Challenges facing non-ferrous metal production

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Keywords: Copper, Nickel, Zinc, Sulphide smelting, Refining, Minority metals, Sustainability

ABSTRACT

The increase in metals demand in the electrifying globe means significant growth in the smelting of e.g., copper, nickel, zinc, and lead, produced from primary sulphide sources or using sulphide mattes as the intermediates of the process chains. This means that leaner and complex mineral deposits will be evaluated as ores and are in the future traded in the commodity market for smelting and refining to pure metals.

An important issue in the trend is the technology metals, like antimony, tellurium, and gallium, which exist as trace elements in sulphide ores and form no ores of their own. Their recovery becomes important in the coming decades as will be the case with growing slag amounts without use in other industries. The key is to produce environmentally acceptable slags in the smelting operations. It sets new boundary conditions to e.g., the treatment of flue dusts. This means that all material streams of smelting and refining must be re-evaluated for the deportments of the main and minority metals.

In copper smelting, the recoveries of precious metals are today important for the feasibility of the custom smelters but due to low prices of many minority metals they are discarded in slag landfills. It is one of the emerging issues also in the secondary copper smelting today and once the demand grows, the same question will be faced also in the mining-beneficiation-smelting-refining chain of the primary production of nickel, zinc, and lead. The distributions of many technology metals in the copper and nickel smelting have been recently studied using methods where the chemically bound trace elements in the slag and its phases at the smelting conditions have been studied. Thus, the key data about options for process modifications and additional processing steps are piling up.

Short processing routes in the metals smelting and refining are attractive due to their simplicity. At the same time, complexity of many raw materials challenges the fluxing at high oxygen partial pressures in low silica slags with high metal concentrations. The compromise between high primary recovery and safe operation is a demanding task in conditions where slag foaming outside the processing window is evident.

The increase in the demand of pure nickel is challenging the raw material basis where low-grade sulphide ores are soon smelted along with nickel laterites to matte. It is a demanding task at high MgO concentrations. The low solubility of MgO in iron silicate slags requires new fluxing strategies and new smelting end points for the operation at reasonable temperatures; the direct nickel matte smelting in one-matte mode may be an option.

INTRODUCTION

The increase in metals' demand anticipated in the electrifying world means growth in the smelting of e.g., copper, nickel, and lead which primarily are produced from primary sulphide minerals or using sulphide mattes as the intermediate product. This means that leaner and more complex mineral deposits will be evaluated and classified as ores and are traded in the commodity market for smelting and refining. Whether this is possible, the key is in the development of agile smelting and refining technologies. The question also is, who will have 'patient money' to carry out and commit to the long term basic and applied research, aiming at CO₂-lean and environmentally lean technologies. Another side of the coin is the common need of less special knowledge and skills to operate the plants and to do that in a safe way. In that e.g., novel on-line measurements, like direct oxygen partial pressure from the smelting vessels, robotics, and AI, will play vital roles.

A simple calculation of global demand of refined copper indicates that 3 % annual growth ends up from the present about 25 Mt pa [Copper 2023] to 50 Mt pa in 2050. This means a significant increase in the mine production, due to the long end-of-life time for copper products. In terms of smelter capacity, it means 1-2 new large scale greenfield smelters each year in 2025 and 2-3 in 2050. This requirement of 'new metal' is stricter for copper than in e.g., alloy steels, where substituting alloys can be developed, whereas most copper use and essentially all future growth is in high-purity metal to be used for heat and in particular for electricity transfer purposes. This means that 99.99 % pure A-grade cathode must be able to be produced also using the low-grade and complex raw materials. At the same time, the discard slag production is at least doubled which lowers the primary yield and increases the production costs, when the slag recycling will be the preferred option instead of landfilling. The same is valid with nickel and zinc as well as to some degree with lead.

Running large scale smelting and refining operations today includes reliable life cycle management of the equipment and forecasting the maintenance needs several months, even more than half a year beforehand, due to the availability and long delivery times of many critical spares. Such vulnerable areas in the non-ferrous smelting and refining are e.g., the refractory bricks, cooling jackets, and many electric and electronic components.

The recovery of all trace elements in copper, nickel, zinc, and lead smelting is a future challenge which requires re-thinking of the process chains for optimising the recoveries and allowing the circular economy also in the small so-called technology metals. They today deport and deplete in slags without hope of recovery. On the other hand, the global distributions of many toxic elements in copper, nickel and lead smelting are very uneven [Risopatron, 2018] which emphasises the need of using available technological advancements for limiting e.g., mercury, arsenic and lead emissions also in the current facilities when increasing the production.

The regulation in industrialised countries today is hostile to metal making. That discourages the activities to develop the present technologies and makes long-term commitment of the industry less attractive. This again has a major impact in the technology development and innovations which lead to new and more green metal making processes in a field where major technology improvements need decades to mature. The development is evident when looking at the distribution of fundamental and engineering publications by country over the last two-three decades.

THE IMPURITY PROBLEM

In the non-ferrous metallurgy, most trace elements in the primary and secondary raw materials are either technology metals or harmful elements. The former must be recovered, and latter eliminated for environmental reasons. The fundamental knowledge in finding the optimal end points e.g., for the processing of matte, converting, and refining steps, includes the elements' equilibrium distributions between matte, slag and gas, and the thermodynamic properties of their species in the phases. Thus, the individual conditions for the maximum deportments of the impurity elements in the various side streams can be evaluated. Such accurate and reliable fundamental data also allows digitalisation of the processing operations.

In the non-ferrous industry, with exception of aluminium production, the use of hydrogen and fossilfree metals in terms of Scope 1, 2 and 3 greenhouse gas emissions [US EPA] will not be as demanding as in the ferrous and especially in ferroalloys industries. There is no fundamental restriction from thermodynamic point of view even if the degrees of utilization of hydrogen in some processing steps, like slag cleaning, may be realised on a relatively low level. The smelter flow sheets of today include closed flue dust circulation which forces all volatile elements into the two existing outlets of the smelter, namely the crude metal/matte and the slag, see Fig. 1. Independently from the slag cleaning technology used, the closed operation mode leads to high trace element concentrations in the metal product and the discard slag when/if they are not removed from the material streams.



Figure 1. Schematic flow sheets of the present closed-type flue dust treatments and an open circuit mode with the suspension smelting technology as an example (FSF-flash smelting furnace; FCF flash converting; PSC – Peirce Smith converting; WHB – Waste heat boiler).

The utilisation of the opportunity of high particle temperature in the gas-concentrate suspension in the copper and nickel in the flash smelting processes and also the vigorous agitation in the bath smelting processes allow us to split several impurity elements from the main metal stream and redirect them into safe treatment instead of mixing them in the discard slag and crude metal. The key trace elements in the copper production by ICSG today and in near future are arsenic, lead and bismuth [Risopatron, 2018].

RECOVERY OF THE TRACE ELEMENTS

The sulphide ores are important sources of several minority metals some of which do not have ores of their own. Typical examples are e.g., selenium, tellurium, antimony, and bismuth. Their recoveries are part of the smelting and refining steps in cases there is economy behind the extraction. Today, a lot of these minor elements (often called technology metals) are lost in the earlier steps prior to smelting due to commercial reasons [Moats et al., 2021; Nassar et al., 2022] i.e., lack of demand and low price.

The deportment of minority components will be a more vital issue in the case where the trace elements from secondary resources will be recovered. The use of standard primary copper smelting circuits is out of question because many elements deport in the smelting and converting slags and cannot be recovered from there in the slag cleaning operations due to their thermodynamic properties and low concentrations [Lennartsson et al. 2018; Faraji et al., 2022]. Thus, the focus of WEEE recycling has been so far on the recovery of the PM and PGM values only. Therefore, the optimal routes for the primary and secondary raw feeds must be evaluated in future from this perspective [Alvear Flores et al., 2020].

Losses of trace elements in beneficiation-smelting-refining chain are evident and often intentional due to penalties involved in concentrate trading. Recent detailed analyses on some trace elements in the primary copper ores and their recovery in the current beneficiation-smelting-refining chains and technologies [Moats et al., 2021; Nassar et al., 2022] indicate that significant fractions are lost or actively suppressed in the gangue or slag streams. Thus, they are led to the tailings at mine site and slag landfills at smelters which seem to contain large quantities of them accumulated as reserves over the past decades.

An important issue in this context is the technology metals in copper, zinc, and nickel smelting, like e.g. antimony, tellurium, molybdenum in copper extraction, and gallium in zinc and alumina processing, which exist as trace elements in many sulphide ores and form no ores of their own. Thus, their increased demand is essentially linked with the use and availability the primary sources of those metals. Many of them are on the critical metals/materials lists of the geographical areas e.g., in EU and USA [EU critical minerals act; US critical minerals]. Their effective recovery may become important in the coming decades as will be the case with growing slag amounts without

sustainable use in the other industries. The key is to produce environmentally acceptable slags and other by-products in the smelting operations which sets new boundary conditions to e.g., the treatment of flue dusts and its volatile elements as well as the hydrometallurgical iron residues [Salminen et al., 2020].



Figure 2. The metal-slag equilibrium distribution coefficients of indium between copper/copper matte and slag as a function of the prevailing oxygen partial pressure at 1300 °C [Sukhomlinov et al., 2020, 2020b].



Figure 3. The metal-slag distribution coefficients of tin between (a) copper (b) copper matte and slag as a function of the prevailing oxygen partial pressure at 1300 °C [Avarmaa et al., 2018; Sukhomlinov et al., 2020b].

The recovery of many technology metals in copper and nickel smelting is problematic because they do not volatilise, and they oxidise in the matte smelting step or converter stage. In many cases they deport in the slag when the extraction process advances from reducing to oxidising. This is clearly seen when studying the equilibrium distributions as the function of the prevailing oxygen partial pressure. The thermodynamic parameter independent of the scale demonstrating the issue can be defined [e.g., Park et al., 1984] as

$$L^{s/m}(Me) = [wt\%Me]_{matte/metal} / (wt\% Me)_{slag}.$$
 (1)

and it can be derived from the thermodynamic properties of the element in the phases in contact or from the assays of the phases in the industrial or laboratory conditions. Typically, they are measured in equilibrium conditions using chemical analyses made from the homogeneous part of the phase at process conditions. That was often neglected in the past, and bulk analyses were used instead of *in situ* phase analyses which leads to too small (apparent) distribution coefficient values if they deviate

strongly (>1000) from unity [Klemettinen et al., 2017]. For this reason, the experiments where the phases were sampled from a large pool of slag and quenched the presence of inclusions is difficult to trace and separate from the 'clean' phase. Then also the chemical composition is only average and contains average values of the phase including the uncertainties of composition gradients (from volatile species) and inclusions (not belonging to the phase) [Jak et al., 2022]. An important issue is that in such cases, volatilisation and inhomogeneities in the phases remain undetected.

A separate recovery step is needed for preventing the loss of trace elements to the discard slag or other residues. This may include re-thinking of the flue dust treatment, as discussed earlier, due to volatile nature of some trace elements. The situations for indium in black copper and copper matte smelting can be seen in Fig. 2 and those of tin in Fig. 3. The matte/metal-slag distribution coefficients are unbiased to the gas-melt equilibria and thus, the volatility of each element and its deportment in the flue dust must be studied as a separate case. For that purpose, typically mass distributions of elements obtained from the mass balance are used [Nakajima et al., 2009]. Particularly problematic is the situation in cases like indium and tin in black copper smelting where the distribution coefficient in reducing conditions is strongly on the metal side and in oxidising conditions in a similar way on the slag side.

Fig. 4 shows an example of copper matte smelting which is one important source of e.g., gold and palladium. All elements with a high distribution coefficient between matte/metal and slag suffer from the systematic technical problem of matte/metal entrainment in the slag. A simple mathematical exercise shows that when the distribution coefficient is $L^{m/s}[M] > 1000$ the apparent values of the experimental results remain at around 10-100 if the separation of matte/metal droplets in the slag is ignored, i.e. assumed negligible without proof, or made unsuccessfully.



Figure 4. The experimental distribution coefficients of (a) gold and (b) palladium between copper matte and iron silicate slag saturated with silica as a function of the matte grade [Avarmaa et al., 2015].

The high accuracy and significantly larger experimental equilibrium values of the distribution coefficients compared with the previous data (e.g., Baba & Yamaguchi 2013) was justified by the spatial accuracy of the used LA-ICP-MS technique which allowed selecting inclusion free phase areas of the slag for the analysis [Klemettinen, 2021]. Also, the isotope fluxes as a function of time in the MS analyses (i.e., TRA signals) provide information about the presence of micro/nano nuggets in the samples [Richter et al., 2004].

The behaviours of many technology metals in the primary and secondary copper and nickel smelting have been recently studied to facilitate their extraction. The used methods have enabled to locate where the chemically bound trace elements in the slag and its phases at the smelting conditions deport in the various processing steps. Thus, the key data for process modifications and additional processing steps for separating them from e.g., the slag, matte and flue dust streams, is gradually piling up and soon allows the assessments of their thermodynamic properties.

IMPORTANCE OF THE SLAG CHEMISTRY AND FLUXING

The short processing routes in the metals smelting and refining are attractive due to their better recoveries and potentially, smaller capital expenditures. The key is to eliminate internal circulations

within the smelter. A fundamental issue is limiting wider use of such processes, namely the shortage of low-iron or high-copper ores. Thus, only less than 10 such smelters exist today. An option for increasing the use of such processing routes is a pre-concentration of standard sulphide concentrates and cleaning of complex bulk concentrates [Tuominen et al. 2005, 2007; Awe 2010; Fuentes et al., 2009]. For such purposes, straightforward processing concepts are needed which eliminate most minority and trace metals and gangue from the copper minerals and at the same time, allow increasing the copper-to-iron ratio.

Another option may be the production of a bulk concentrate and to split that into two streams at mine site, one with a high Cu/Fe ratio and the other with most impurities and low copper for hydro-metallurgical processing which can handle the impurities in a comprehensive way [Risopatron, 2018]. This strategy would allow deposition of the nasties in a concentrated form and avoid their spreading at low concentrations e.g., in the slag landfills.

In the direct-to-blister copper smelting, the shorter process chain means the absence of the entire converter isle which allows more compact building and the movement of all molten materials in covered launders which eliminates scattered fugitive emissions at the smelter. An example of the streamlined lay-out is in Fig. 5 which also indicates the lack of internal material circulations in the process and the option of selecting the slag cleaning technology based on the local needs.



Figure 5. A schematic of the direct-to-blister flash smelter: feed preparation, the furnace-waste heat boiler-ESP, and the auxiliary crude copper, off-gas, and slag treatments steps prior to the electrolytic refining to 4N copper cathodes; the material flows are also demonstrated (Outotec).

In the high-grade matte or direct blister production, major increase in the oxidation degree exposed to the charge brings challenges to the fluxing at the prevailing high oxygen partial pressures in low silica slags with high copper concentrations. The compromise between high primary recovery and safe operation is a demanding task in the conditions where slag foaming outside the processing window is evident.

The complexity of sulphide concentrates in nickel smelting does not limit the use of the direct highgrade nickel matte smelting which allows in a flexible way the use of all possible nickel sulphide concentrates either as such or together with the EF matte which fulfil the heat balance at reasonable oxygen enrichments.

Case studies: direct-to-blister copper smelting

The shortest way and smelter chain in sulphide smelting is the direct production of metal or its intermediate high-grade matte for refining in one smelting step. Such industrial examples are the direct-to-blister smelting of copper [Kojo & Huppe, 2011; Taskinen 2011], direct-to-high grade matte smelting of nickel [Mäkinen et al., 2005] and direct lead smelting by suspension technologies [Bryk et al., 1966]. In those technologies, the feed mixture with its gangue minerals goes through the heating and combustion steps in the reaction shaft of the smelting vessel. There in copper and lead

smelting, the oxidation conditions have been adjusted for oxidising almost all sulphur and iron from the matte allowing production of low-sulphur metal. In the direct nickel matte smelting, the product is essentially iron-free sulphide matte. Thus, the fluxing in metal making conditions must take into consideration also the gangue components.

The forming slag is determined in such conditions, at much higher oxygen partial pressures than conventionally, by the endpoint of the crude metal in copper smelting and in nickel that of the high-grade matte smelting. To achieve this condition, the metal droplets generate a large volume of SO₂ in the reaction shaft and the forming slag must dissolve the iron oxides together with gangue and maintain exactly the correct degree of oxidation for the iron oxides present. An example of the challenges is given in Fig. 6 where the high-silica sulphide concentrate will form silica-saturated slags without any fluxing i.e., it locates within the primary field of silica (the red circle). Note the steep saturation boundaries of silica (tridymite on the right) and pseudo wollastonite (on the left side) which indicate that the correct fluxing is the key for avoiding foaming.

The correct operation of the smelting may need some sort of preprocessing for the complex and low calorific value concentrates for removing selected harmful sulphide minerals and gangue components. This will stabilise the smelting step and remove slag fluidity problems when the composition of the feed mixture can be kept within narrow bounds in terms of its iron and sulphur concentrations.



Figure 6. Operation line of slag in a DtoB smelter when it is fluxed with lime depicted on an isothermal, quasiternary Gibbs triangle at constant oxygen partial pressure of 3×10⁻⁵ atm and 10 wt% Cu₂O; blue line shows fluxing as a function of CaO and the red circle is the unfluxed slag of the feed mixture (MTDATA).

Auxiliary fuel in sulphide smelting:

Another issue is the smelting of low-calorific value sulphide concentrates which need additional fuel for the smelting for maintaining the process temperature. For effective recovery of minority components, the primary smelting step or matte making may end up at matte grades lower than the present 60-65 % Cu which additionally limits the heat generation in the smelting step. A fossil-free low-CO₂ alternative is the use of pyrite as fuel, but the downside is increased S/M ratio and the growing slag amount which requires improved copper recovery and lower residual copper in the discard slag.



Figure 7. Extra enthalpy generated by FeS₂ when added in a lean chalcopyrite concentrate, producing a fixed matte grade of 65 % Cu and fluxing the slag to 30 wt% (SiO₂); a simplified heat balance without considering the effects of gauge minerals on the slag chemistry (MTDATA 7.4 with MTOX database 8.2).

Thermodynamic equilibrium calculations at fixed matte grade of 65 % Cu indicate that the slag amount is doubled at a pyrite addition of slightly less than 50 wt% of chalcopyrite content of the feed mixture (in case CuFeS₂ is the only copper carrier). The extra heat provided by pyrite is, however, significant as shown in Fig. 7. An addition of about 42 wt% FeS₂ doubles the heat input in copper smelting in a case where high oxygen enrichment is used in the Flash Smelting Furnace (see the used constraints of Fig. 7). No process gas preheating was assumed [Pesonen et al., 2022], all raw materials were at 25 °C, and the products at 1300 °C.

Thus, from the point of view of the CO_2 footprint, it is more sustainable to use pyrite as additional fuel than the present hydrocarbons or coal/coke.

SUMMARY AND CONCLUSIONS

If countries and geographic areas are truly worried about the criticality of metals and minerals, that should be not the interest of commercial actors only. In the copper making the environmental and fugitive emissions must be eliminated and the recovery of trace elements need significant technological advancements. The deficiency of nickel and cobalt output will be a clear challenge which needs totally new technologies for the extraction.

Radical improvements in technology have so far not emerged without thorough fundamental information about the physics, chemistry, and engineering behind the inventions. This fact requires significant RTD input from the mining and smelting community for decarbonising their operations and maximising the metal value yields to the thermodynamic limits.

The environmental awareness of the consumers is an important issue of today which supports transparency to the entire production chain of metals. Carbon free metals and e.g. sulphuric acid over the production chain are today's slogan but when that option is reality in many mining operations in remote areas is a question mark. It will be seen whether the consumers are willing to pay premium for environmentally friendly metals' options in the end use. That also means, to cover the cost of recycling the metals when the demand will be 2-5 % larger next year to the present and some investment goods have a life span on several decades instead of 6 months of the cell phones of today. Or is such an option viable that you're allowed to get a new cell phone, car battery, or PC only when you after payment return the old one to an authorised dealer for reuse or recycling?

In copper and nickel sulphide smelting, the recoveries of precious metals are today important for the feasibility of the custom smelters, but due to low prices of many minority metals they are discarded in slag landfills. It is one of emerging issues in the secondary copper smelting today. Once the demand of the trace elements 'technology elements' grows, the same question will be faced also in the mining-beneficiation-smelting-refining chains of the primary production of nickel, zinc, and lead. The distributions of many technology metals in the copper and nickel smelting have been recently

studied using methods where the chemically bound trace elements in the slag and its phases at the smelting conditions have been studied. Thus, the key data about options for process optimisation, modifications, and additional processing steps are piling up.

An important issue in the process development is the needs of mode accurate fluxing control in the intensive processing technologies compared with the old processes. Then, the practical operation must more and more rely on on-line or off-line computational tools for maintaining the heat balance and the intended fluxing. For that purpose, digital tools and AI may bring added value.

ACKNOWLEDGEMENTS

The authors are indebted to several R&D programs funded by Tekes and Business Finland over the years 2013-2023 (e.g., ARVI, SIMP, SYMMET, TOCANEM) as well as Metso-Outotec and Boliden for their encouragement, industrial contribution, and financial support.

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