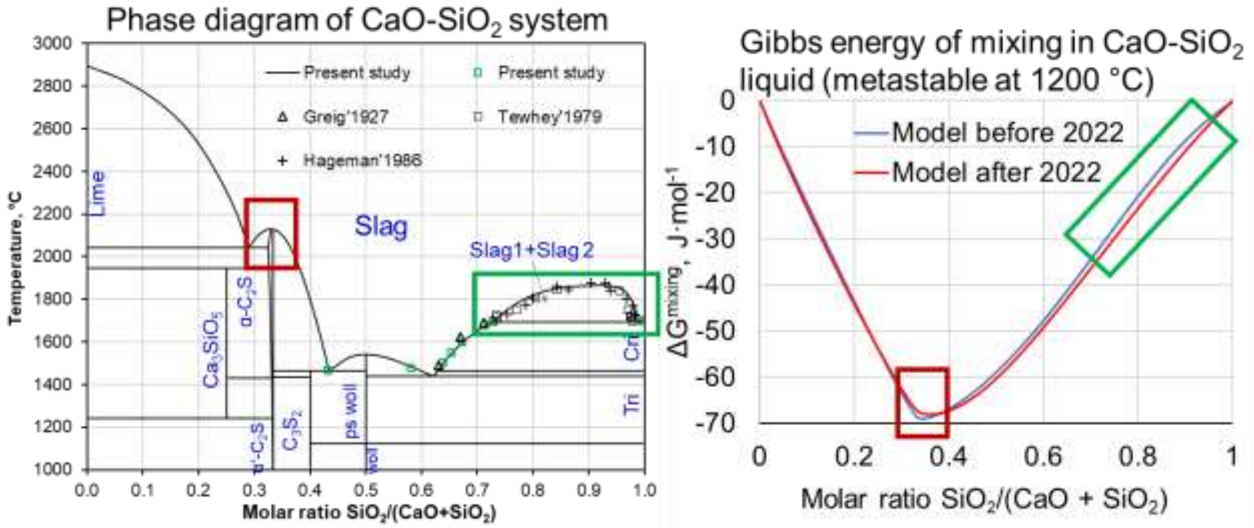

FIG 4. Two regions in the CaO-SiO$_2$ system which required significant revision of model within the MQF, not just the revision of model parameters: enthalpy of mixing is too sharp near Ca$_2$SiO$_4$ and excess curvature of Gibbs energy of mixing near SiO$_2$.

Unusual excess parameters – non-ionic slags

The models for slags developed using the MQF typically require few model parameters to describe the main features of thermodynamic properties and phase diagrams. The use of multiple parameters to describe experimental data, especially series of negatively correlated parameters, is discouraged and may indicate internal inconsistencies in the experimental data series. Also, it is unusual to use excess parameters with high powers, i.e. $g_{AB}^{i,j}$ where *i* or *j* > 6, except for the Me-Si-O systems (Me = Li$^+$, Ca^{+2}, Mg^{+2}, Fe^{2+}, Fe^{3+}, Zn^{+2}, Cu, Ni^{+2}, Co^{+2}, Cr^{+2}...). Parameters with high power on SiO$_2$ have been commonly used for the to introduce the miscibility gaps in slag close to SiO$_2$ (Konar et al., 2017; Prostakova et al., 2012; Prostakova et al., 2013; Hidayat et al., 2017b; Wu et al., 1993b; Jung et al., 2007). An example of miscibility gap in slag is shown in FIG 4 (left, green area). Furthermore, these parameters often contained large entropy terms to reproduce the closing the miscibility gaps at high temperature. For many systems the experimental data on the miscibility gaps were rare and controversial, so little attention was given to the values of these parameters. Recent EPMA measurements in high-SiO$_2$ areas of the ternary and higher-order systems (Shevchenko et al., 2022; Khartcyzov et al., 2022; Cheng et al., 2021) revealed that predicted miscibility gaps extended systematically too far into the multicomponent compositional space compared to experimental data, and could not be described well enough using ternary parameters. This indicated that Gibbs energy of mixing was too concave in many Me-Si-O systems in the region shown using green area in FIG 4 (right). Less concave Gibbs energy of mixing, but similar shape of the miscibility gap could be achieved using excess parameters with higher power on SiO$_2$, more than 9. These parameters were never used before. It is believed the need to use unconventional parameter series is attributed to the fact that the model for slags assumes fully ionic behaviour. The high-SiO$_2$ liquids are not fully ionic (weak electrolytes), and exhibit long-range electrostatic interactions between the uncompensated charged Me^{x+} cations and O^{2-} anions, an effect similar to the Debye-Hückel model and clustering well known to be present in the diluted aqueous solutions. The Gibbs energy of mixing of the components can be better represented as a polynomial sequence, to simulate the long-distance ionic interactions (FIG 4). After the introduction of the polynomial sequences in some systems, unrealistic entropy contributions to excess parameters were no longer necessary, resulting in better description of tridymite liquidus at temperatures below the miscibility gap for many systems, particularly CaO-FeO-Fe$_2$O$_3$-SiO$_2$. Systematic replacement of parameters for high-SiO$_2$ liquids is expected to provide step-like improvement in many other systems.

Alternative approach was used in a PhD thesis by Nekhoroshev (2019), who introduced dimers of (Na$_2$)$^{+2}$ and (K$_2$)$^{+2}$ to better describe liquidus in high-SiO$_2$ region of the Na$_2$O-SiO$_2$ and K$_2$O-SiO$_2$ systems. Still, this approach, if applied to the multicomponent database, would result in many undefined excess parameters among dimers and other components of the solutions. In the

PYROSEARCH model, a combination of $g^{0,8}_{\mathrm{Na^{+1}Si^{+4}}}$ and $g^{0,15}_{\mathrm{Na^{+1}Si^{+4}}}$ was tested for Na_2O-SiO_2 and good description of SiO_2-rich was achieved as shown in FIG 5.

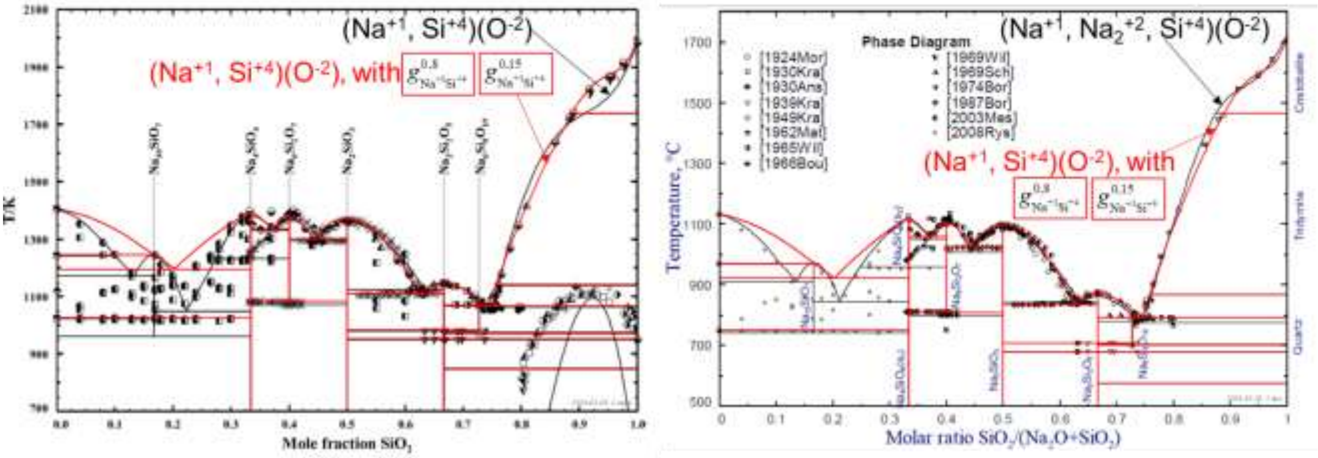

FIG 5. Phase diagrams of the Na_2O-SiO_2 assessed using different models within the MQF: Black lines are earlier works (Lambotte and Chartrand, 2011) and (Nekhoroshev, 2019), red lines are PYROSEARCH model results.

Liquid matte/metal/speiss

Apart from differences in chemistry, the choice to treat Liquid matte/metal/speiss as a separate model from slag and salt comes from the technical limitation of FactSage©. For the equilibrium calculations, a maximum of three immiscibilities within the same solution model is allowed, which is indicated by using the J-option in the user interface. In theory, more immiscible liquids of the same solution can be included in the calculation by creating copies of the same solution with different names and slightly different properties, but stability and speed of such calculations is questionable. Even three-phase equilibria in the multicomponent system pushes FactSage© to the limit, and sometimes gives incorrect results. A generalized model for slags, mattes, metals and speiss within the MQF is theoretically possible but not practical. We observe slag/matte/metal/speiss equilibrium in experimental results (see FIG 1, right). It would not be possible to reproduce this in the calculation, if all these phases were described using a single solution.

Sublattices and species

The first model for mattes within the MQF was developed in 1990s (Dessureault and Pelton, 1993; Decterov et al., 2000; Kongoli et al., 1998). One-sublattice approach was used, with the main goal of describing strong SRO between metals and sulphur. The species were not charged. In theory, this approach allows the description of liquids within the complete range of composition from metals to sulphides, and to elemental sulphur. Still, in these publications, mattes were artificially separated from molten copper and from molten lead metal solutions to benefit from existing models for these metallic solutions. The one-sublattice approach was expanded by Waldner and Pelton (2004b, 2005); Waldner and Sitte (2011) and Waldner and Pelton (2004a). Metallic copper and matte were merged and included in FactSage software as FTmisc database (FTsulf since version 8.2), but the results of this work were not published until much later (Waldner, 2020; Waldner, 2022).

Multiple coordination numbers for elements

The concept of treating metals and mattes within the same solution was accepted by the developers of the PYROSEARCH model. When expanding the database towards non-ferrous applications, it was also necessary to describe the solubility of oxygen in metals and mattes. The selected model within the MQF was also applicable to oxide liquids (see FIG 3 left) in cases when Second Nearest Neighbour SRO was not that important, i.e. for oxide liquids without SiO_2.The Cu-O and Fe-O systems had two compositions of SRO each, which was solved by introducing extra species intro the model. They had different thermodynamic properties and coordination numbers, i.e. Cu^{I} and Cu^{II}, Fe^{II} and Fe^{III}. (Shishin and Decterov, 2012; Hidayat et al., 2015; Shishin et al., 2013). The notations ^{I}, ^{II} and ^{III} have the meaning of valency with O^{II} and S^{II}, and determined by the ratio of coordination numbers. A drawback of this approach was that thermodynamic properties of pure liquid O^{II}, Cu^{II}, Fe^{III} were ill-defined, since they don't exist.

Heat capacity term in excess Gibbs energy

Within the selected model, the heat capacity of liquids at the compositions of maximum SRO, for instance at Cu_2S, is an additive function of endmembers, i.e. liquid Cu^{I} and S^{II}, which is not a very good approximation from the physical point of view. The bonds between atoms give a significant contribution towards heat capacity. Liquid copper has metallic bonds, Cu_2S is believed to have large proportion of ionic bonds, while S should retain much of covalent bonds in the liquid state. Still, uncertainties in heat capacities are significantly smaller compared to metal-sulphur and metal-oxygen interactions, so very good description of experimental results have been obtained by the introduction of composition-dependent excess Gibbs energy functions. Still, in the case of Cu_2S, a correction of heat capacity may be required, since the only experimental work on this topic indicates lower value (FIG 6). The problem of heat capacity was not addressed in a recent publication (Waldner, 2020). Typically, excess Gibbs energy dependence on temperature (T) is expressed as a + bT, but additional cTln$T$ term should be used in this case. Of course, such a correction would initiate the re-assessment of all parameters in systems related to the Cu-S, i.e. Cu-As-S (Prostakova et al., 2021), Pb-Cu-S (Shishin et al., 2020a), and dozens more. Optimistically this may help resolving some of the accuracy issues explained in sections below.

FIG 6 shows another important concept. The reasonable function is used for liquid Cu_2S for temperatures below melting and down to 0 K. Large portions of FactSage public database do not have reasonable heat capacity functions far below melting temperatures, which is compensated by excess Gibbs energy functions. Further improvements in the accuracy of predictions demonstrated the need to revise these functions. In the Calphad community, the need to invest resources into re-assessments of the systems due to corrections in heat capacity below 298 K is often justified by using the term "3rd Generation" Calphad database, with publications appearing for single-component (He et al., 2022) and binary-system re-assessments. In some cases the use of this highly publicized term results in the publication of low-quality assessments (Abdul et al., 2023).

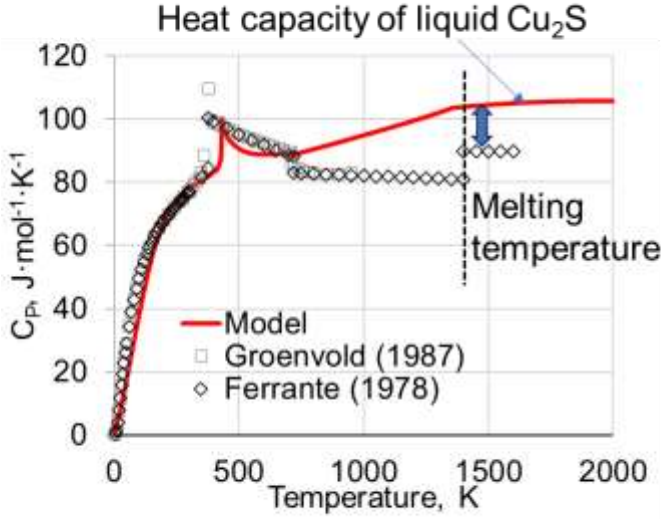

FIG 6. Heat capacity of Cu_2S. Symbols are experimental data (Groenvold and Westrum, 1987; Ferrante et al., 1978). Line is calculated using the PYROSEARCH model for the liquid phase at the composition of Cu_2S. Double arrow indicates that heat capacity of liquid should be corrected using the cTln$T$ term in excess Gibbs energy.

Lack of direct parameters between sulphides

The analysis of slag/matte equilibria with the Cu-Fe-O-S-Si and higher order systems (Shishin et al., 2018b; Shishin et al., 2018a) indicates possible need for the re-assessment of the Cu-Fe-S system. The predicted $P(O_2)$ vs. wt% Cu in matte, a systematic deviation of about +0.15 in $\mathrm{Log}_{10}[P(O_2)$, atm] is observed, when compared to experimental data obtained using the equilibration with the flow of CO-CO_2-SO_2-Ar gas. No apparent reasons for this deviation can be found from the analysis of existing data within the Cu-Fe-S (matte) (Waldner, 2022) or Cu-Fe-O-Si (slag) (Hidayat et al., 2017a) subsystems. The data in the Cu-Fe-O-S system (Shishin et al., 2015) is somewhat scattered, and no systematic deviation is observed. So, the slag/matte data indirectly indicates the systematic deviation of the activity “FeS” according to the reaction:

“FeS” (in Cu-Fe-S matte) + O_2 (activity fixed) = “FeO” (in Fe-Si-O slag, activity predicted) + SO_2 (activity fixed)

This assumes the achievement of equilibrium and correct calibration of the gas flow in these complicated experiments.

Another case is the Cu-Ni-S system, where the data on the tie-lines between metallic phase and matte could not be successfully re-conciliated with the matte-digenite phase diagram data by Walder or in the PYROSEARCH database.

The current working theory is that accumulated deviation of Gibbs energy exist for the Cu_2S (as in FIG 6), or a misbalance in Gibbs energy between Cu_2S and other sulphides, i.e. FeS or NiS. In the case of Slag, these types of inconsistencies can be compensated by binary parameters between end-members. In one-sublattice model for mattes, ternary parameters must be used. As shown in FIG 7, main ternary parameters do not act along the line of maximum SRO, which makes it very hard to compensate issues in certain areas of the diagram, without affecting other areas. It is tempting to introduce the associates inside the MQF, such as Cu_2S, FeS, possibly NiS to get access more excess parameters. It would be possible to describe the existing binary system data, and very likely, ternary data due to larger and more flexible set of available binary parameters. It is hard though, to predict how such model would behave in a system with many elements. Logically, Cu_2O, FeO, etc. associates would need to be introduced as well. Computational time will increase significantly, since FactSage still needs to calculate the bond fractions between all species on the sublattice, such as Cu-Cu_2S, Cu_2S-FeO, etc.

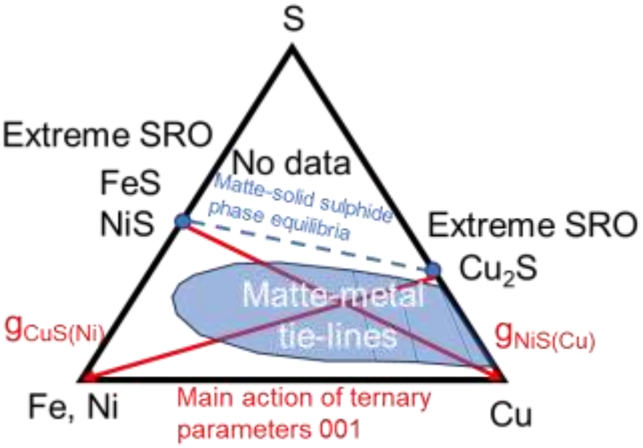

FIG 7. The problem of ternary parameters in one-sublattice model for Liquid matte/metal/speiss. No direct parameters along the FeS-Cu_2S and NiS-Cu_2S lines.

Geometric interpolation

Within the current model, the obvious interpolation method in binary parameters into higher-order space is Kohler-Toop with sulphur being an asymmetric component. With the expansion of the database towards As, Sb and Sn, the strong interaction between copper, iron, and these metalloids (Shishin et al., 2019; Shishin et al., 2023) was described using the same model within the QMF. Same model, but slightly different parameters were used in parallel studies by (Kidari and Chartrand, 2023b; Kidari and Chartrand, 2023a). Unlike the sulphide systems, where barely any data exist for the sulphur-rich region beyond the composition of maximum SRO, the regions AsS-Cu_2S-S and AsS-Ag_2S-S were relatively well studied experimentally. In these systems, the choice of geometric interpolation is not obvious. For the Ag-As-S, silver was selected as an asymmetric component (Kidari and Chartrand, 2023a). It is worth mentioning, that no liquid immiscibility experimental data within the Ag-Ag_2S-Ag_3As area of the diagram were available, even though the gap was predicted by the model. In the case of Cu-As-S, Muggianu-type of interpolation provided reasonable results, even though the mathematical expressions of the Muggianu-type interpolation of excess parameters written in terms of pair fraction may be incorrect in FactSage software. It was very challenging to describe experimental data on the immiscibility within the Cu-Cu_2S-Cu_3As together with other areas of the diagram, indicating that different types of interpolation techniques may be required for different areas of the diagram. This can only be achieved by introducing the associates within the existing MQF. While helping some systems, choice of geometric interpolations between associates and all other components can be a daunting task.

Salt

The choice of the model for salt was largely inspired by the works of Coursol et al.(2005a) and Coursol et al. (2005b). It was decided not to merge slag and salt within the same solution but introduce the O^{-2} anions into the salt model (see TABLE 2). Antimony and arsenic in the +5 oxidation state will in all probability dissolve in sulphate liquids, forming antimonates and arsenates. Sulphate liquids have been demonstrated to remove As and Sb from copper metal (Coursol et al., 2004), and these studies are of interest for lead refining. Formation of liquid sulphates should be controlled, as it accelerates the hot corrosion of furnace components during the lead smelting and may also cause the formation of dust accretions in off-gas pathways. A possible further expansion is the introduction of SbO_4^{3-}, AsO_4^{3-} anions.

CONCLUSIONS

This review demonstrates the versatility of the Modified Quasichemical Formalism (MQF) for developing various molten phase models. The choice of the model is a balance between the predicting power of and the flexibility to provide the accurate description of reality through the optimisation of model parameters. When the focus is on multicomponent solutions, the developments in experimental techniques and generation of abundant and accurate experimental become critical. The data generated in 2014-2024 pushed the existing models to the limit in terms of accuracy, and challenged some decisions that were made at the early stages of the development.

Examples of long standing issues that have been resolved recently by introducing unconventional model choices into MQF, including: 1) Combining Bragg-Williams and Quasichemical negative contributions into the slag model for the CaO-SiO_2, which made the tip at the enthalpy of mixing less sharp; 2) Introducing the excess Gibbs energy parameters with powers of > 9 to describe non-ionic behaviour of slags near pure SiO_2. An example of issue that has not been resolved yet is the inability to reconcile the activity, distribution of elements and phase equilibria for several Cu-S-containing systems. It is possible that the choice of one-sublattice approach without associates for Liquid matte/ metal/ speiss limits the model flexibility and results in: 1) incorrect heat capacity at the composition of maximum SRO requiring systematic introduction of the $T\ln T$ term in excess Gibbs energies; 2) Inability to introduce direct excess binary parameters between two sulphides at the compositions of maximum SRO; 3) Inability to create different geometric interpolation techniques for different areas of the ternary system X-Cu-S.

The issues and potential solutions often originate in systems of 2 or 3 components, but become evident only in multicomponent systems. For the established multicomponent thermodynamic database, any changes in low-order systems require significant efforts and iterative re-assessment of model parameters in hundreds of related higher-order systems. This phenomenon is often compared in the Calphad community to re-building the foundation of the inverted pyramid. To perform re-assessments effectively, large datasets of hundreds of thousands experimental points, and tools for their effective management must be developed. Newly obtained experimental information should trigger the semi-automated re-assessment. In this way, alternative model approaches potentially providing further improvements can be tested in timely manner.

ACKNOWLEDGEMENTS

The research funding and technical support is provided by the consortium of copper and lead producing companies: Anglo American Platinum (South Africa), Aurubis AG (Germany), BHP Billiton Olympic Dam Operation (Australia), Boliden (Sweden), Glencore Technology (Australia), Metso Oy (Finland), Peñoles (Mexico), RHI Magnesita (Austria), Rio Tinto Kennecott (USA) and Umicore NV (Belgium), as well Australian Research Council Linkage program LP190101020 “Future copper metallurgy for the age of e-mobility and the circular economy". Present study would not be possible without the facilities and technical assistance of the staff of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy and Microanalysis in The University of Queensland.

REFERENCES

Abdul, W., Mawalala, C., Pisch, A. & Bannerman, M. N. 2023. CaO-SiO_2 assessment using 3rd generation CALPHAD models. *Cem. Concr. Res.,* 173**,** 107309.

Bale, C. W., Belisle, E., Chartrand, P., Decterov, S. A., Eriksson, G., Gheribi, A. E., Hack, K., Jung, I. H., Kang, Y. B., Melancon, J., Pelton, A. D., Petersen, S., Robelin, C., Sangster, J., Spencer, P. & Van Ende, M. A. 2016. FactSage thermochemical software and databases, 2010-2016. *CALPHAD,* 54**,** 35-53.

Castillo-Sanchez, J.-R., Oishi, K., St-Germain, L., Ait-Amer, D. & Harvey, J.-P. 2023. The power of computational thermochemistry in high-temperature process design and optimization: Part 1 - Unit operations. *CALPHAD,* 82**,** 102593.

Chartrand, P. & Pelton, A. D. 2001. The Modified Quasichemical Model. III - Two Sublattices. *Metall. Mater. Trans. A,* 32**,** 1397-1407.

Chartrand, P., Wang, K. & Gheribi, A. E. 2024. Recent developments for the Modified Quasichemical Model in the Quadruplet Approximation for applications in slags, molten salts, mattes and liquid alloys. *Molten 2024.* Brisbane.

Cheng, S., Shevchenko, M., Hayes, P. C. & Jak, E. 2019. Experimental Phase Equilibria Studies in the FeO-Fe_2O_3-CaO-SiO_2 System in Air: Results for the Iron-Rich Region. *Metall. Mater. Trans. B,* 51**,** 1587-1602.

Cheng, S., Shevchenko, M., Hayes, P. C. & Jak, E. 2021. Experimental Phase Equilibria Studies in the FeO-Fe_2O_3-CaO-SiO_2 System and the Subsystems CaO-SiO_2, FeO-Fe_2O_3-SiO_2 in Air. *Metall. Mater. Trans. B,* 52**,** 1891-1914.

Coursol, P., Pelton, A. D., Chartrand, P. & Zamalloa, M. 2005a. The $CaSO_4$-CaO-$Ca_3(AsO_4)_2$ phase diagram. *Can. Metall. Q.,* 44**,** 547-553.

Coursol, P., Pelton, A. D., Chartrand, P. & Zamalloa, M. 2005b. The $CaSO_4$-Na_2SO_4-CaO phase diagram. *Can. Metall. Q.,* 44**,** 537-545.

Coursol, P., Stubina, N., Carissimi, E., Zamalloa, M. & Mackey, P. J. 2004. Industrial development of a novel sulfate system for copper pyro-refining. *Jom,* 56**,** 41-45.

Decterov, S. A. 2018. Thermodynamic database for multicomponent oxide systems. *Chimica Techno Acta.,* 5**,** 16-48.

Decterov, S. A., Dessureault, Y. & Pelton, A. D. 2000. Thermodynamic Modeling of Zinc Distribution among Matte, Slag and Liquid Copper. *Can. Metall. Q.,* 39**,** 43-54.

Decterov, S. A. & Pelton, A. D. 1996. Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the CrO-Cr_2O_3-SiO_2, and CrO-Cr_2O_3-SiO_2-Al_2O_3 Systems. *J. Phase Equilib.,* 17**,** 488-494.

Dessureault, Y. & Pelton, A. D. An optimized thermodynamic database for matte, slag, speiss and metal phases in lead smelting. 1993. Can. Inst. Min. Metall. Pet., 143-151.

Dilner, D. & Selleby, M. 2017. Thermodynamic description of the Fe-Ca-O-S system. *CALPHAD,* 57**,** 118-125.

Ferrante, M. J., Stuve, J. M., Daut, G. E. & Pankratz, L. B. 1978. Low-temperature heat capacities and high-temperature enthalpies of cuprous and cupric sulfides. Albany Metall. Res. Cent., Bur. Mines, Albany, OR, USA.

Gorsse, S. & Senkov, O. N. 2018. About the reliability of CALPHAD predictions in multicomponent systems. *Entropy,* 20**,** 899.

Groenvold, F. & Westrum, E. F., Jr. 1987. Thermodynamics of copper sulfides. I. Heat capacity and thermodynamic properties of copper(I) sulfide, Cu_2S, from 5 to 950 K. *J. Chem. Thermodyn.,* 19**,** 1183-1198.

He, Z., Haglöf, F., Chen, Q., Blomqvist, A. & Selleby, M. 2022. A Third Generation Calphad Description of Fe: Revisions of Fcc, Hcp and Liquid. *Journal of Phase Equilibria and Diffusion,* 43**,** 287-303.

Hidayat, T., Fallah Mehrjardi, A., Abdeyazdan, H., Shishin, D., Shevchenko, M., Hayes, P. C. & Jak, E. 2020. Integrated experimental and thermodynamic modelling study in the Pb-Fe-O-S-Si system: Effect of $p(SO_2)$ on slag-matte equilibrium. *Metall. Mater. Trans. B*.

Hidayat, T. & Jak, E. 2014. Thermodynamic modeling of the "Cu_2O"-SiO_2, "Cu_2O"-CaO, and "Cu_2O"-CaO-SiO_2 systems in equilibrium with metallic copper. *Int. J. Mater. Res.,* 105**,** 249-257.

Hidayat, T., Shishin, D., Decterov, S. & Jak, E. 2017a. Critical assessment and thermodynamic modeling of the Cu-Fe-O-Si system. *CALPHAD,* 58**,** 101-114.

Hidayat, T., Shishin, D., Decterov, S. A. & Jak, E. 2016a. Critical thermodynamic re-evaluation and re-optimization of the CaO-FeO-Fe_2O_3-SiO_2 system. *CALPHAD,* 56**,** 58-71.

Hidayat, T., Shishin, D., Decterov, S. A. & Jak, E. 2016b. Thermodynamic optimization of the Ca-Fe-O system. *Metall. Trans. B,* 47**,** 256-281.

Hidayat, T., Shishin, D., Decterov, S. A. & Jak, E. 2017b. Experimental Study and Thermodynamic Re-evaluation of the FeO-Fe_2O_3-SiO_2 System. *J. Phase Equilib. Diffus.,* 38**,** 477-492.

Hidayat, T., Shishin, D., Jak, E. & Decterov, S. 2015. Thermodynamic Reevaluation of the Fe-O System. *CALPHAD,* 48**,** 131-144.

Hillert, M. 2001. The Compound Energy Formalism. *J. Alloys Compd.,* 320**,** 161-176.

Hillert, M., Kjellqvist, L., Mao, H., Selleby, M. & Sundman, B. 2009. Parameters in the compound energy formalism for ionic systems. *CALPHAD,* 33**,** 227-232.

Hillert, M., Sundman, B. & Wang, X. 1990. An assessment of the calcia-silica system. *Metall. Trans. B.,* 21B**,** 303-312.

Jafarian, M., Arjomandi, M. & Nathan, G. J. 2017. Thermodynamic potential of molten copper oxide for high temperature solar energy storage and oxygen production. *Appl. Energy,* 201**,** 69-83.

Jak, E., Decterov, S. A., Wu, P., Hayes, P. C. & Pelton, A. D. 1997a. Thermodynamic Optimisation of the Systems PbO-SiO_2, PbO-ZnO, ZnO-SiO_2 and PbO-ZnO-SiO_2. *Metall. Mater. Trans. B,* 28B**,** 1011-1018.

Jak, E., Hidayat, T., Prostakova, V., Shishin, D., Shevchenko, M. & Hayes, P. C. 2019. Integrated experimental and thermodynamic modelling research for primary and recycling pyrometallurgy. *EMC.* Düsseldorf, Germany: GDMB Verlag.

Jak, E., Zhao, B. & Hayes, P. C. 1997b. Experimental determination of phase equilibria in lead/zinc smelting slags and sinters. *Proc. Int. Conf. Molten Slags, Fluxes Salts '97, 5th***,** 719-726.

Jantzen, T., Yazhenskikh, E., Hack, K., Baben, M. T., Wu, G. & Mueller, M. 2021. Addition of V_2O_5 and V_2O_3 to the CaO-FeO-Fe_2O_3-MgO-SiO_2 database for vanadium distribution and viscosity calculations. *CALPHAD,* 74**,** 102284.

Jo, Y., Lee, H.-G. & Kang, Y.-B. 2013. Thermodynamics of the MnO-FeO-MnS-FeS-SiO_2 system at SiO_2 saturation under reducing condition: immiscibility in the liquid phase. *ISIJ Int.,* 53**,** 751-760.

Jung, I.-H., Decterov, S. A. & Pelton, A. D. 2007. Thermodynamic modeling of the CoO-SiO_2 and CoO-FeO-Fe_2O_3-SiO_2 systems. *Int. J. Mater. Res.,* 98**,** 816-825.

Jung, I.-H. & Van Ende, M.-A. 2020. Computational Thermodynamic Calculations: FactSage from CALPHAD Thermodynamic Database to Virtual Process Simulation. *Metall. Mater. Trans. B,* 51**,** 1851-1874.

Kang, Y.-B. & Pelton, A. 2009. Thermodynamic Model and Database for Sulfides Dissolved in Molten Oxide Slags. *Metall. Mater. Trans. B,* 40**,** 979-994.

Khartcyzov, G., Shevchenko, M., Cheng, S., Hayes, P. C. & Jak, E. 2022. Experimental phase equilibria studies in the "$CuO_{0.5}$"-CaO-SiO_2 ternary system in equilibrium with metallic copper. *Ceram. Int.,* 48**,** 9927-9938.

Kidari, O. & Chartrand, P. 2023a. Thermodynamic Evaluation and Optimization of the Ag-As-S system. *J. Phase Equilib. Diffus.,* 44**,** 269-299.

Kidari, O. & Chartrand, P. 2023b. Thermodynamic evaluation and optimization of the As-Co, As-Fe and As-Fe-S systems. *CALPHAD,* 82**,** 102589.

Konar, B., Van Ende, M.-A. & Jung, I.-H. 2017. Critical evaluation and thermodynamic optimization of the Li-O, and Li_2O-SiO_2 systems. *J. Eur. Ceram. Soc.,* 37**,** 2189-2207.

Kongoli, F., Dessureault, Y. & Pelton, A. D. 1998. Thermodynamic Modeling of Liquid Fe-Ni-Cu-Co-S Mattes. *Metall. Mater. Trans. B,* 29B**,** 591-601.

Lambotte, G. & Chartrand, P. 2011. Thermodynamic optimization of the (Na_2O + SiO_2 + NaF + SiF_4) reciprocal system using the Modified Quasichemical Model in the Quadruplet Approximation. *J. Chem. Thermodyn.,* 43**,** 1678-1699.

Lambotte, G. & Chartrand, P. 2013. Thermodynamic modeling of the (Al_2O_3 + Na_2O), (Al_2O_3 + Na_2O + SiO_2), and (Al_2O_3 + Na_2O + AlF_3 + NaF) systems. *J. Chem. Thermodyn.,* 57**,** 306-334.

Nekhoroshev, E. 2019. *Thermodynamic Optimization Of The Na_2O-K_2O-Al_2O_3-CaO-MgO-B_2O_3-SiO_2 System.* Ph. D. thesis, Polytechnique Montréal.

Pelton, A. D. & Blander, M. Computer-Assisted Analysis of the Thermodynamic Properties and Phase Diagrams of Slags. *In:* FINE, H. A. & GASKELL, D. R., eds. Proceedings of the Second International Symposium on Metallurgical Slags and Fluxes, TMS-AIME, Warrendale, PA, 1984. 281-294.

Pelton, A. D. & Blander, M. 1986. Thermodynamic Analysis of Ordered Liquid Solutions by a Modified Quasi-Chemical Approach. Application to Silicate Slags. *Metall. Trans. B,* 17B**,** 805-815.

Pelton, A. D. & Chartrand, P. 2001. The Modified Quasichemical Model. II - Multicomponent Solutions. *Metall. Mater. Trans. A,* 32**,** 1355-1360.

Pelton, A. D., Chartrand, P. & Eriksson, G. 2001. The modified Quasichemical Model. IV - Two Sublattice Quadruplet Approximation. *Metall. Mater. Trans. A,* 32**,** 1409-1415.

Pelton, A. D., Decterov, S. A., Eriksson, G., Robelin, C. & Dessureault, Y. 2000. The Modified Quasichemical Model. I - Binary Solutions. *Metall. Mater. Trans. B,* 31**,** 651-659.

Pelton, A. D. & Kang, Y.-B. 2007. Modeling short-range ordering in solutions. *Int. J. Mater. Res.,* 98**,** 907-917.

Prostakova, V., Chen, J., Jak, E. & Decterov, S. 2013. Experimental study and thermodynamic optimization of the MgO-NiO-SiO_2 system. *J. Chem. Thermodyn.,* 62**,** 43-55.

Prostakova, V., Chen, J., Jak, E. & Decterov, S. A. 2012. Experimental study and thermodynamic optimization of the CaO-NiO, MgO-NiO and NiO-SiO_2 systems. *CALPHAD,* 37**,** 1-10.

Prostakova, V., Shishin, D. & Jak, E. 2021. Thermodynamic optimization of the Cu-As-S system. *CALPHAD,* 72**,** 102247.

Selleby, M. 1997. An Assessment of the Ca-Fe-O-Si System. *Metall. Trans. B,* 28B**,** 577-596.

Selleby, M. & Sundman, B. 1996. A Reassessment of the Ca-Fe-O System. *CALPHAD,* 20**,** 381-392.

Shevchenko, M., Shishin, D. & Jak, E. 2022. Integrated phase equilibria experimental study and thermodynamic modeling of the Cr-Si-O, Fe-Cr-O and Fe-Cr-Si-O systems. *Ceram. Int.*

Shevchenko, M., Shishin, D. & Jak, E. 2024. Advancement in experimental methodologies to produce phase equilibria and thermodynamic data in multicomponent systems. *Molten 2024.* Brisbane.

Shishin, D., Chen, J., Hidayat, T. & Jak, E. 2019. Thermodynamic modelling of the Pb-As and Cu-Pb-As systems supported by experimental study. *J. Phase Equilib. Diff.,* 40**,** 758–767.

Shishin, D., Chen, J. & Jak, E. 2020a. Thermodynamic Modeling of the Pb-S and Cu-Pb-S Systems with Focus on Lead Refining Conditions. *J. Phase Equilib. Diffus.,* 41**,** 218-233.

Shishin, D. & Decterov, S. A. 2012. Critical assessment and thermodynamic modeling of Cu-O and Cu-O-S systems. *CALPHAD,* 38**,** 59-70.

Shishin, D., Fallah Mehrjardi, A., Shevchenko, M., Hidayat, T. & Jak, E. 2020b. Experimental study, thermodynamic modeling and industrial implications of slag/matte/metal equilibria in the Cu-Pb-Fe-O-S-Si system. *J. Mater. Res. Technol., in Press*.

Shishin, D., Hidayat, T., Chen, J., Hayes, P. C. & Jak, E. 2018a. Experimental Investigation and Thermodynamic Modelling of the Distributions of Ag and Au between Slag, Matte and Metal in the Cu-Fe-O-S-Si System. *Journal of Sustainable Metallurgy,* 5**,** 240-249.

Shishin, D., Hidayat, T., Chen, J., Hayes, P. C. & Jak, E. 2018b. Integrated Experimental Study and Thermodynamic Modelling of the Distribution of Arsenic between Phases in the Cu-Fe-O-S-Si System. *J. Chem. Thermodyn.,* 135**,** 175–182.

Shishin, D., Hidayat, T., Jak, E. & Decterov, S. 2013. Critical assessment and thermodynamic modeling of Cu-Fe-O system. *CALPHAD,* 41**,** 160-179.

Shishin, D. & Jak, E. 2018. Critical assessment and thermodynamic modeling of the Cu-As system. *CALPHAD,* 60**,** 134-143.

Shishin, D., Jak, E. & Decterov, S. A. 2015. Thermodynamic assessment and database for the Cu–Fe–O–S system. *CALPHAD,* 50**,** 144-160.

Shishin, D., Shevchenko, M., Starykh, R., Sineva, S., Prostakova, V. & Jak, E. 2023. Development and application of matte/speiss/metal thermodynamic database for optimization of processing of drosses, dusts and reverts from lead, zinc and copper production. *10th International Conference on Lead and Zinc Processing.* Chansha, China.

Sineva, S., Shishin, D., Prostakova, V., Fallah-Mehrjardi, A. & Jak, E. 2023. Experimental Study and Thermodynamic Analysis of High-temperature Processing of mixed Ni-Cu sulfide feed. *The 62nd Annual Conference of Metallurgists: COM 2023.* Toronto, Canada: MetSoc of CIM.

Sundman, B. 1991. Modification of the Two-sublattice Model for Liquids. *CALPHAD,* 15**,** 109-119.

Sundström, A., Eksteen, J. J. & Georgalli, G. A. 2008. A review of the physical properties of base metal mattes. *Journal of The South African Institute of Mining and Metallurgy,* 108**,** 431-448.

Waldner, P. 2020. Gibbs Energy Modeling of the Cu-S Liquid Phase: Completion of the Thermodynamic Calculation of the Cu-S System. *Metall. Mater. Trans. B*.

Waldner, P. 2022. The High-Temperature Cu-Fe-S System: Thermodynamic Analysis and Prediction of the Liquid–Solid Phase Range. *J. Phase Equilib. Diff.*

Waldner, P. & Pelton, A. D. 2004a. Critical Thermodynamic Assessment and Modeling of the Fe-Ni-S System. *Metall. Mater. Trans. B,* 35**,** 897-907.

Waldner, P. & Pelton, A. D. 2004b. Thermodynamic modeling of the Ni-S system. *Z. Metallkd.,* 95**,** 672-681.

Waldner, P. & Pelton, A. D. 2005. Thermodynamic modeling of the Fe-S system. *J. Phase Equilib. Diff.,* 26**,** 23-28.

Waldner, P. & Sitte, W. 2011. Thermodynamic modeling of the Cr-S system. *Int. J. Mater. Res.,* 102**,** 1216-1225.

Wang, K. & Chartrand, P. 2021. Generic energy formalism for reciprocal quadruplets within the two-sublattice quasichemical model. *CALPHAD,* 74**,** 102293.

Wang, K., Li, D., Zou, X., Cheng, H., Li, C., Lu, X. & Chou, K. 2023. Generic bond energy formalism within the modified quasichemical model for ternary solutions. *J. Mol. Liq.,* 370**,** 120932.

Wen, X., Shevchenko, M. & Jak, E. 2021. Experimental study of "$CuO_{0.5}$"-"FeO"-SiO_2 and "FeO"-SiO_2 systems in equilibrium with metal at 1400-1680°C. *J. Alloys Compd.,* 885**,** 160853.

Wen, X., Shevchenko, M., Nekhoroshev, E. & Jak, E. 2023. Phase equilibria and thermodynamic modelling of the PbO–ZnO-“$CuO_{0.5}$”-SiO_2 system. *Ceram. Int.*

Wu, P., Eriksson, G. & Pelton, A. D. 1993a. Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the Calcia-Iron(II) Oxide, Calcia-Magnesia, Calcia-Manganese(II) Oxide, Iron(II) Oxide-Magnesia, Iron(II) Oxide-Manganese(II) Oxide, and Magnesia-Manganese(II) Oxide Systems. *J. Am. Ceram. Soc.,* 76**,** 2065-2075.

Wu, P., Eriksson, G., Pelton, A. D. & Blander, M. 1993b. Prediction of the Thermodynamic Properties and Phase Diagrams of Silicate Systems - Evaluation of the FeO-MgO-SiO_2 System. *ISIJ Int.,* 33**,** 26-35.