Improving industrial copper processing operations through the application of thermodynamic fundamentals and advanced predictive tools

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ABSTRACT

Mineral resources are becoming more complex in composition and structure making it more difficult to produce clean concentrates for primary metal smelting. In parallel, providing technological solutions to the recycling and recovery of end-of-life materials is becoming more important in moving towards the goal of increasing circularity. The availability of fundamental thermodynamic data and advanced thermodynamic tools greatly assists in evaluating these complexities and their impact on existing and new processes. In addition, it is fundamental to support the economic performance of smelters. This paper describes several examples on how fundamental work can be applied to industrial processing.

INTRODUCTION

Primary and secondary sources of base metals are gradually increasing complexity. This complexity is expressed in terms of lower grade materials and increase in concentration of minor metals and slagging elements. This pattern has clearly affected the non-ferrous metal production, increasing operating costs and investment required to ensure the sustainable production of metals.

Alvear et. al. [2018, 2020] discussed some key elements associated with the increasing complexity for primary copper production. They pointed out that this behaviour was observed in the processing of primary and secondary materials, with increasing complexity and reduction in the concentration of base and precious metals in the sourced raw materials.

The processing of complex materials in non-ferrous smelting has traditionally been approached as a niche opportunity to capture the economic value contained in the mined resources [Alvear, 2020]. Mining companies, on one side, have sometimes adopted processing options, such as ultra-fine grinding, alternative flotation circuits, or hydrometallurgical processes to address the impact of the complexity on the value of their product. Smelters, on their side of the equation, have addressed complexity either by modifying their operational setpoints or when strictly necessary developing new processes.

In recent times, as sustainable solutions are more and more demanded, synergies and cooperation between base metal processing facilities have improved recovery and waste management. Good examples of these collaboration have been integrated processing, such as the efforts of Codelco and Ecometales to process complex dust from roasting and smelting, [Alvear, 2018], the Albion dust leaching process at the Glencore Mount Isa Smelter [Alvear, 2013] and the Nutton process proposed by Rio Tinto [2024] among others.

Other examples of integrated operations across the globe, the Aurubis multi metal smelter network, the Kazzinc Pb-Zn-Cu integrated flowsheet and the Japanese non-ferrous smelting companies, have demonstrated how base metals integration can support more effective metal processing and recovery of valuable elements. Chinese non-ferrous processing companies have also developed integrated solutions following similar principles. The synergic, multi-metal process approach as shown in Figure 1, is required to ensure that maximum possible value is extracted from the natural resources. Examples of these flowsheets are discussed by the author in another publication [Schlesinger et al., 2022].

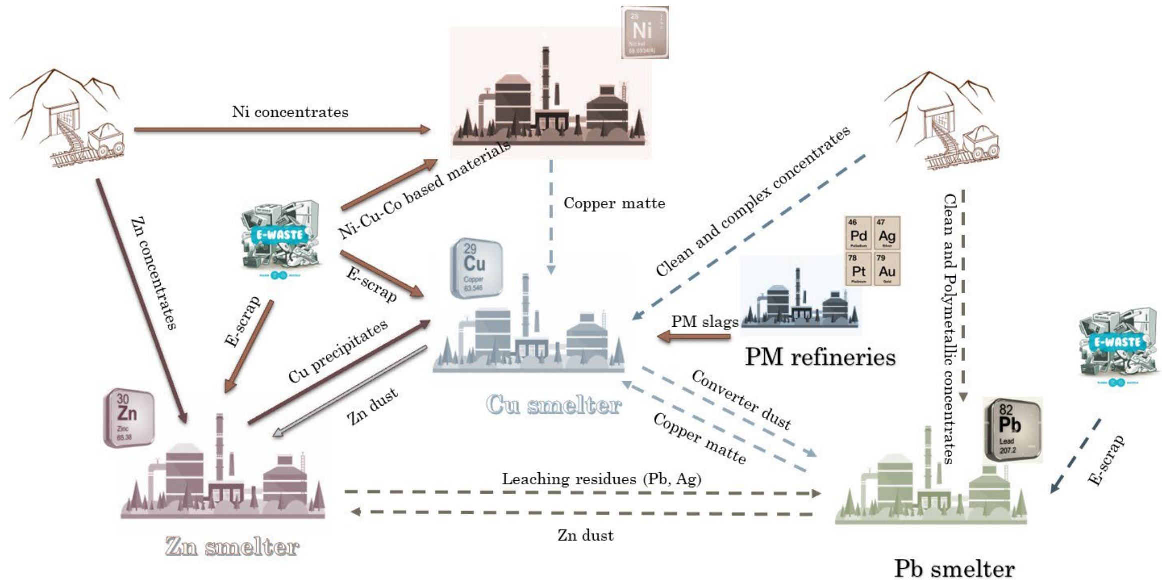

FIG 1 – Multi metal processing approach using base metals as collectors, modified from Alvear [2020]

However, in most cases, the copper industry has used dilution as the main response, either by blending complex materials in central facilities or by diluting small quantities in large feed streams to smelters. This approach has gradually been challenged by the need to minimize waste, reduce the environmental footprint, and the need to develop different methods to valorise mining and metal projects.

This pattern places smelters in a constant questioning of their competitiveness and with the need of a regular evaluation of cost-effective measures to remain competitive. It is in here, where producers are facing the most critical question: How to differentiate from each other in a business that has been traditionally regarded as a commodity business with commodity-based technologies used for this purpose. [Alvear, 2018]

Valid questions to ask are; How is fundamental knowledge evolving? What research support is needed to be able generate the fundamental knowledge to enable industry to achieve this transformation? and How can this fundamental knowledge be integrated with emerging approaches such as advanced analytics, and artificial intelligence to provide more effective integrated solutions?

DEVELOPMENTS IN THE COPPER INDUSTRY

Figure 2 shows a timeline representing the copper smelting industry development for the last fifty years [Schlesinger, 2022]. Over this period, the copper smelting processing has dramatically evolved. New bath smelting technologies have claimed their territory, and along with flash smelting, increased the processing intensity and proposed new slag chemistry targets.

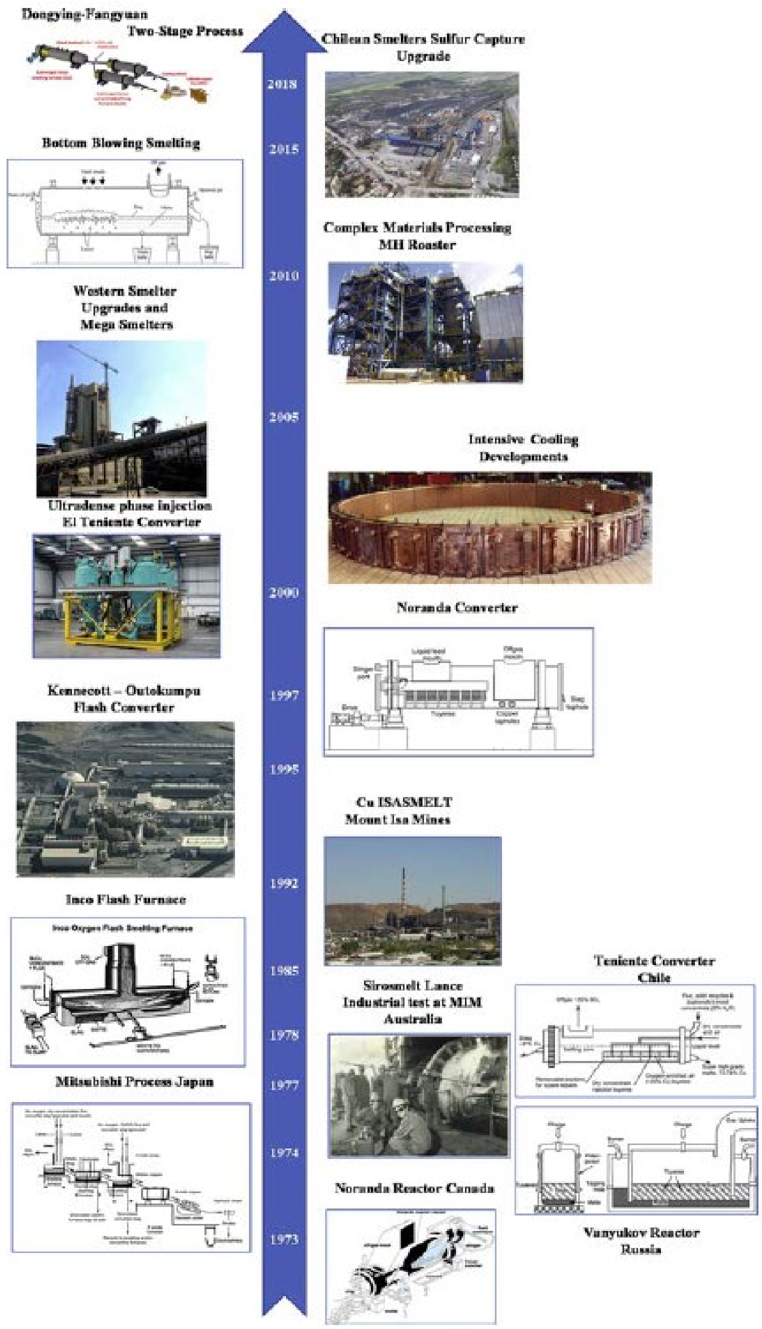

FIG 2 – Examples of some of the relevant technological developments in the copper smelting industry since 1973, Schlesinger et al. [2020]

Copper technology developments have focused on increasing the process intensity by using tonnage industrial oxygen, this has translated into increasing processing capacities. An example of the processing intensity by means of the increasing of the copper concentrate smelting feed rates in a number of different technologies is shown in Figure 3. Modern smelting plants can achieve over 250 tonnes/hour of fresh feed.

This path of increasing process intensity has been accompanied by a systematic improvement in the determination of the required thermodynamic properties. The development and consolidation of advanced thermodynamics database have allowed scientists to increase the accuracy of critical predominance and phase diagrams that play a relevant role in supporting the understanding of modern copper smelting. Some examples are shown in the next section of this paper.

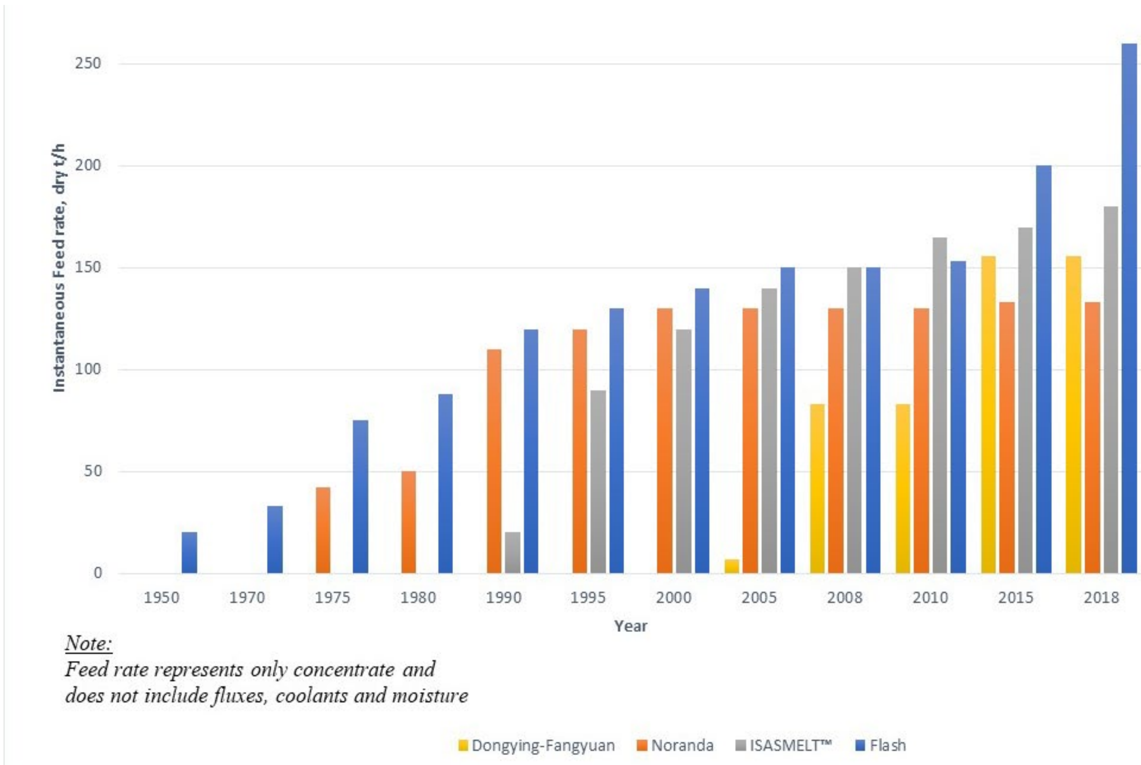

FIG 3 – Instantaneous concentrate feed rate evolution since 1950 in selected copper sulphide smelting technologies. Figure modified from Schlesinger et al. [2020]

Example 1 The Cu-S Predominance Diagram

A classic example of key fundamental knowledge is the Cu-S predominance diagram proposed by Professor Akira Yazawa. Despite the technical relevance of this diagram, still there are many metallurgists across smelters that they do not know how to use the contained information to better understand their processes. Figure 4 shows a newly recalculated Cu-S predominance diagram at 1300 C, prepared with support of Pyrosearch, University of Queensland, using the FactSage public database [Jak et al., 2016]. The figure also shows the original boundary lines calculated by Yazawa [1979] and allows you to identify the main “metallurgical road” for copper processing, A / B / C(C’) / D / E and B / B’, as follows:

Copper smelting: Following the path A / B copper concentrates are gradually combusted (oxidized) to a given matte grade by controlled oxygen addition. Through this process, iron is oxidized, sulfur is combusted to SO_2, and slag is formed by adding silica as a flux.

Slag/Matte separation: Following path B / B', matte and slag are, given appropriate process conditions, allowed settle and physically separate.

Batch Converting

Slag Blowing following path B / C: Copper matte is oxidized to finalize the controlled oxidation of iron.

Copper Blowing following path C / D: After removal of slag generated in the previous step, the high-grade matte is converted to blister copper,

Continuous Converting follows the path B (close to the 70% Cu matte grade)

Direct to Blister: Copper matte is directly converted to blister, avoiding an intermediate step.

For special concentrates, normally low in iron, it is possible to produce blister copper in a single step. This follows the path A / C'.

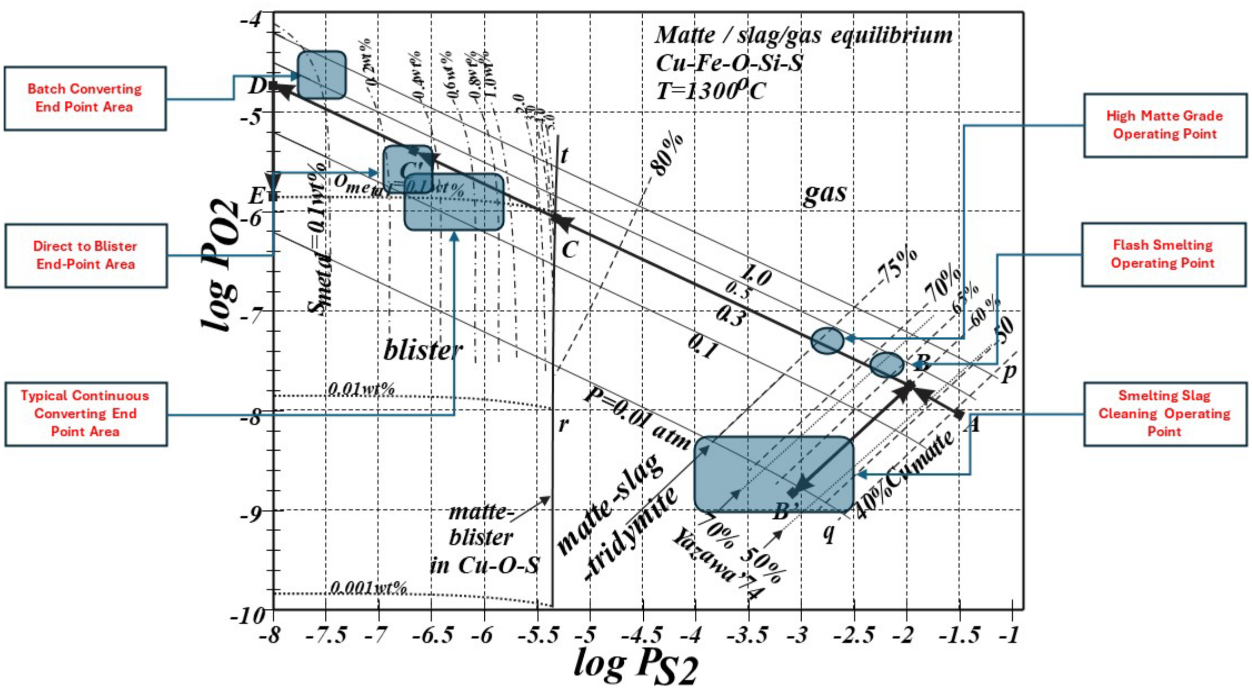

FIG 4 - Predominance diagram describing copper making process at 1300 °C based on calculations using FactSage public data base and original Yazawa diagram [Jak 2016, Yazawa 1979, Schlesinger 2022].

Example 2 The FeO-Fe_2O_3-SiO_2 Phase Diagram and Copper Smelting

The selection of an appropriate slag system is also important to maximize the capacity of slags for the required elements and minor oxides. The selection of the slag system is governed by the chemical and physical properties of the slags, such as liquidus temperature and viscosity. In primary copper smelting, the FeO-Fe_2O_3-SiO_2 phase diagram is the main system used to define the equilibrium conditions between copper matte and smelting slags.

The physical chemistry properties of slag in copper smelting were reviewed forty years ago by Mackey [1982]. In his review, Mackey commented: “Despite many changes, the smelter man still relies largely on art and experience, especially with regard to slag control and in taking care of the slag”. He also added: “Copper smelting is still largely an art but is emerging into science of copper smelting and the understanding of processes develops on sound metallurgical engineering principles”.

Mackey discussed chemical and physical properties of copper smelting and converting slags. Figure 5 shows a comparison of a section of the FeO-Fe_2O_3-SiO_2 phase diagram from his original publication and the re-calculated phase diagram using FactSage database [Mackey, 1982, Hidayat, 2017].

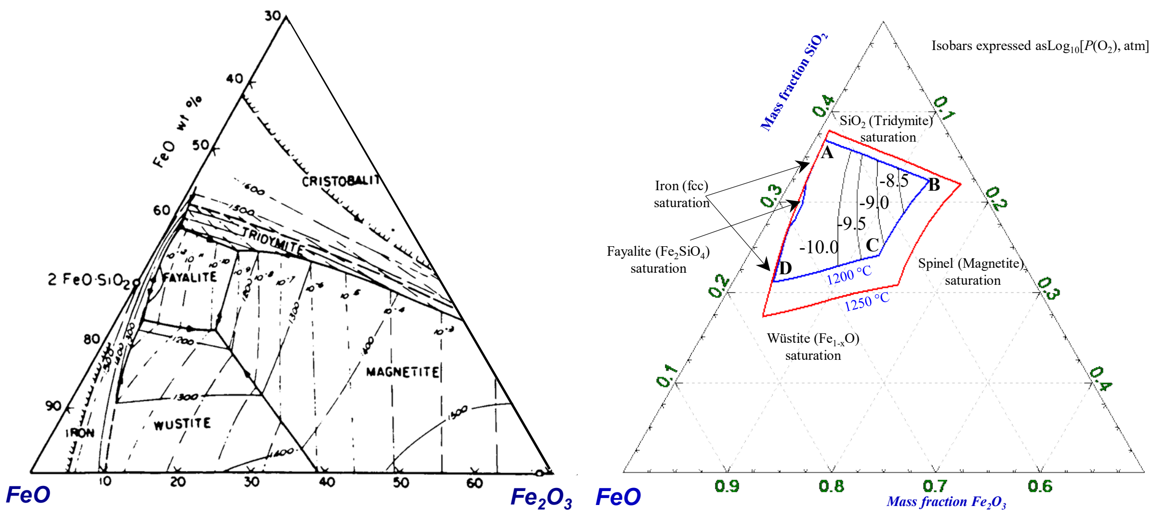

FIG 5 – Liquidus surfaces of the Fe-O-Si system describing copper smelting slags at 1300 °C based on calculations using the FactSage public data base and original Yazawa diagram [Mackey 1982, Hidayat 2017].

The slag system described by Figure 5 is a simplification of the real chemistry involved in the primary smelting. Moreover, as complexity is increasing, the participation of minor oxides becomes relevant not only to understand the real slag composition but also to determine, the required amount of fluxing, the heat load requirements of the process and the impact of these minor oxides into the overall chemical and physical properties of the system.

The work at Advanced Research Centres, such as Pyrosearch, developing a more accurate data base evaluating impact of minor oxides in the system is enabling metallurgical engineers to design in a more precise fashion new metallurgical processes and estimate the impacts of complex feeds on well-established metallurgical processes.

Figure 6 shows the impact of minor oxides in the Fe/SiO_2 ratio as function of copper matte grade for the iron silicate slag system at 1200 °C and pSO_2 = 0.25 atm [Shishin, 2018]. The figure shows the impact of minor oxides in the liquidus region for different Fe/SiO_2 ratios and highlights the importance of understanding these facts to properly estimate flux requirements for the process.

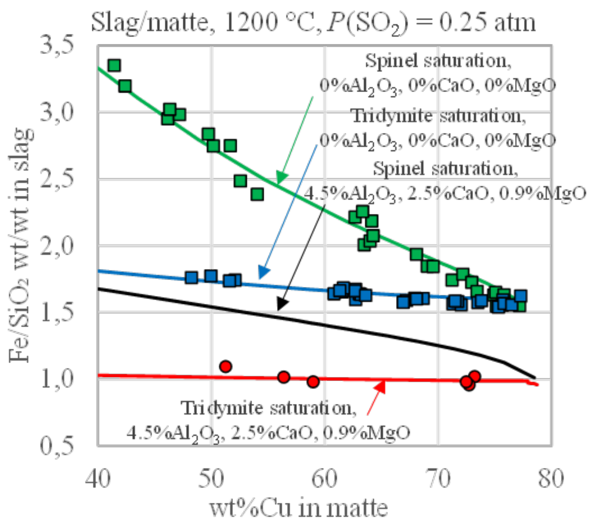

FIG 6 - Impact of minor oxides in the limiting Fe/SiO_2 ratios as function of copper matte grade for the iron silicate slag system at 1200 °C and pSO_2 = 0.25 atm [Shishin 2018, Schlesinger 2022].

An interesting example of the impact of minor oxides in primary and secondary copper smelting is the effect of alumina in the liquidus temperature, viscosity, and overall copper recovery of copper and other valuable elements.

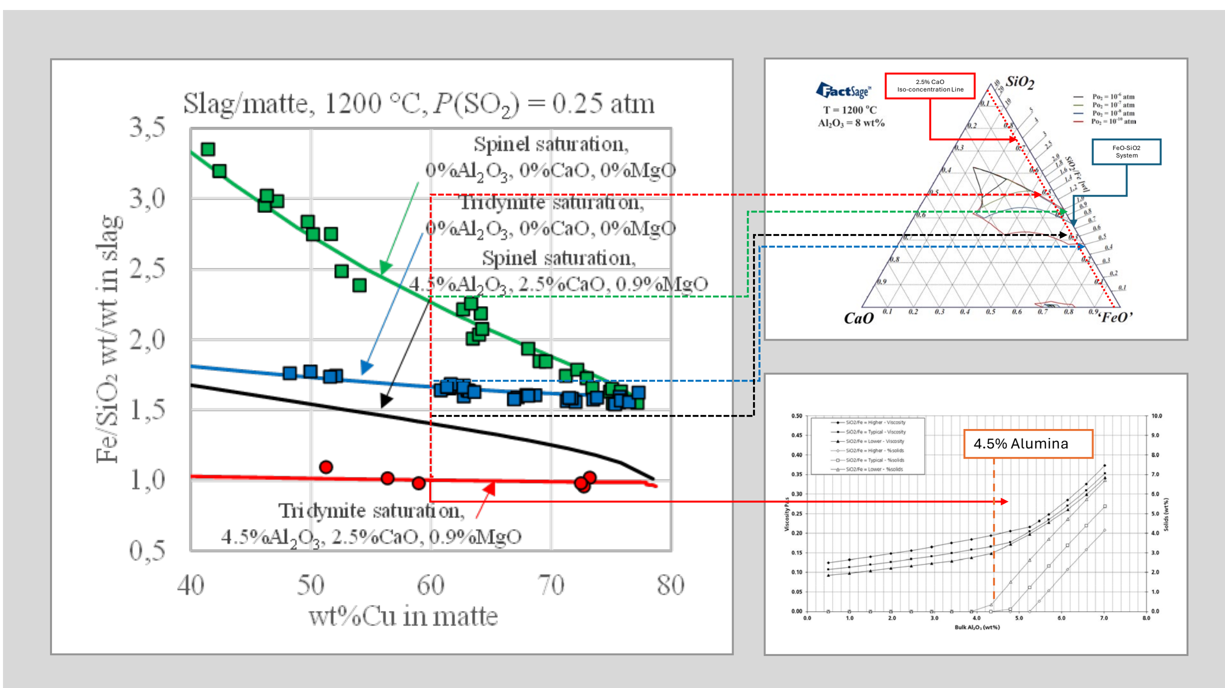

FIG 7- Impact of minor oxides in the limiting Fe/SiO_2 ratios as function of copper matte grade for the iron silicate slag system at 1200 °C and pSO_2 = 0.25 atm [Shishin 2018, Schlesinger 2022] and viscosity of the slag for a given alumina and CaO concentration [Alvear, 2013].

In the primary copper, an increment in alumina has direct impact on the fluxing regime as additional silica is required to slag the alumina and the potential use of CaO requires revision.

Alvear [2013] reported the impact of alumina in the viscosity of fayalite slags. Figure 7 exemplifies the impact of minor oxides in the liquidus region for a 60% copper matte grade and how lime impacts in the liquidus region. The viscosity calculations reported by Alvear (2013) shows how viscosity is increased when alumina concentration increases and how the liquidus is affected at 8% alumina in the slag at different oxygen partial pressures. Solids precipitation is avoided until over 5 wt% alumina in the slag.

Defining a proper slag composition has direct impact on the overall economics of the smelting business. Fluxing must be maintained to the minimum requirements to maximise the copper recovery and the potential slag valorisation required for the slag as a subproduct of the smelting process. In this aspect, some smelters have decided to use slag flotation as the main process to recover the slag while others use the traditional slag cleaning by means of settling and reduction of magnetite in electric furnaces. Klaffenbach [2023] has undertaken extensive work on evaluating slag as product of economic use for other applications, such as the cement industry. Regardfless of the used method, minimizing copper content in the slag and amount of fluxing required will have a direct impact on the profitability of the business. This can be easily demonstrated using Value in Use modelling to estimate the impact of copper losses on the overall profit margin of the smelting business.

As this author was preparing this manuscript, sadly the passing of Professor Bill Davenport was announced. Coincidentally, Mackey and Alvear [2014] presented a review on the advances in copper smelting at the Davenport Symposium. In that work, gaps in fundamental knowledge were recognised and in the last 10 years since then, Pyrosearch with the support of key industrial partners, has been assessing these gaps and generating the required fundamental work. A number of major industrial companies, such as Aurubis, Umicore, Boliden and other consortium members have also supported and worked in this field. Table 1 shows some of the gaps identified in 2014 and some advances since then.

Table 1 –Gaps in Fundamental Knowledge in Copper Smelting Identified in 2014 and Some Advanced Since Then

Process/Area	Gaps in Fundamental Knowledge in 2014	Some Knowledge Developed Since 2014
Primary Copper Smelting	• Correction and refinement in minor element activity coefficients in matte phase. • Minor element partial pressure under smelting conditions	• Review and thermodynamics analysis in copper smelting liquid mattes, metals, slags, speiss and solids phases, Shishin et al., (2022) • Phase Equilibria and Minor Element Distributions in Copper/Slags/Matte Systems, Sineva et al., (2020) • Thermodynamic Consideration of Copper Matte Smelting Conditions with Respect to Minor Element Removal and Slag Valorisation, Klaffenbach et al., (2018)
Copper Converting	• High matte grade batch converting process control and link with Physic-chemical data	• Equilibria of Iron Silicate Slags for Continuous Converting Copper-Making Process Based on Phase Transformations, Sun et al., (2020)

Process/Area	Gaps in Fundamental Knowledge in 2014	Some Knowledge Developed Since 2014
Slag Cleaning	• Electric furnace modelling • Minor element distribution improvements	• Comprehensive review on metallurgical recycling and cleaning of copper slag, Tian et al., (2021) • Copper Smelting Slag Cleaning in an Electric Furnace by Using Waste Cooking Oil, Wei et al., (2020) • Sustainable and Comprehensive Utilization of Copper Slag: A Review and Critical Analysis, Klaffenbach et al., (2023)
Secondary Copper Smelting	• Minor element modelling at reducing conditions	• Experimental Study and Thermodynamic Modelling of Modelling Equilibrium Distribution of Ni, Sn, and Zn between Slag and Black Copper for E-Scrap Recycling Applications, Sineva et al., (2023)
Anode Refining	• Continuous anode refining	• Dongying Fangyuan application for continuous converting and refining
Polymetallic Systems	• Further development in the Cu_2S-FeS-PbS-Cu-Fe-Pb system	• Fundamental Analysis of Improved Multi Metal Recovery by Combining Copper and Lead Metallurgy, Zschiesche et al., (2019).
General	• Incorporation of fundamental data in software packages for modelling	• Effort done at Pyrosearch by updating FactSage with fundamental thermodynamic data generated in the Copper Consortium.

Example 3 Minor Element Distribution and Recovery

Copper resources processed in the primary and secondary smelting processes are accompanied of minor oxides and minor elements. Minor oxides, such as alumina, magnesia or lime can be removed with appropriate fluxing as shown in the previous discussed example. In the case of minor elements, they will distribute in between the phases, with partitions define by the distribution equilibria between the molten phases and the volatilization degree of these minor elements.

The topic minor elements distribution has been given a great degree of importance by Japanese researchers and thermodynamic models such as the Degree of Volatilization, *S*, has been proposed by Professor Kimio Itagaki [1982]. CSIRO also did review thermodynamic properties of minor elements and incorporated them into their modelling tools [Chen, 2010].

There have been a lot of discussions about the role of technology selection on the maximization of the removal of impurities from copper sources. It is the opinion of the author that the maximisation of the removal of impurities is associated with the oxidation/reduction ability of the element to be removed, the reactor characteristics (plug reactor or equilibrium reactor) and the selection of appropriate slag systems.

A method to quantify the potential of removing a minor element in the secondary copper is the refining ability. Since almost all the impurities contained in the copper scrap have a high oxygen affinity, oxidation refining is normally used as an appropriate alternative method for the copper scrap refining after a first reductive smelting step.

Fujisawa et al., [1997] proposed the Oxidizing Refining Ability Index, as a parameter to preliminary qualify and quantify the potential for minor elements removal in copper scrap refining. The oxidation of a minor element was defined by equation 1.

$$\mathrm{X}(\mathrm{in\ \ metal}) + (\nu/4)\mathrm{O}_2 = \mathrm{XO}_{\nu/2}(\mathrm{in\ slag}) \quad (1)$$

$$A_\mathrm{X} = K_{(1)} \cdot \gamma_\mathrm{X} \cdot p_{\mathrm{O}_2}^{\nu/4} \quad (2)$$

The refining ability of a minor element x, A_x, is defined by the expression of equation 2, were $K_{(1)}$ is the equilibrium constant of reaction (1), γ_i is the Raoultian activity coefficient of component i, in liquid copper and p_{O_2} is the standardized oxygen partial pressure at the slag-metal interface. The index was estimated based on the following approximations:

(1) [n_T], defined as the molar amount of 100 g metal can be approximated to pure copper,
(2) (n_T), defined as the molar amount of 100 g slag does not change so much among the slag systems under study,
(3) p_{O_2} can be approximated to the equilibrium value for the Cu_2O/Cu system, since the main component of the slag is Cu_2O, and
(4) γ_X can be approximated to that at infinite dilution, γ°_X, when the impurity content in copper is low.

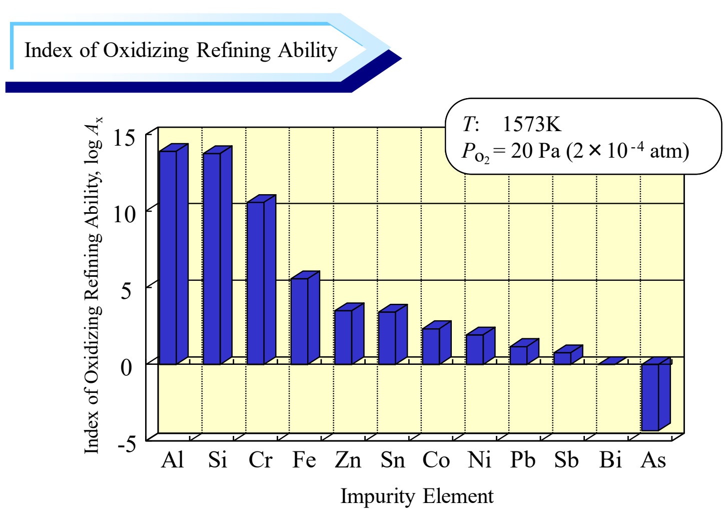

FIG 8 - Index of Oxidizing Refining Ability. Fujisawa et al., [1997]

Figure 8 shows the estimated refining ability index for several minor elements potentially contained in copper secondary sources at 1573 K at Cu/Cu_2O equilibrium. The index decreases in the following order: Al, Si, Cr, Fe, Zn, Sn, Co, Ni, Pb, Sb, Bi and As. Fujisawa, stated that most of the above-mentioned elements can form stable complex oxides with Cu_2O-SiO_2, Cu_2O-B_2O_3

and Cu_2O-Fe_2O_3 slags. Following these estimations, several experimental distribution experiments were conducted to estimate the distribution ratio, L, between copper and slags. It should be mentioned that at the time of this research (In which the author of this paper was part of) tools like FactSage were not very well developed and a lack of fundamental data under these conditions was observed.

The early work conducted at Nagoya University as part of the Research Centre for Advanced Waste and Emission Management, was summarised and reported as part of the Super Smelter Project, an effort between Japanese universities and Japanese copper processing companies to evolve in the processing of copper secondary sources. Figure 9 shows the results reported by Fujisawa, Alvear et al [1997] for different copper-based slag systems.

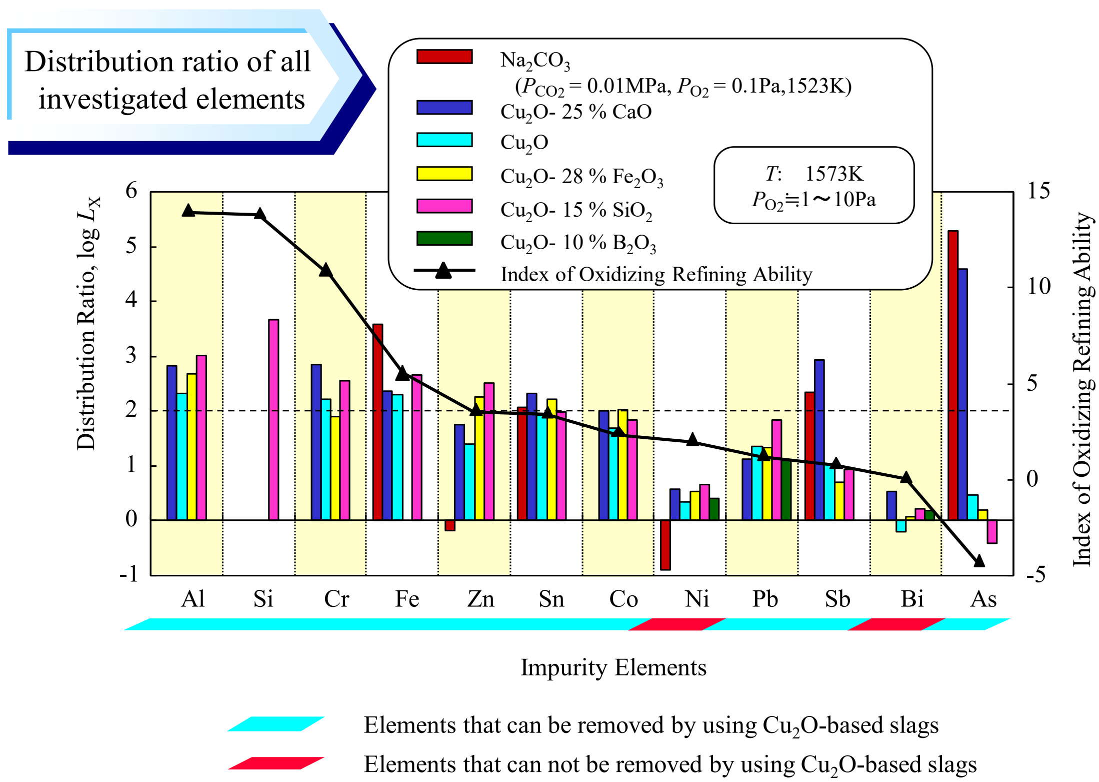

FIG 9 - Index of Oxidizing Refining Ability Fujisawa, Alvear et al [1997] for different copper-based slag systems.

The results indicated that:

- Al, Si and Cr present can be eliminated even without slag addition and by simply blowing oxygen or air into the scrap melt.
- Fe, Zn, Sn, Co and Pb can be efficiently removed by using Cu_2O-SiO_2 slags.
- Co, Sb and As, Cu_2O-CaO slag can be efficiently used for their elimination.
- Ni and Bi, the results indicate that their elimination cannot be expected by using Cu_2O-based slags.

A particular impurity of great concern for the primary concentrate process has been arsenic. Arsenic is present in most of copper concentrates exported by Chilean and Peruvian miners and in some cases, the concentration can exceed the import limits defined by local authorities (i.e., China has a maximum concentration of 5,000 ppm in concentrates). The impact on As in the copper anode was reported by Moats [2016] in his surveys of copper refineries, in which he reported over 80% increase in As concentration in anodes compared with levels in 2003.

Pyrosearch reported the As distribution between copper matte and slags between 60 and 75% matte grade, showing good agreement with selected plant data. Their main conclusions indicated that the thermodynamic model demonstrate the decreasing order As > Pb > Bi for the distribution coefficient. Thermodynamic predictions indicate the decreasing order Zn > Sb > Sn > As > Pb > Bi > Ni > Ag > Au for the slag/matte distribution coefficient in the matte grade range up to 70 wt. % Cu [Sineva, 2020].

In the refining of copper, Alvear [1998] reported the impact of oxygen concentration on the simultaneous elimination of As and Sb from molten copper using sodium carbonate slags. A mechanism for the simultaneous elimination of As and Sb was observed, depending on the relative compositions of these elements and oxygen in the melt. For instance, under similar concentrations of impurities and oxygen, as shown in Figure10, the removal of arsenic will occur until the arsenic concentration is low enough to enable free oxygen to react with antimony.

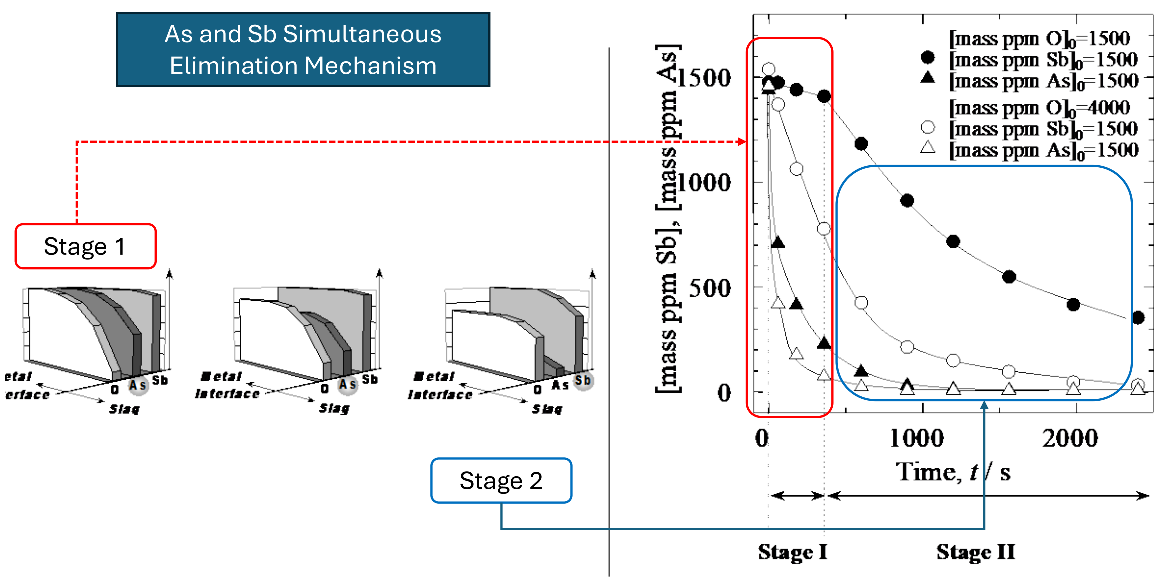

FIG 10 – Simultaneous Elimination Mechanism of As and Sb Mechanism from Molten Copper using Sodium Carbonate Slags at 1523 K, Alvear [1998]

All the fundamental work undertaken to determine distribution ratios of minor elements, activity coefficients and physical properties need to be added to simulation tools to allow process engineers to estimate process indicators and anode impurity capacities in more robust fashion. Moreover, following these process fundamental estimations, these calculations are vital to estimate financial performance of the process and estimate the anode impurity capacities of each plant. These advanced predictive capacities will allow to determine the financial performance of each plant depending on the material portfolio they will be processing.

CONCLUSIONS

The copper industry has evolved in the last fifty years, significantly increasing process intensity. As processes have been developed, and resources are becoming more complex, highly advanced thermodynamic tools are required to support scientist and process designers in the task of developing process operating windows.

Minor oxide and minor elements play an important in the chemical and physical properties of slags as well as in the final composition of copper produced in the pyrometallurgical processing of primary and secondary sources.

Despite this fact, there are some classical diagrams, such as the Cu-S stability diagram Yazawa Diagram and the FeO-Fe_2O_3-SiO_2 ternary diagram that still relevant to support the process development in copper smelting.

The knowledge developed at Pyrosearch to support the copper smelting industrial has been vital to the success of these companies in the copper business.

Integration of fundamental findings firstly to process modelling tool platforms is fundamental to allow process engineers and business analysts to balance material portfolios for different plants, assess potential processing of complex materials and evaluate synergies between plants to improve multi-metal recovery and extraction of valuable metals from primary and secondary resources.

There is still work to be done from the fundamental perspective, with the verification of physical properties, such as viscosities and partial pressures of minor elements under different conditions. In addition, properties of secondary products, such as dusts, and the recycling to primary and secondary vessels requires a deeper understanding of their respective mechanisms.

A more complete understanding of these properties will allow companies to better assess processing of complex materials at optimum processing cost, and maximum utilization of their resources, with particular focus on the optimisation of multi-metal operations.

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