Fusion of Molten Phase R&D into the Metallurgical Industry to Drive Circularity.

S. Nikolic[1]*, A. Burrows*[2]*, S.L. Nicol*[3]*, O.J. Mendoza*[4] *and B.J. Hogg*[5]

1. Manager - Technology, Glencore Technology, Brisbane, QLD, 4000. Email: stanko.nikolic@glencore.com.au
2. Project Lead – Smelters, Glencore, Baar, 6340, Switzerland Email: alistair.burrows@glencore.com
3. Senior Metallurgist, Glencore Technology, Brisbane, QLD, 4000. Email: stuart.nicol1@glencore.com.au
4. Senior Metallurgist, Glencore Technology, Brisbane, QLD, 4000. Email: oscar.mendoza@glencore.com.au
5. Principal Metallurgist, Glencore Technology, Brisbane, QLD, 4000. Email: ben.hogg@glencore.com.au

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ABSTRACT

The Top Submerged Lance (TSL) technology, developed in the 1970s, is now widely used for the processing of a range of materials. The key advantage the ISASMELT™ TSL technology provided was the ability to process feed materials in a highly turbulent bath, reaching close to equilibrium conditions, uniquely allowing for operation below the liquidus of the molten slag phase. The details on what happened below the liquidus line in the phase diagram became critical for the successful operation of the technology. During the development of the ISASMELT™ technology this led to a collaboration between the Process Technology group of Mount Isa Mines, now part of Glencore Technology, and the Pyrometallurgy Research Centre (PYROSEARCH) at The University of Queensland. The fusion of the phase equilibria research into the technology development allowed for understanding of the behaviour of molten splash, reliable tapping of the furnace, and the ability to operate the furnace with a refractory lining and achieve a year campaign life in excess of four years. The outcome has allowed for the highly successful adaption of the ISASMELT™ technology to recycling of complex feed streams necessary to drive circularity in our modern global economy.

INTRODUCTION

The development of the top submerged lance (TSL) technology began in the 1970's and started with investigations on how to improve tin smelting processes. This work led to the development of the SiroSmelt lance, which through collaboration between the Commonwealth Scientific Industrial Research Organisation (CSIRO) and Mount Isa Mines, now part of Glencore, by the 1990s had expanded the TSL technology, ISASMELT™, to industrial implementations in both primary concentrate smelting and secondary recycling targeting the processing of the carrier metals copper, nickel, zinc and lead (Burford 2009; Hogg, Nikolic and Voigt, 2018).

The ability of the ISASMELT™ technology to process a wide variety of feeds in the same furnace arrangement is because it is a turbulent molten slag reaction process. The slag phase itself is both continuously produced and continually provided with fresh oxidant or reductant, depending on the process reactions taking place, by the feed materials and the inlet air/oxygen/reductant being added down the centrally positioned lance. Unlike other high temperature processes, which either over or under oxidise the feed through a burner or pass the oxygen through a matte/metal layer, necessitating thermal control, slag phase reaction allows for near thermal and chemical equilibrium to be achieved. Proper understanding of the operation of the furnace requires detailed knowledge of the phase equilibria of the molten phases and their interactions.

Information present in the literature during the development of the technology was either focused on binary/ternary systems or analysis of the behaviour of complex phases taken from furnace rebuilds. The understanding of the fundamental compositional and physical properties of the molten slag in the multi-component systems, such as phase equilibria and viscosity, was missing from the earlier research and it would be vital for the process implementation, optimization and control of the ISASMELT™ technology. This led to a collaborative effort beginning in the late 1990's between the Process Technology group of Mount Isa Mines, now part of Glencore, and the Pyrometallurgy Research Centre (PYROSEARCH) at The University of Queensland for the purpose of investigating the fundamental phase equilibria of multi-component systems with their rapid quenching electron probe x-ray microanalysis technique (Jak, Hayes and Lee, 1995; Jak and Hayes, 2004 and Ilyushechkin, Hayes and Jak 2004).

UNDERSTANDING SLAG CHEMISTRY FOR REFRACTORY FREEZE LININGS

The main concerns in the early development of the Lead ISASMELT™ process were to minimise dust production from the vaporisation of the lead sulphide in the feed during the smelting step. This led to a minimisation of the operating temperature as this has a direct correlation with the fuming rate. A surprising observation on the demonstration plant scale, later confirmed on the commercial scale, was that there was effectively no refractory wear in the walls of the smelting vessel.

Samples taken from the operating furnace by PYROSEARCH staff as a part of an industry-sponsored research program in the mid-1990s shed light on this mystery. The samples showed that at typical smelting temperatures the ISASMELT™ slag in the lead smelter at Mount Isa Mines Ltd.

was not a homogenous liquid. As shown in Figure *1*, slags obtained by careful sampling, followed by rapid quenching, contained a mix of reaction products in both solid and liquid states as a result of the smelting process.

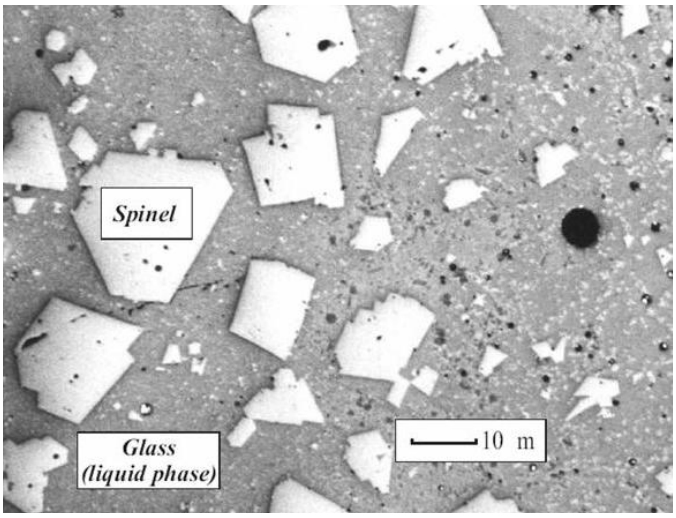


Figure 1 - Photomicrograph of slag from the lead ISASMELT™ process (Jak, Liu, Lee and Hayes, 1994). Many euhedral spinel particles, up to a particle size of 10 µm, are suspended inside a liquid.

The lead ISASMELT™ furnace at that time operated, as those still operating do today, below the slag liquidus temperature. Tiny particles of solids, in addition to floating in the bath of high-density slag, gradually accumulate on solid surfaces inside the furnace that are exposed to splashed slag. The liquid part of the slag drains off quickly, leaving behind a few solid particles each time, developing a spinel coating that provides protection for the furnace side wall refractory from upset over temperature conditions that may occur. A view inside a nicely spinel coated ISASMELT™ furnace is shown in Figure *2*.

Figure 2 - Lead ISASMELT™ Furnace side wall bricks, exposed mid-campaign, showing widespread spinel coating (Hogg *et al.* 2018)

It was later shown that the proportion of spinel present in the lead smelting slag in air for a given bulk composition and temperature could be deduced from the experimentally determined equilibria presented on pseudo-ternary sections Fe_2O_3-ZnO - (PbO+CaO+SiO_2) for given CaO/SiO_2 and PbO/(CaO+ SiO_2) ratios (Jak and Hayes, 2002).

Copper ISASMELT™ Furnace Lining Development

When considering the copper ISASMELT™ furnace technology in Mount Isa it was initially justified on a two (2) year campaign length. However, this target was not achieved for the first 6 campaigns from 1992 to 1998, refer to Figure *3*, with most campaigns lasting between 45-65 weeks. A review was completed on implementing some form of copper cooling - either of the bricks, interwoven with the bricks, or direct freeze lining of the slag bath. However, experience from operation of the lead ISASMELT™ process and the demonstration plant for the copper ISASMELT™ process indicated that a ninety (90) week refractory campaign life was achievable (Burford, 2009).

Although similar levels of solids, as seen in lead smelting, were not possible to be maintained in the copper process it led to a renewed focus on maximising the campaign life through temperature management and understanding of the slag phase equilibria to produce spinel crystal structures. Based on this daily review, plant operating set points were adjusted, and the result was an extension to the campaign length for a record 105 weeks. Management of the ISASMELT™ plant has continued to improve with a four (4) year campaign life becoming the new standard for operation, refer to Figure *3*.

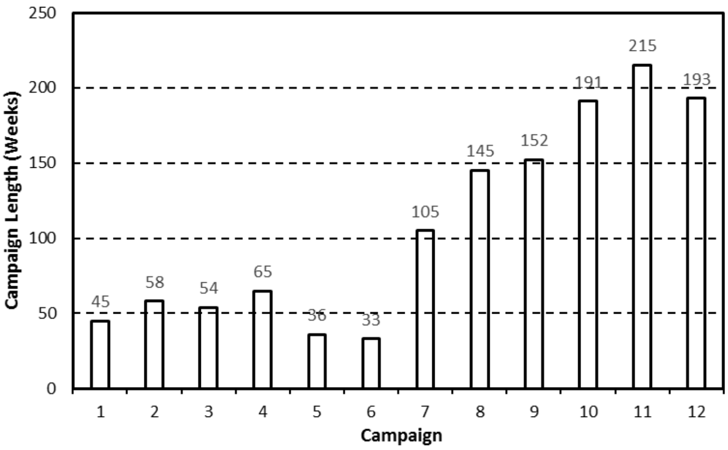


Figure 3 – Mount Isa copper smelting ISASMELT™ campaign life.

Once the correct metallurgical recipe and operating temperature regime has been obtained, side wall brick-wear can be minimised in the Copper ISASMELT™ process. This has been proven time and again at ISASMELT™ furnaces around the world as is evident when operating temperatures are elevated, as shown on the left portion of Figure *4*. Against when the furnace temperature control is optimized, to below the liquidus, as shown on the right side of Figure *4*. The ISASMELT™ refractory wear can be minimized to a point where it is almost non-existent. This is possible, and highly repeatable, with the ISASMELT™ process due to the reaction zone location and the combination of the knowledge provided by the phase equilibria research with the process control incorporated within the technology.

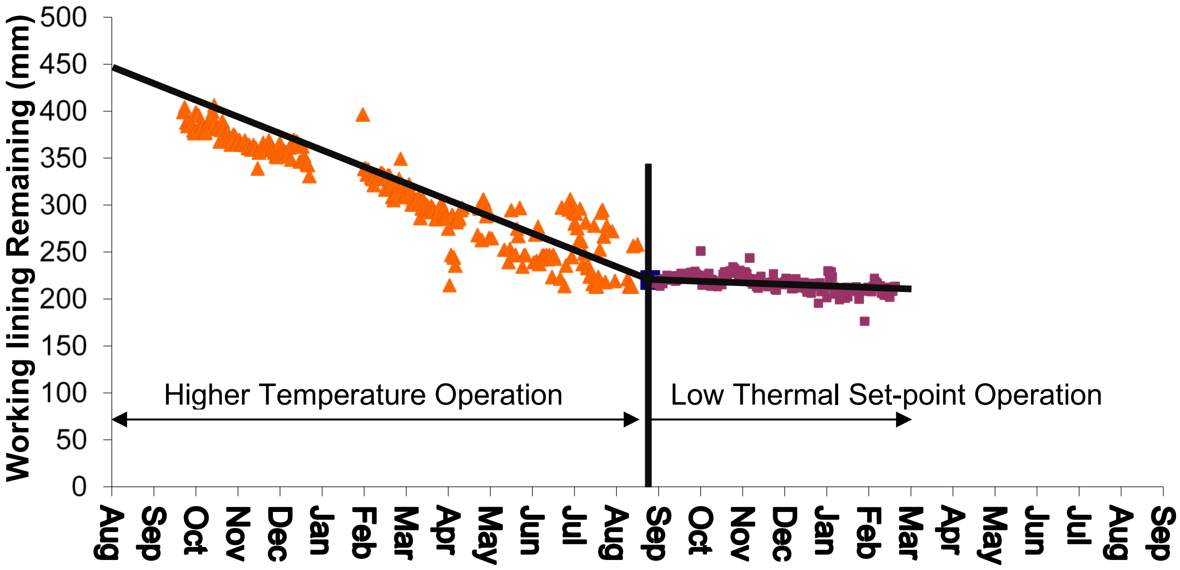


Figure 4 - ISASMELT™ brick wear trend showing high temperature operation and optimal temperature operation.

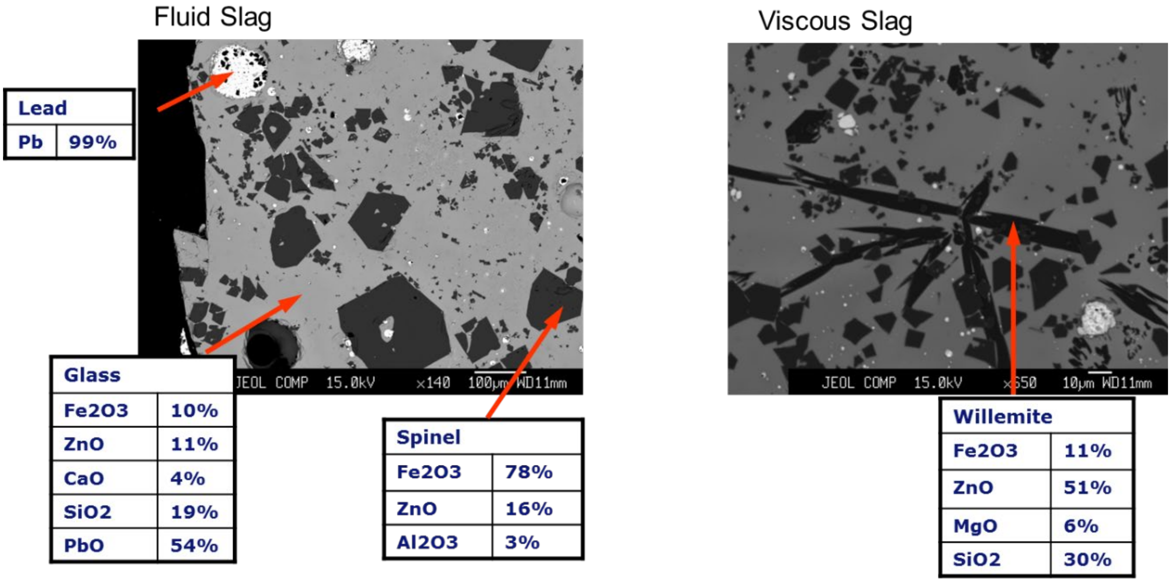
PHASE EQUILIBRIA AND TAPPING IN THE ISASMELT™ PROCESS

The lead ISASMELT™ process has been implemented in Australia, China, and Kazakhstan. The closely related ISASMELT™ process for recycling lead-acid batteries was developed in the late 1980s and has additionally been operated in England and Malaysia (Burford, 2009). In each case lead-rich feeds are smelted and slags are created that are rich in lead oxide. Removal of the slag through a tap hole in the wall of the furnace has been the subject of numerous efforts of design, improvement, re-design, and modification.

Operating the furnace with the aim to minimise lead fuming and maximise refractory life presented a challenge with the tapping of essentially a liquid molten slurry from the furnace. This came into focus during the period when the industrial-scale lead ISASMELT™ furnace in Mount Isa was being commissioned. The taphole in the oxidation furnace was to be operated as an overflow taphole, with a minimum head of liquid slag inside the oxidation furnace. Challenges with process constraints (unrelated to tapping) determined that continuously feeding the furnace and tapping the slag batchwise was a more appropriate option.

Tapping sub-liquidus slag was next tried in China when the Isa-YMG process was commissioned in Qujing (Errington, Arthur, Wang and Dong, 2005). Although the production capacity of Chihong Zinc & Germanium Company's smelter in China was intended to be greater than that at Mount Isa Mines, there was a comparatively reduced amount of lead-rich slag owing to the high grade of concentrate being smelted and the production of some lead bullion inside the ISASMELT™ furnace.

There was also a tendency for the slag at Qujing to change from 'tappable' to 'untappable' throughout the day, with little apparent change in temperature or bulk composition. This phenomenon was investigated further with the PYROSEARCH Centre through a sponsored research program. This work identified that at the microscopic level fluid slags, refer to Figure 5, tended to look very similar to those at Mount Isa a decade earlier: a slurry of spinel particles suspended in a lead oxide-rich liquid. But the viscous slags looked different. There were some additional particles with the approximate composition of willemite. The crystals of willemite tended to appear as acicular needles, which were very different from the shape of spinels.



Lead	
Pb	99%

Glass	
Fe2O3	10%
ZnO	11%
CaO	4%
SiO2	19%
PbO	54%

Spinel	
Fe2O3	78%
ZnO	16%
Al2O3	3%

Willemite	
Fe2O3	11%
ZnO	51%
MgO	6%
SiO2	30%

Figure 5 - Photomicrographs of slags, tapped at sub-liquidus temperatures, from Qujing lead ISASMELT™ furnace (Zhao *et al, 2005*).

The absence of acicular crystals was found to be a prerequisite for achieving a reliable slag flow. It was already known that the presence and crystal-shape of the suspended solid particles in a sub-liquidus lead oxide-rich slag could vary with slag composition. Zhao *et al*. (2005) reported this observation with respect to melilite particles. Accumulated knowledge about sub-liquidus crystal types now seemed to be knowhow that was transportable to the more practical application of understanding whether a slag would exhibit good tapping behaviour at sub-liquidus temperatures.

The Campforts Diagram

To be able to adapt this knowledge, so that it was understandable and relatable to the industrial process, a new approach had to be undertaken. Separate research being done in collaborations that PYROSEARCH completed with other universities and industry partners offered a new approach. In a series of published papers (Campforts *et al*, 2007; Campforts *et al*, 2008 and Campforts, Blanpain and Wollants, 2009) the authors calculated the proportion of phases present at various temperatures using the FactSage™ package and associated database (Jak et al. 1997, 1998; Bale, Pelton and Thompson, 2007). The proportion of solids was graphically presented as pseudo-unary phase diagrams, as shown in Figure 6. With a variation in the slag bulk composition, the nature and proportion of solids changes, with a unique pseudo-unary diagram for each slag composition and oxygen partial pressure. It was a useful method to explain the topic of freeze lining formation. By chance, it is also a useful method to explain the chemistry of sub-liquidus slags. In the interests of brevity, and because these cited papers are the first in which the authors saw this type of diagram, it is referred to hereafter as the 'Campforts Diagram'.

For two different slags rich in lead oxide, Campforts predicted different proportions of stable condensed oxide phases at each temperature (Campforts, Blanpain and Wollants, 2009). Compositions of slags M1 and S1 are shown below.

Table 1 - Compositions used in analysis of the Campforts diagram (Campforts, Blanpain and Wollants, 2009)

Slag	CaO	SiO_2	PbO	ZnO	Fe_2O_3	Al_2O_3
M1	10.57	13.81	45.79	3.28	20.28	6.27
S1	3.70	9.56	55.80	4.44	21.35	4.90

For both of these slags it was predicted that only about 90 % of the mass of condensed oxides is going to be in liquid form at the temperature of 1150°C. However, it was also predicted that there were significant differences in the solid phases present. Referring to Figure 6, it is clear that for slag M1 at 1150°C the solids are predicted to be mostly melilites, whereas for slag S1 at the same temperature those solids will be exclusively spinels.

In the experiments performed by Campforts (2009) and under the conditions investigated, melilite was observed to form acicular crystals that were able to be interlocked, while spinel was observed as individual and isolated crystals. This ability for spinel crystals to form individual phases whilst crystals involving silica formed interlocking structures was consistent with that observed by other researchers in other slag systems (Hidayat, Henao, Hayes and Jak, 2012). From experience with sub-liquidus slag tapping, and informed by the Campforts diagrams of these two slags, it is possible to predict that slag M1 will need to be tapped at a temperature of about 1200°C, but it would be possible to tap slag S1 at a temperature of 1100°C. Note that this is completely the opposite of the conclusions that would be drawn if the liquidus temperature alone were considered. i.e. Slag S1 has a higher liquidus temperature than slag M1, but it is possible to tap slag S1 at a lower temperature.

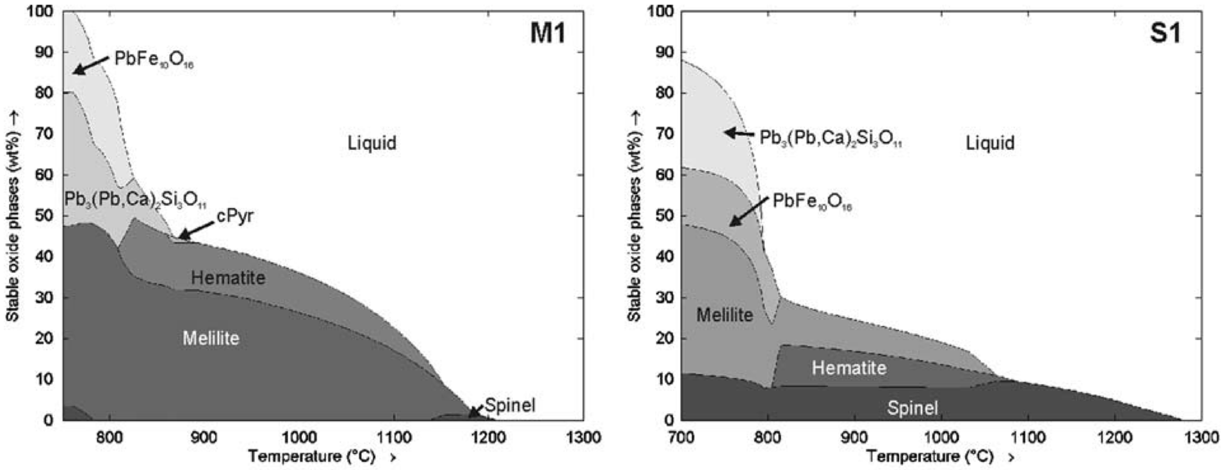


Figure 6 - Campforts diagrams for two different slags (denoted M1 and S1) (Campforts, Blanpain and Wollants, 2009).

MOLTEN PHASE RESEARCH DRIVING THE CIRCULAR ECONOMY AND RECYCLING

At the end-of-life of a given component, product or material, implementation into circularity involves a large number of steps - from the initial collection stage and preliminary sorting, which generally involves some degree of physical upgrading and separation, through to the final processing stages to produce pure renewed starting materials or byproducts. In the case of complex intermediate streams, which cannot be separated or reused directly in the circular economy, recycling of the contained metal values is required. All steps in this process are important, but due to the energy intensity and requirement for extractive processing, the near-final recycling processing step producing a payable metal product, is the step that is ultimately the key to achieving sustainability.

The application of ISASMELT™ for the treatment/recycling of complex feed streams was implemented in Europe at the Umicore Precious Metals Refining Hoboken Plant in Belgium and the Aurubis AG Lünen plant in Germany in the 1990s (Vanbellen and Chintinne, 2006; Ayhan, 2001). Umicore focused on the processing of complex lead/copper materials, containing valuable minor elements in a two-step smelting and converting ISASMELT™ process, shown in Figure *7*. The Aurubis Lünen plant focused on treating copper secondary and recycling materials in a process that can involve a number of steps in a single ISASMELT™ reactor - such as smelting, reduction and converting to maximise the recovery of the targeted elements to the gas phase, slag phase or copper phase in each stage of the batch process. This is shown in Figure *8*.

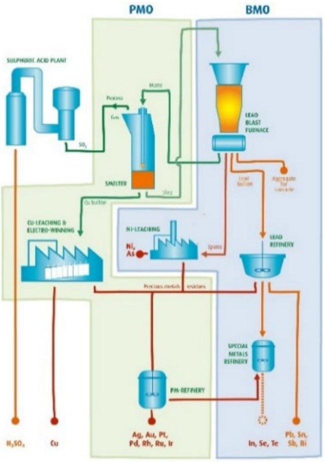


Figure 7 - ISASMELT™ Furnace in the Umicore, Hoboken Plant Operations Flowsheet (Vanbellen and Chintinne, 2006)

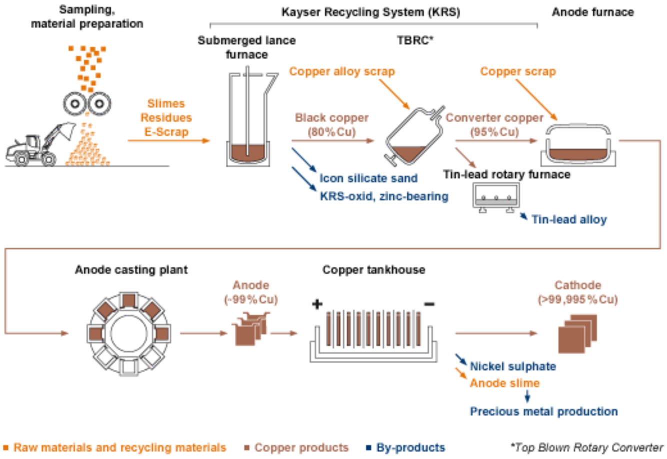


Figure 8 - ISASMELT™ Furnace in the KRS Flowsheet at Aurubis Lünen, Germany (Aurubis, 2011)

The core of the application of the ISASMELT™ within both flowsheets was the ability of the technology to maintain a turbulent slag bath that allows for rapid integration of all feed materials to their molten metal equivalents. Both sites used this to their advantage as once in the molten phase base metals can then be used as the collectors for the contained value, predominately the precious and platinum group metals present in the feed. Recovery of these, as well as the base metals, can only be optimised through the selective oxidation possible with a batch ISASMELT™ process. Thermodynamic calculation packages can be used to simulate these requirements. For example, under appropriate oxygen and sulphur potentials conditions (oxidative smelting) lead can be selectively oxidised and transferred to the slag as copper remains in a sulphide/metallic phase as oxidation progresses.

To be able to take advantage of the ability of the ISASMELT™ to operate across the oxidative range a more robust thermodynamic calculation process was required than what was offered by generic databases and software. As illustrated in the previous examples maintaining a spinel crystal presence in the ISASMELT™ melt is critical to the longevity of an operation. The work of the PYROSEARCH Centre to increase the available information used in thermodynamic packages has been critical to the ability to calculate the multi-component phase equilibria in these types of systems. To illustrate this a set of ternary diagrams, produced by FactSage™ (Bale, Pelton and Thompson, 2007) and using databases developed from the outcomes of work at PYROSEARCH, calculating the impact of oxygen partial pressure, representing operational conditions from reductive smelting to converting at a fixed alumina content in a typical fayalite slag at 1200 and 1300°C is shown in Figure *9*.

Within a batch process, typically in the first step the furnace is run in pseudo-continuous operating conditions whilst one of the molten phases is built up in the vessel. During this period the operational targets of slag fluxing and operating temperature of the furnace would be conducive to building a protective spinel lining. This would represent the base condition and, for example, would be operating at 1200ºC with a low oxygen partial pressure of 10^{-10} atm and a SiO_2/Fe ratio in the slag of 0.7, when considering the lime concentration. During the subsequent step in the batch cycle a more oxidative oxygen partial pressure would normally be practiced. When considering the impact of oxygen potential on the proportion of solids in the melt at 1200°C this would reach unacceptable levels if the slag operating temperature and fluxing are not managed. Using the information in the calculations it is possible to calculate the necessary increase in temperature against the oxygen potential of the bath to maintain the proportion of solids in the melt required to maintain the integrity of the furnace.

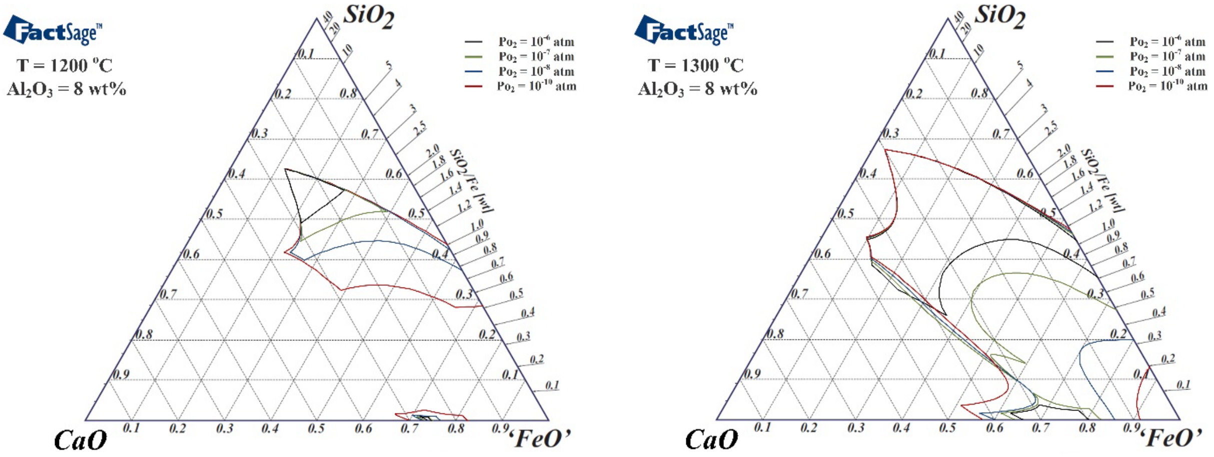


Figure 9 – FactSage calculations for the effect of oxygen partial pressure on slag liquidus on alumina containing fayalite slag at 1200°C and 1300°C.

Although these changes can be predicted it should be noted that slag liquidus alone is not sufficient in this regard. Operating regions need to be selected that allow for the most sustainable outcome. One where appropriate levels of metals are recovered, whilst the versatility and usability of the waste materials from the process is maximised by allowing them to be used as feed materials for other industries.

CONCLUSIONS

ISASMELT™ technology's vertical submerged lance injection, with a resulting highly turbulent bath, allows for a different approach to be taken for the design and implementation of a furnace system. To be able to take full advantage of this the understanding of the fundamental compositional and physical properties of the molten slag in the multi-component systems was required to be applied to the technology process development. Through the collaborative efforts, beginning in the late 1990's, between Glencore Technology and PYROSEARCH, this allowed for the understanding of the behaviour of freeze linings on refractories through molten splash, reliable tapping of the furnace and the adaptation of the technology to recycling of complex feed streams.

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