Understanding the Side-Blown Furnace Slag System at Glencore Nordenham´s Lead Plant: From Theory to Industrial Application

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ABSTRACT

Lead has the ability to collect and carry valuable metals such as copper, bismuth, antimony, tin, and precious metals for their downstream recovery. Therefore, lead metallurgy is key for the raw material supply that our society demands. Lead smelters, excluding lead-acid battery recyclers, tend to process more complex primary and secondary raw materials, which are mostly processed via the pyrometallurgy route. Accordingly, understanding the slag system of these metallurgical processes is key for the efficient industrial operation and recovery of minor elements.

Glencore Nordenham is an integrated lead and zinc smelter in northern Germany with a production of 92 000 tonnes of lead and 164 700 tonnes of zinc in 2022. The lead production line processes complex lead-bearing raw materials through the direct smelting process. Firstly, the feed mix is smelted in a Top Submerged Lance (TSL – Ausmelt®) furnace, where a lead bullion containing minor metals and a lead-rich slag are produced. Then, the lead-rich slag from the TSL is tapped (via launder) into a Side-Blown Furnace (SBF), where lead oxide is reduced to produce lead bullion (with minor elements) and discard slag. The lead bullion from both stages is refined to produce lead (> 99.9 %) and recover the minor elements (Cu, Ag, Au, Sb, Te, Bi, etc).

This paper reflects the experience of operating the SBF after the first 5 years of operation and describes its 'PbO-SiO_2-FeO_x-CaO-ZnO' slag system. Firstly, the slag system, the furnace operating region and the potential solid phases present are discussed from a theoretical point of view. This theoretical study has been performed using FactSage 8.2 and the database developed by the Pyrosearch group at the University of Queensland, Australia (UQPY). Then, the FactSage simulations are compared with industrial slag measurements. Finally, some examples on how the slag knowledge gained at Glencore Nordenham can help the industrial operation of the SBF are discussed.

INTRODUCTION: GLENCORE NORDENHAM´S INTEGRATED LEAD AND ZINC PRODUCTION

The metallurgical infrastructure of non-ferrous base metals such as lead, zinc, copper or nickel is key for supplying the materials that society demands. Many minerals, alloys or technology products contain at least two of these metals together with other minor elements. These materials are often processed in the base metal´s metallurgical infrastructure where the base metals are refined, and the accompanying minor elements are recovered as by-products. The ability of base metals to dissolve and carry other minor elements throughout their refining process enables it.

Lead can collect valuable metals such as precious metals, copper, bismuth, antimony, tin and/or zinc for their downstream recovery. Furthermore, by-products containing copper, nickel, cadmium, lead or precious metals are obtained when zinc is produced. Therefore, there is a close interconnection within the non-ferrous metallurgical infrastructure to maximize metal recovery through the exchange and treatment of its by-products. This interconnection becomes more important day by day because of the increase on the complexity of raw materials and the necessity of moving towards a circular economy (Reuter, Matusewicz and van Schaik, 2015).

Ores are decreasing their grade and becoming more complex in terms of minor elements, while chemical elements representing half the periodic table can be present in other products such as modern vehicles or waste electrical and electronic equipment (WEEE). Moreover, the processing of these complex materials generates higher quantities of by-products that should be treated to maximize material recovery. These are a few examples of raw materials that the metallurgical infrastructure has to process nowadays to supply the metals that society demands.

Glencore Nordenham is an integrated lead and zinc smelter aiming at becoming a modern and flexible polymetallic smelter that can process a wide range of complex materials by making the most out of the synergies between lead and zinc metallurgies. The zinc plant has a roasting-leaching-electrowinning (RLE) configuration combined with Glencore´s Albion Process™ direct-leaching technology. The production of zinc was 164 700 tonnes in 2022 as master and die-casting alloys, special high grade (SHG) zinc and zinc alloys for continuous galvanizing. Additionally, by-products such as sulfuric acid, lead and silver secondaries, copper cement or cadmium metal are also produced.

The lead smelter uses the direct smelting process to produce over 100 000 tonnes of lead per year as soft and fine lead and lead alloys. Additionally, sulfuric acid and silver-gold alloys are also produced. The flowsheet of the lead smelter is shown in Figure 1. The process starts with the feed blend preparation of primary and secondary materials. Different types of concentrates, residues and secondaries are blended with internal recycle materials and fluxes. This feed blend is then smelted in a top submerged lance (TSL) furnace, Ausmelt®, where a lead bullion containing minor elements and a lead-rich slag (~ 50 wt% Pb) are produced. The lead bullion is sent to copper drossing before being sent to the pyrometallurgical lead refinery. The lead-rich slag from the TSL flows via a launder to a side-blown furnace (SBF), where the lead oxide in the slag is reduced to recover the lead as lead bullion together with other minor metals. The SBF slag is then landfilled. The lead bullion of both furnaces is sent to a pyrometallurgical lead refinery to refine the lead and recover the dissolved minor metals such as Ag, Au, Bi, Cu, Sb, Sn or Te.

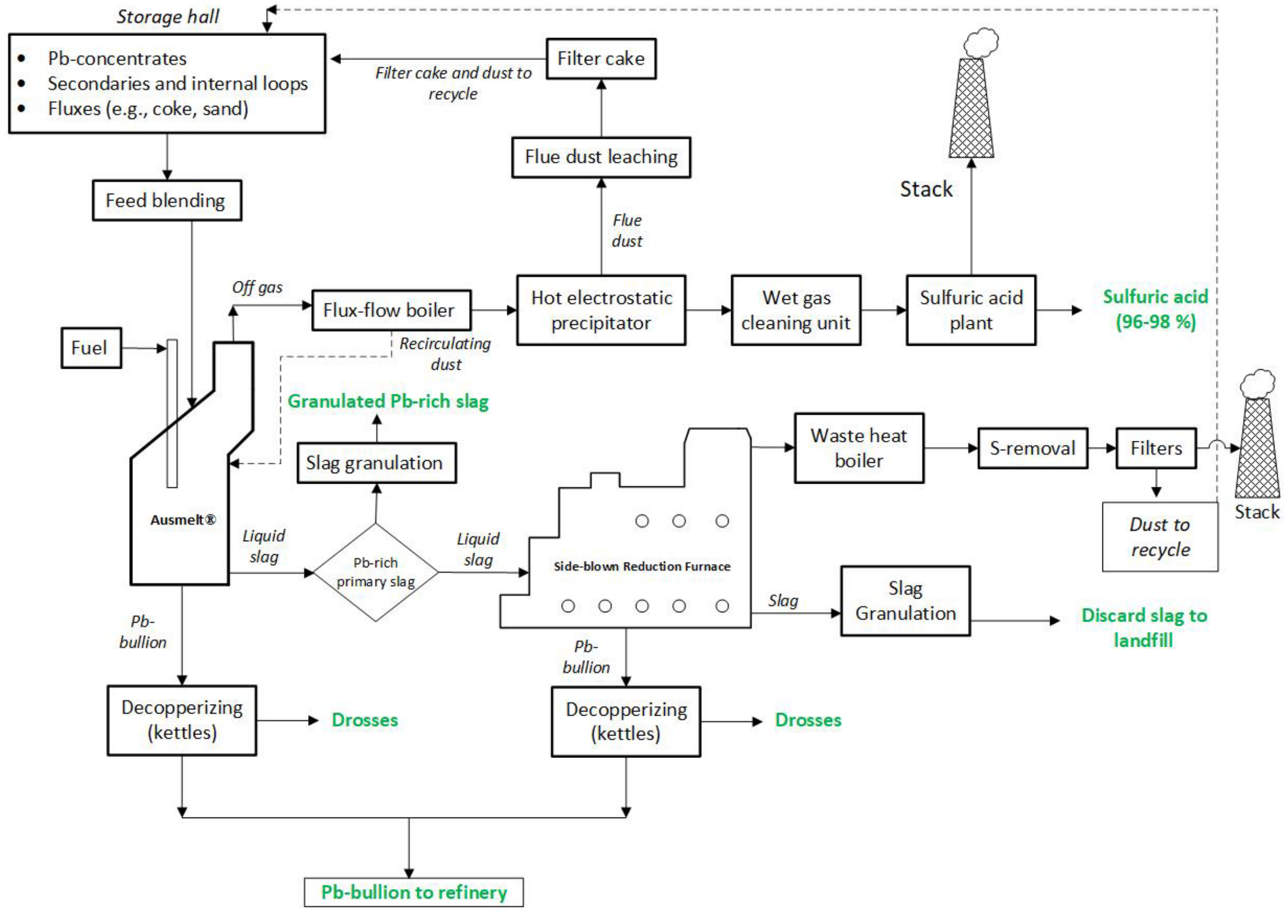


Figure 1. Flowsheet of Lead plant at Nordenham Metall GmbH, Germany (Kandalam *et al.*, 2023).

The TSL furnace and its latest upgrades at Glencore Nordenham have been already described by Kandalam et al. (Kandalam *et al.*, 2023). Therefore, this paper describes the SBF and the experience after 5 years of operation. Particularly, the ‘PbO-SiO_2-FeOx-CaO-ZnO’ slag system used in the SBF is described theoretically. Additionally, few examples on how the theoretical knowledge of the slag system is used in furnace operation are explained.

LEAD SLAG REDUCTION FURNACE AT GLENCORE NORDENHAM

The SBF at Glencore Nordenham is a submerged-tuyere furnace constructed with a long and narrow rectangular hearth that becomes wider at the top of the furnace (Wei *et al.*, 2019). It was commissioned in 2018 to process the lead-rich slag of the TSL furnace, increase the lead recovery of the plant, and enable the recovery of minor metals when complex raw materials are treated.

A schematic of the SBF is shown in Figure 2, while data of the furnace are gathered in Table 1. Four main regions can be distinguished in the SBF:

- Lead region: a refractory-lined region at the bottom of the furnace and below the tuyeres where the lead bullion is settled and transferred to the copper drossing kettles via siphon.
- Slag region: a water-cooled copper panels region in the middle part of the furnace. The tuyeres are situated in this region to blow enriched air into the slag.
- Freeboard region: a water-cooled copper panels region above the slag region, where the gases in the furnace are post-combusted with air from the secondary tuyeres.
- Off-gas region: lined with concrete and steel anchors, this region carries the post combustion gases to the waste heat boiler (WHB).

The slag flows from the TSL furnace via launder into the SBF hot slag feed port. Moreover, the coal for heating and reduction is fed through a feed port located at the top of the furnace. Fluxes and cold material can also be fed through this feed port if needed. Final slag is tapped through a taphole, granulated, and then landfilled, while a siphon transfers the lead bullion to two copper drossing kettles. The furnace operates in batch mode with three stages: (i) charging, (ii) reduction and (iii) tapping. The batch time is around 2 hours.

After five years of operations (from 2018 till 2023), the SBF has treated around 600 000 tonnes of lead-rich slag from the TSL furnace with an availability of > 98 % (excluding planned maintenance and shut-downs), producing a slag with a lead content below 1.5 wt% suitable for landfilling. Additionally, the SBF has enabled the recovery of accompanying metals such as Ag, Bi, Cu, Sb, Sn and Te when they are present in the TSL slag. Therefore, a wide range of complex raw materials can be treated at Glencore Nordenham. This flexibility has enabled the treatment of more than 50 different raw materials such as lead-bearing concentrates, residues and recyclates (excluding internal loops and fluxes).

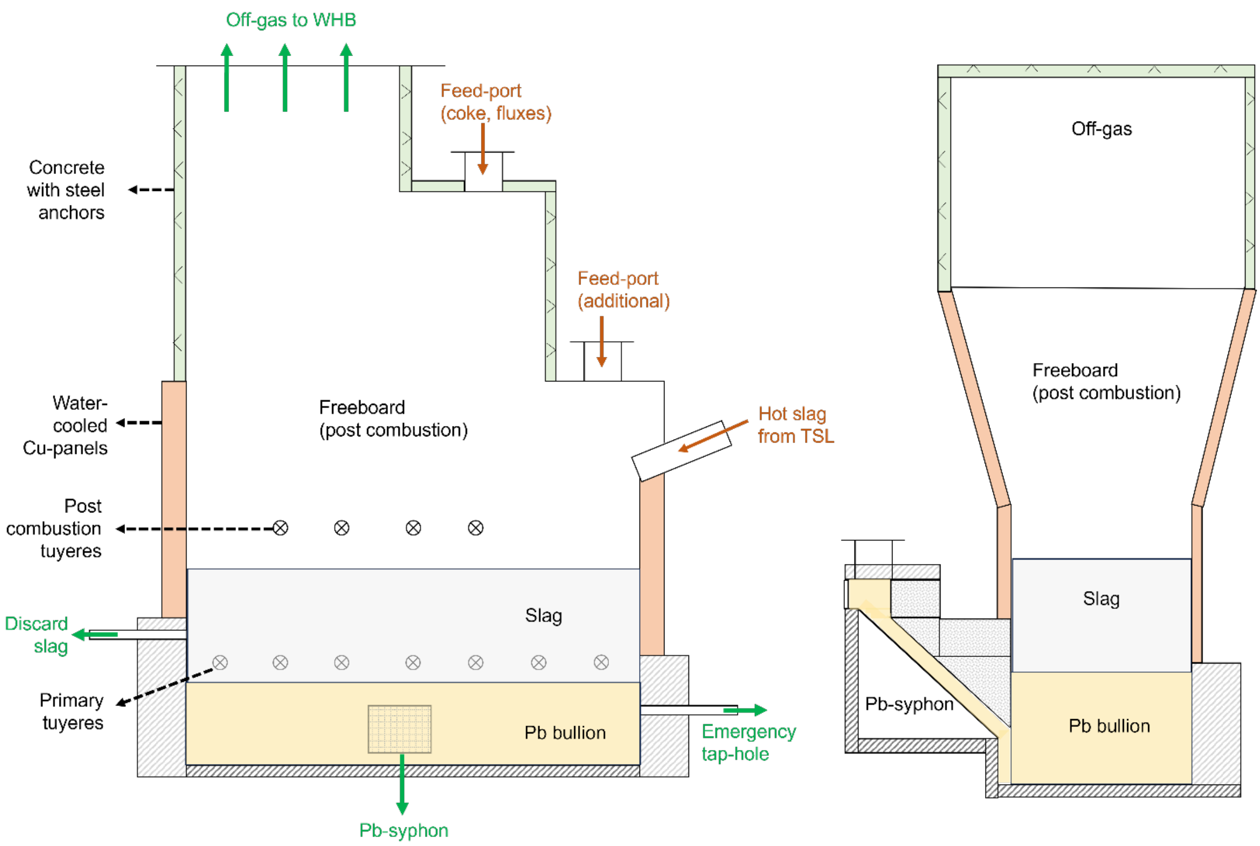


Figure 2. Schematic representation of Side-Blown Furnace (SBF) at Nordenham Metall GmbH, Germany.

Table 1. Glencore Nordenham´s SBF data.

Commissioned	August 2018
Length * width [m]	6.35 * 2.80
Height [m]	8
Number of tuyeres	22
Slag charge [t]	34-38
Pb in input TSL slag [wt%]	48-54
Pb in output slag [wt%]	< 1.5
Slag tapping target temperature [°C]	1250
Batch time [min]	120
Slag treated per year [t/a]	140 000

SLAG SYSTEM OF THE SLAG REDUCTION FURNACE

The slag composition and phases present vary during the SBF batch, particularly, during the charging and reduction stages. The SBF works best when the slag is fluid, above the liquidus temperature. But owing to the batchwise operation of the SBF the slag temperature constantly changes throughout each batch. Moreover, the SBF is not refractory lined in the slag region. Therefore, a slag freeze lining forms on the water-cooled copper panels. The life of the water-cooled copper panels is long and does not determine the furnace campaign duration. However, an excessive freeze lining build-up might create issues during operations, e.g. a reduction of the SBF volume. Therefore, understanding the slag system of the SBF is essential for its optimal operation.

The major components of the slag at Glencore Nordenham are FeO_x, SiO_2, CaO, PbO and ZnO. Other slag components such as Al_2O_3 or MgO are also present but in lower concentrations (< 1 wt%). To understand the SBF slag during a batch, the TSL slag should be discussed briefly. A simplified phase diagram containing the representative phase fields of the TSL slag (Figure 3) has been created using FactSage 8.2 (Bale *et al.*, 2016) and the database of the Pyrosearch centre at the University of Queensland, Australia (UQPY). This database has been particularly developed for the slag/matte/metal systems of the copper and lead industries (Shishin *et al.*, 2020, 2022; Hidayat *et al.*, 2023). The TSL slag composition range (striped green circle) is also shown in Figure 3. The TSL slags operate below liquidus temperature and are in the ‘liquid slag + melilite + spinel’ phase field of the phase diagram. Therefore, the hot slag that is charged into the SBF is a source of some suspended solids.

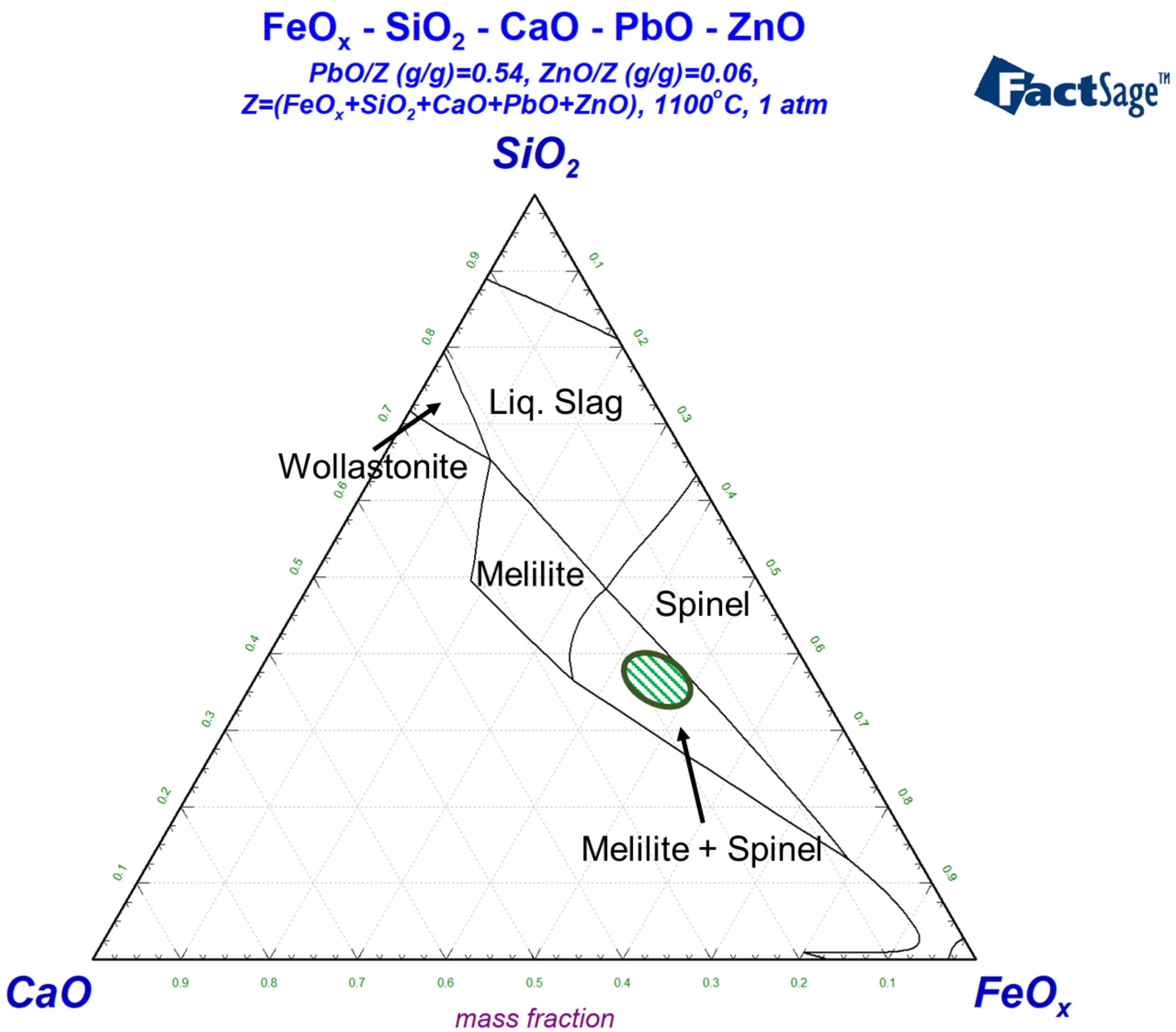


Figure 3. Simplified phase diagram for the TSL slag at 1100 °C showing the slag composition range (striped green area). Liquid slag is also present in the phase fields containing solid phases. A lead content of 50 wt% and zinc content of 5 wt% are set as constant values for this phase diagram calculation. The partial pressure of O_2 (pO_2) has been calculated and set for a slag in equilibrium with metallic lead.

When the lead-rich slag of the TSL flows to the SBF at the beginning of the batch (charging stage), it mixes with a slag heel from the previous batch (< 2 wt% Pb). This results in the starting slag composition for the reduction stage in the SBF. The starting slag has a lead and zinc content around 20 wt% and 12 wt% respectively.

A phase diagram for the starting slag in the SBF after charging has been created for these conditions using FactSage and the UQPY database. This phase diagram (see Figure 4) shows how the liquid slag region becomes larger when the temperature of the starting slag increases. At the end of the charging phase, the temperature is between 1175 °C and 1200 °C. Therefore, the slag is in the 'liquid slag + spinel' area. As the bulk slag composition is close to the liquid slag phase field, the solids content in the bulk slag would be around 5 wt% based on FactSage calculations.

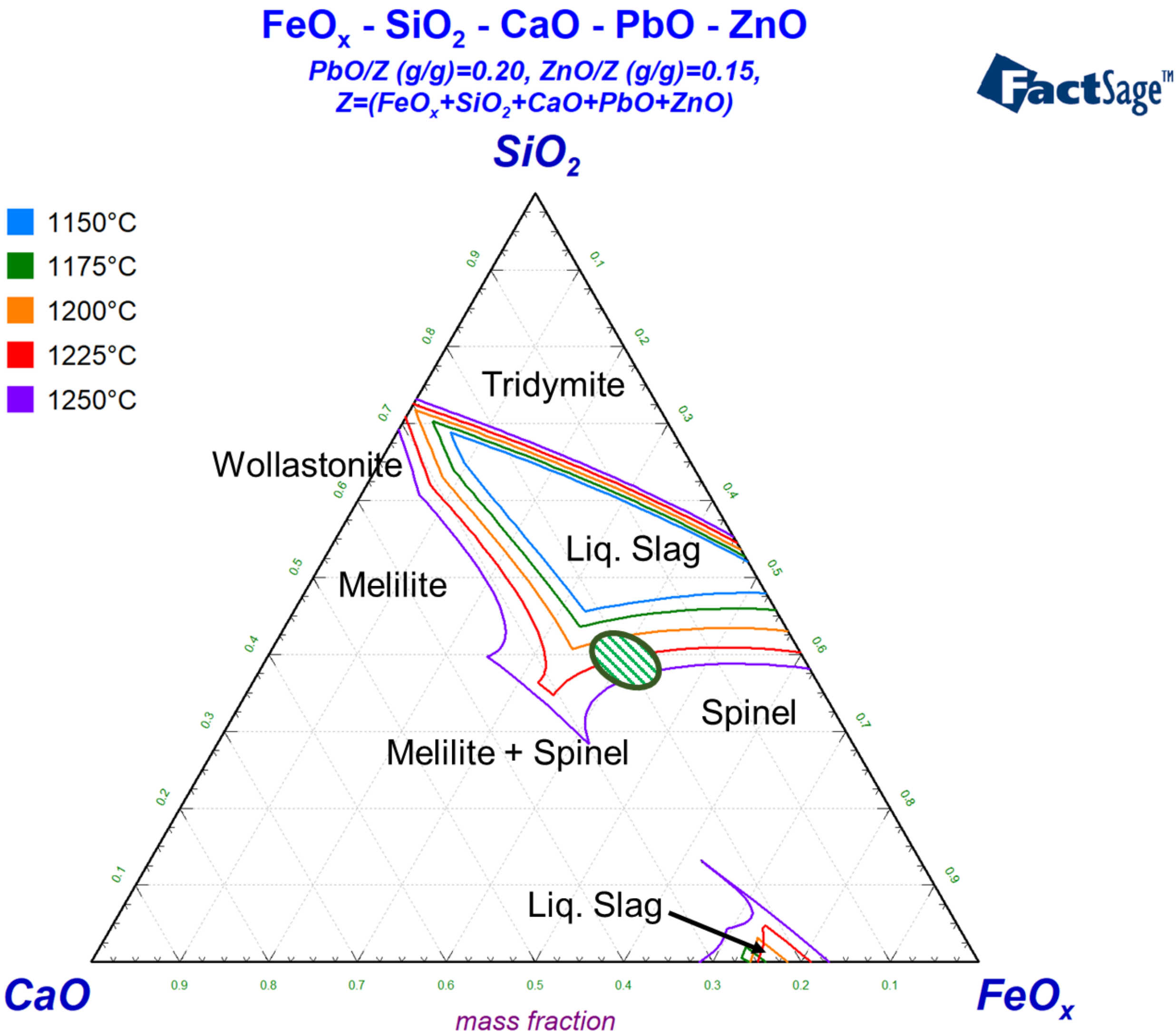


Figure 4. Phase diagram for the starting SBF slag composition after slag charging showing the liquid slag area for different temperatures and the slag composition range (striped green area). A lead content of 19 wt% and zinc content of 12 wt% are set as constant values for phase diagram calculations. The pO_2 is calculated and set for a slag in equilibrium with metallic lead at the different temperatures.

Then, the reduction phase begins. During reduction, the lead content decreases from around 20 wt% to less than 2 wt%. The reduction process can be represented in a phase diagram if the ratio between CaO, FeO_x or SiO_2 is fixed and PbO is included in the ternary diagram. In this case, a phase diagram with a representative CaO/SiO_2 ratio has been plotted using FactSage and the UQPY database (see Figure 5). As discussed before, the starting slag composition is in the 'liquid slag + spinel' phase field below 1200 °C. However, the final slag composition is inside the liquid slag phase field at this temperature. Moreover, the slag temperature increases slightly during the reduction phase. Therefore, a decrease in the solids content is expected to happen during the reduction phase.

When the lead content in the slag is reduced below 2 wt%, the tapping phase of the batch begins. Here, the temperature is increased to around 1250 °C to produce a slag with good lead oxide reduction kinetics and free from entrained lead bullion. According to Figure 5, the slag is expected to be fully liquid at this temperature, which avoids the generation of solid phases and decreases the viscosity of the slag.

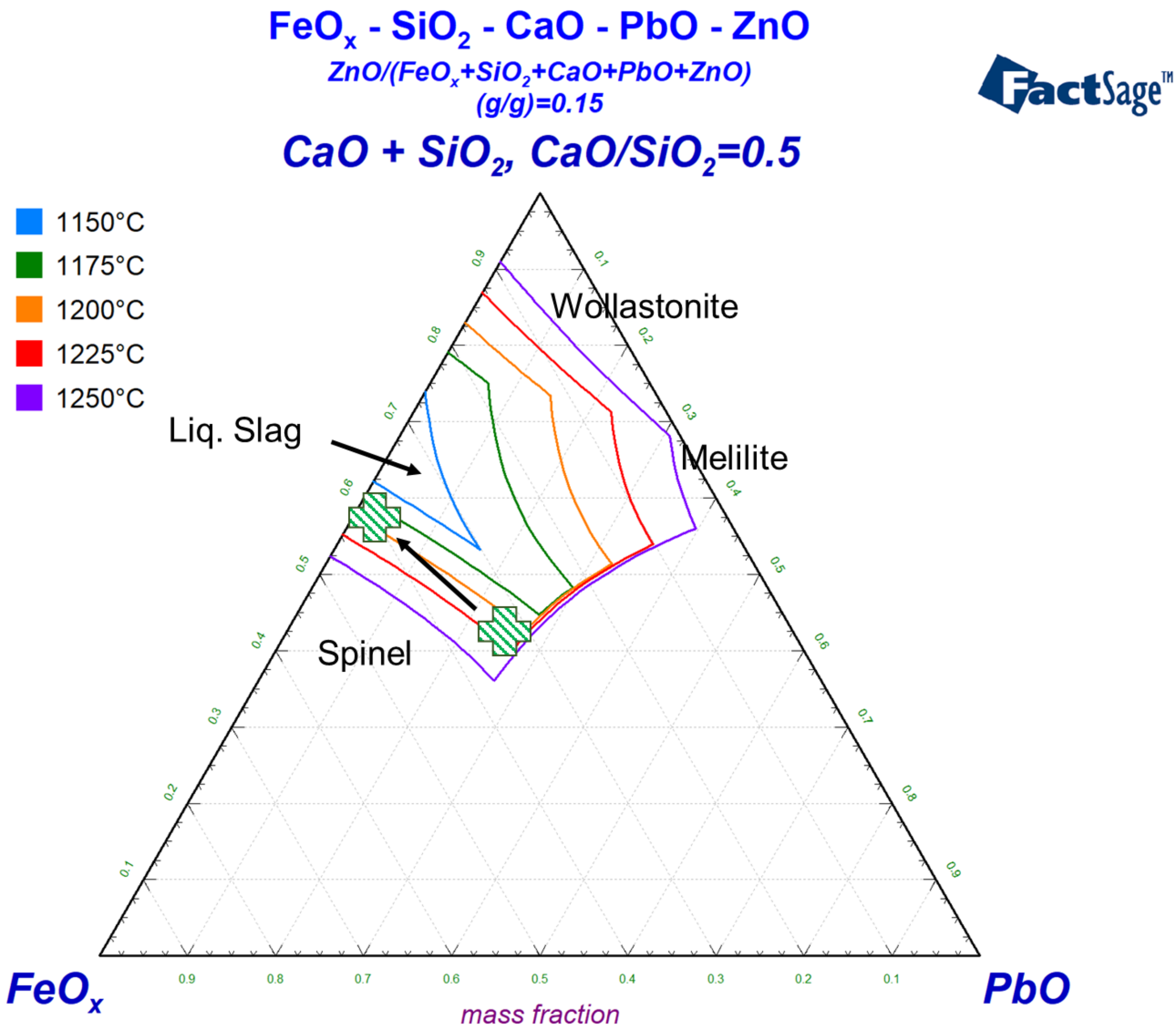
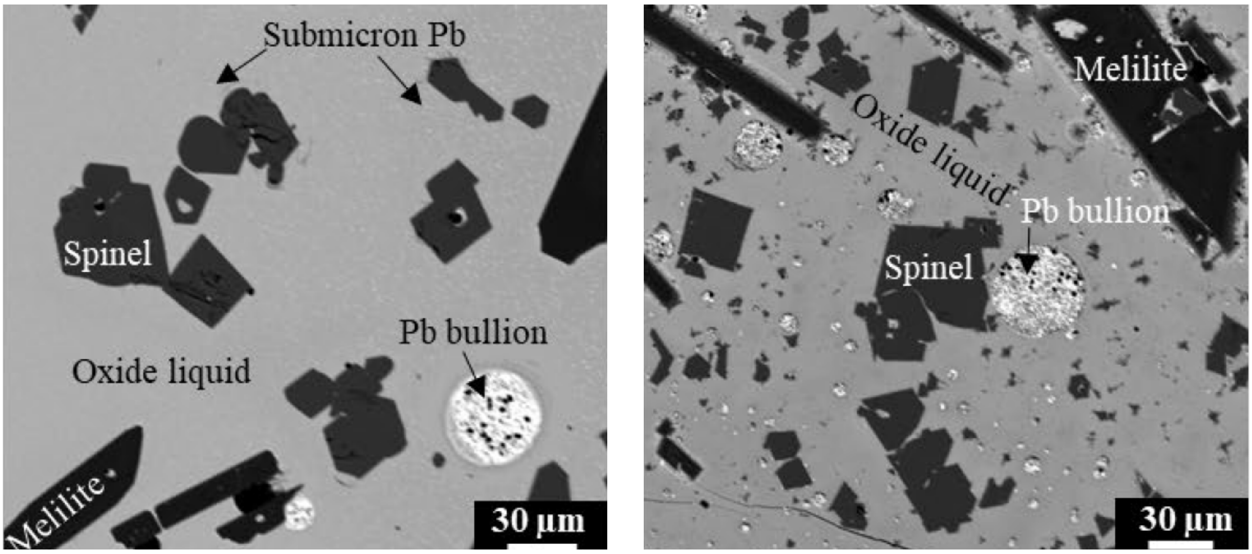


Figure 5. Phase diagram for the reduction phase of the SBF batch showing the liquid slag area at different temperatures and the starting and final slag composition range (striped plus symbol). CaO and SiO_2 are combined as compound in the ternary diagram with a CaO/SiO_2 ratio of 0.5, while the zinc concentration is set to 12 wt%. The pO_2 is calculated and set for a starting slag in equilibrium with metallic lead at the different temperatures.

INDUSTRIAL APPLICATION OF SLAG CHEMISTRY FUNDAMENTALS

The previous section explains the slag chemistry of the SBF batch from a theoretical point of view based on FactSage modelling and the use of the UQPY database. When these theoretical results are compared with actual industrial samples, a good correlation exists. For example, the microscope images of two different TSL slags at Glencore Nordenham analysed by UQPY are shown in Figure 6. As expected, the solid phases present in the bulk slag are spinel (square/polygonal shape) and melilite (elongated shape). Some droplets of lead bullion can be also seen in both samples because of incomplete settling/entrainment. In terms of phase proportions, the proportion of solid phases calculated theoretically with FactSage and the UQPY database also correlates with the value range measured in industrial samples, which is around 10 – 15 wt% solids in bulk TSL slag.



(a) (b)

Figure 6. Optical microscope images of two TSL slag samples entering the SBF, analysed by UQPY.

This good correlation between modelling and actual industrial values allows the application of slag chemistry fundamentals through modelling for analysis, prediction and optimization of the metallurgical processes performed at Glencore Nordenham. A few real examples will be discussed in this section.

As discussed before, the slags at Glencore Nordenham contain solid phases. The solid phases in the slag help the formation of a freeze lining in the furnaces that protects the refractory and water-cooled copper panels (see Figure 7), extending their campaign time before relining and maintenance. However, viscosity-related issues may appear if an excessive proportion of solids is present in the slag.

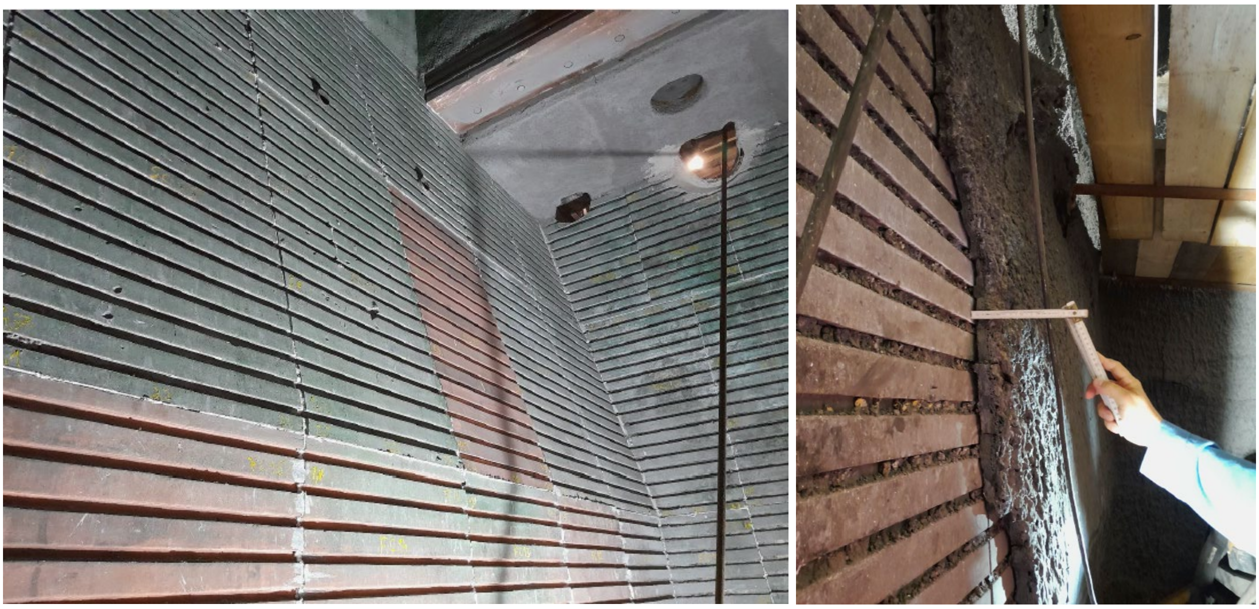


Figure 7. **Left:** Freshly cleaned water-cooled Cu-panels inside SBF. **Right:** Slag freeze layer (~ 3 cm) on the Cu-panels observed during the maintenance shut-down of SBF.

During the slag charging phase of the SBF, only spinel is expected to be present in the slag (see Figure 4). However, a slight increase in the CaO content of the slag at 1175 °C because of feed material variability might move the slag composition inside the 'melilite + spinel' phase field, and melilite would also be formed. The phase diagrams shown in the previous section and FactSage are used to predict the effect of these slag composition variations on the solid phase proportions.

The calculated proportion of spinel and melilite phases in the SBF slag after charging is shown in Table 2. A slight increase in the CaO content at 1175 °C would lead to a melilite proportion in slag of 1.9 wt%, while the total proportion of solids would increase from 7.5 to 10.6 wt%. However, if the temperature of the SBF slag after charging is 1200 °C, melilite would not be formed while the increase in the total proportion of solids would be lower than at 1175 °C (from 4 to 4.9 wt%). These results can be used to help the furnace operations department develop a set of directions for the operators when variations in feed are expected.

Table 2. Solid phase proportions in bulk slag calculated with FactSage and the UQPY database for two different slags. Values in wt%

	Solid phase	**1175 °C**	**1200 °C**
$SiO_2/(SiO_2 + CaO + FeO_x) = 0.40$	Spinel [wt%]	7.5	4
$CaO/(SiO_2 + CaO + FeO_x) = 0.19$	Melilite [wt%]	0	0
$FeO_x/(SiO_2 + CaO + FeO_x) = 0.41$	Total solids [wt%]	7.5	4
$SiO_2/(SiO_2 + CaO + FeO_x) = 0.39$	Spinel [wt%]	8.7	4.9
$CaO/(SiO_2 + CaO + FeO_x) = 0.21$	Melilite [wt%]	1.9	0
$FeO_x/(SiO_2 + CaO + FeO_x) = 0.40$	Total solids [wt%]	10.6	4.9

Another common consequence of processing a wide portfolio of lead-bearing raw materials at Glencore Nordenham is the variability of the zinc content in slag. Zinc in slag promotes the formation of zinc compounds/endmembers in the melilite and spinel solid phases present in lead slags such as hardystonite in melilite ($Ca_2ZnSi_2O_7$) or zinc ferrite in spinel ($ZnFe_2O_4$). Therefore, an increase in the solid phase proportion in the slag can be expected if the zinc content increases. This can be seen in the phase diagram plotted using FactSage and the UQPY database and shown in Figure 8. Here, the liquid slag phase field is plotted for different zinc content values in the slag after SBF charging. When the zinc content in the slag increases, the liquid slag phase field moves away from the slag composition range in the diagram.

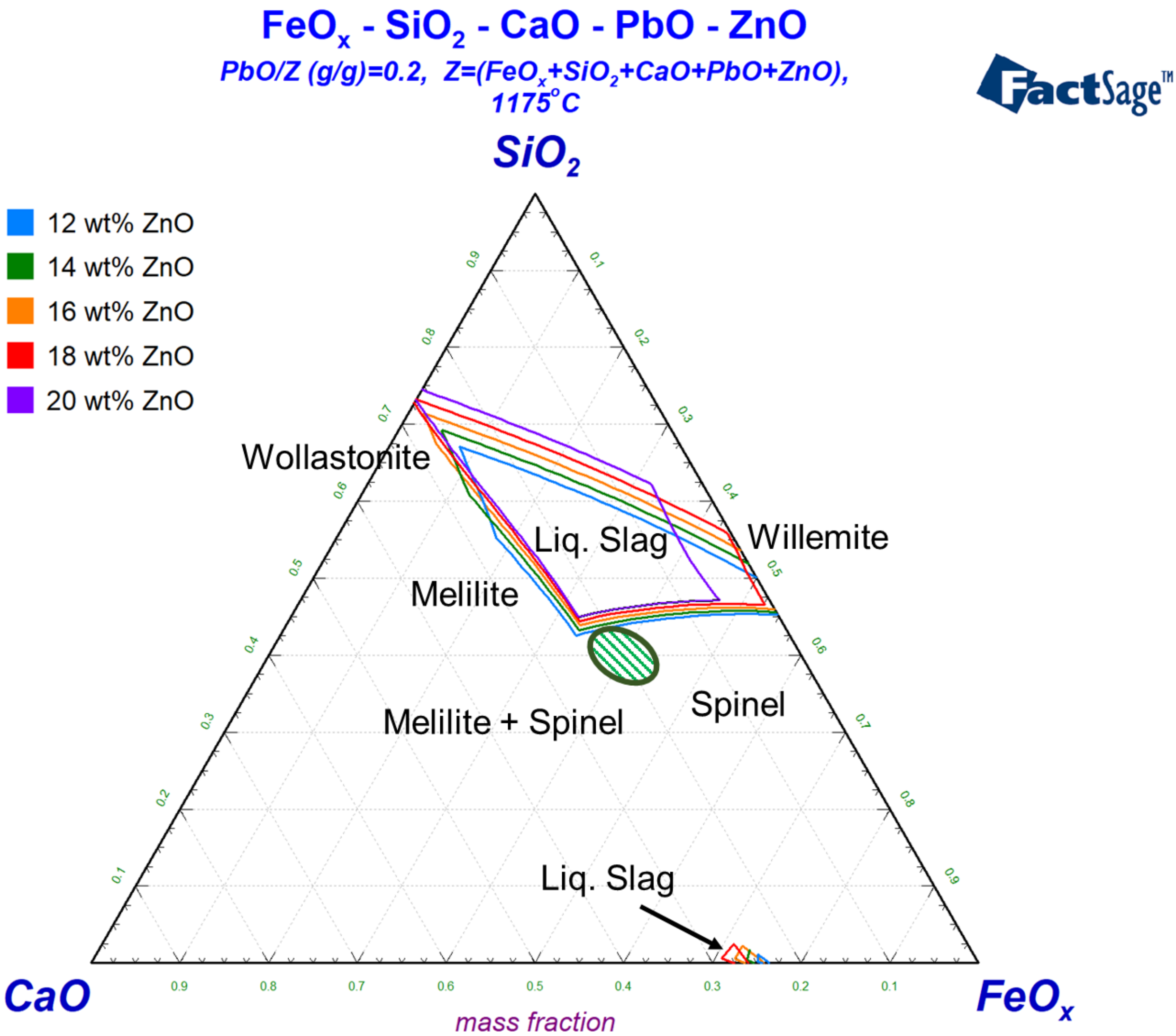


Figure 8. Phase diagram for the starting SBF slag composition after slag charging showing the liquid slag area for different ZnO contents and the slag composition range (striped green area). A lead content of 19 wt% and a temperature of 1175 °C are set as constant values for phase diagram calculations. The pO2 is calculated and set for a slag in equilibrium with metallic lead.

The proportion of solids can also be estimated for the different zinc content values in the slag using FactSage and the UQPY database. The results of the FactSage simulations are shown in Table 3. The solid phase formed for the selected slag composition would be spinel for all the simulated ZnO content values. The solid phase proportions would increase from 6.4 wt% in a slag containing 12 wt% of ZnO to 9.1 wt% for a ZnO value of 20 wt%. Therefore, a more viscous slag may be expected after SBF slag charging, and the operations department can advise the operators how to operate the furnace under the specific batch conditions.

Table 3. Solid phase proportions in bulk slag calculated with FactSage and the UQPY database for different ZnO contents. Values in wt%.

Solid phase proportions [wt%]	**12 wt% ZnO**	**14 wt% ZnO**	**16 wt% ZnO**	**18 wt% ZnO**	**20 wt% ZnO**
$SiO_2/(SiO_2 + CaO + FeO_x) = 0.40$ $CaO/(SiO_2 + CaO + FeO_x) = 0.19$ $FeO_x/(SiO_2 + CaO + FeO_x) = 0.41$	6.4	7.1	7.8	8.5	9.1

CONCLUSIONS

Glencore Nordenham is transforming into a modern polymetallic smelter with high raw material flexibility. This is enabled by the integration of the lead and zinc smelters and their modern and innovative technology. The commissioning of the side-blown furnace (SBF) in 2018 for the reduction of lead-rich slags enabled the recovery of elements such as Ag, Au, Bi, Cu, Sb, Sn and Te and the treatment of more complex raw materials. Till the end of 2023, the SBF has treated around 600 000 tons of lead-rich slag, has increased the overall secondary materials in feed to up to 80% and has enabled the treatment of more than 50 different raw materials.

The transformation of Glencore Nordenham into a flexible smelter requires metallurgical knowledge of slags containing FeO_x, SiO_2, CaO, PbO and ZnO. Nowadays, there is chemical thermodynamics software such as FactSage containing comprehensive thermochemical databases for pyrometallurgical processes such as the one developed by the Pyrometallurgy Innovation Centre at the University of Queensland (UQPY), Australia. The ability of this software of representing the thermochemical processes occurring in industrial furnaces helps understand their slag systems, predict how variations in the operating conditions affect them and optimize the operating parameters. Two real examples on the application of this approach at Glencore Nordenham have been explained, showing how the knowledge on fundamental slag chemistry is applied to industrial operations. This way, the operations teams have more information on the furnace to act faster and with confidence, creating a safe working environment. These quick decisions taken confidently are essential for the optimal and safe furnace operation in flexible smelters like Glencore Nordenham.

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