ISASMELT™ SLAG CHEMISTRY AND COPPER LOSSES IN THE ROTARY HOLDING FURNACES SLAG AT ILO SMELTER

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ABSTRACT

Ilo Smelter has been operating since February 2007 with a copper ISASMELT™ furnace as a single smelting unit (1,200,000 tpy), associated with two Rotary Holding Furnaces (RHF). Due to the liquid bath agitation, matte and slag (fayalite) do not separate in the ISASMELT™ vessel but instead are tapped out together into the RHF, where separation and removal of matte and slag occurs.

The RHF provides surge capacity between the continuous ISASMELT™ furnace and the batch Peirce Smith Converters, as well as to settle matte globules from ISASMELT™ slag to produce a discard quality slag (expected to be less than 0.8 wt% Cu). In this way the RHF slag mass and its copper content has a big influence in the copper recovery of the new Ilo Smelter.

This paper discusses the operational issues and the actions that have been implemented in order to obtain a discard RHF slag. One of them is the change of the slag chemistry at the ISASMELT™ Furnace.
INTRODUCTION

In response to environmental concerns, the Ilo Smelter has been operating since February 2007 with an ISASMELT™ furnace as a single primary smelting unit, which is associated with two Rotary Holding Furnaces (RHF). Figure 1 shows the new smelter flow diagram.

The ISASMELT™ technology is a bath-smelting process in a vertical refractory-lined vessel in which a specially designed submerged-combustion lance is inserted into the bath of molten material. The furnace is fed continuously with copper concentrates and fluxes; oxygen-enriched air is injected into the bath through the lance, creating very intense bath agitation and a rapid reaction rate.

The bath principally consists of molten iron-silicate slag and molten copper matte. Due to the agitated state of the bath, the matte and slag are periodically tapped out together through a single taphole to either of two RHF via water cooled copper launders. The RHF are required to provide a phase separation, allowing clean slag and matte to be poured separately.

The RHF is not a smelting vessel because it is not designed to conduct any chemical reactions, any un-smelted particles may, however, react in the RHF with slag phase. RHF also provide surge capacity between the continuous operation of the ISASMELT™ furnace and the batch Peirce Smith Converters (PSC) cycles.

The Rotary Holding Furnaces are steel-shelled brick lined vessels, 15.3 meters long by 4.7 meters in diameter. The temperature of the RHF is maintained by burners located in the roof and end wall of each furnace. An oxygen-fuel (No. 6 fuel oil) end wall burner, opposite the feed end, delivers the bulk of the energy required.

Each furnace is rotated by a hydraulic drive linked to the furnace by a chain. By rotating the furnace one way or the other, the operator can either pour the slag into the hauler pot or pour matte into a pot in the aisle. The maximum rate of slag skimming is controlled to minimize the copper content of the slag. When matte is tapped, the slag carryover is minimized by using a small spout and rotating quickly through the slag layer.

Pig iron is added periodically to each RHF through two addition ports on the roof near the center of the furnace to control the bottom build up.
ISASMELT™ FURNACE PROCESS CONTROL

In the ISASMELT™ smelting process, the main control variables are: $\text{SiO}_2/\text{Fe}$ and $\text{SiO}_2/\text{CaO}$ ratios in slag, matte grade and bath temperature, and were fixed by practical experience and considerations of productivity, brick wear and slag loss, by this way:

Matte Grade

The target (61 - 62% Cu) was fixed in order to ensure that the PS Converters can treat all the matte produced by the ISASMELT™ furnace. Matte grade is controlled adjusting oxygen addition that enters by the lance, considering matte sample assays.

$\text{SiO}_2/\text{Fe}$ and $\text{SiO}_2/\text{CaO}$ Ratios in Slag

The $\text{SiO}_2/\text{Fe}$ ratio should be maintained at 0.80 – 0.82, in order to help the slag - matte phase's separation and obtain a proper slag mass and slag viscosity. By the other hand sea shell is added in the feed to further drop the melting point of slag, the $\text{SiO}_2/\text{CaO}$ ratio is set around 7.5. These ratios are controlled adjusting the silica and sea shell fluxes additions, considering RHF slag samples assays.

In order to get a proper feed back, the RHF slag and the ISASMELT™ matte samples are processed promptly by the on site x-ray facilities. The chemical assays are provided to the control room operator in less than 25 minutes.

Magnetite Content in Slag

The magnetite content in the slag which will be produced at equilibrium with the operating parameters above defined, was calculated by around 8 – 10%, applying a thermodynamic model of iterative calculation [1]. The magnetite content of the ISASMELT™ slag agrees with this theoretical range.

When slag is cooled, magnetite precipitates out, and this is the magnetite content which is measured in the slag samples with a Satmagan instrument, but these magnetite analyses using cooled solid samples has the problem that the amount of precipitated magnetite crystals varies with the cooling rate of the melt. The slower cooling rate of the sample the more magnetite content is measured, and this cooling rate depends on the slag sampling method.

Figure 2 shows a photograph of slag sampling methods in the ISASMELT™ furnace and RHF. The ISASMELT™ slag samples were taken in a spoon during tapping, while the RHF slags were taken by a paddle when the slag was skimmed off. All samples were cooled at room temperature. By this reason the ISASMELT™ slag samples have a lower cooling rate and this would explain the higher magnetite contents reported in comparison with the RHF slag.

![Figure 2: Slag sampling in ISASMELT™ furnace (tapping launder) and RHF (skim spout)](image)
In order to control the copper loss, the magnetite content target in the RHF slag should be less than 7%, according the sampling method above mentioned. By this reason coal is added to the ISASMELT™ bath in order to control the magnetite content in the slag, and by other hand it would be possible that coal remainder enter to the RHF, which also would explain the less magnetite content in the RHF slag.

**Bath Temperature**

Bath temperature was set between 1175°C and 1195°C in order to get a good slag viscosity and have a proper control of the magnetite activity. At the same time this target leads to have an appropriate thickness of the magnetite coating to protect the bricks.

The bath temperature is measured on line, and it is automatically controlled adjusting mainly the oxygen enrichment of the process air. The bath temperature is periodically checked using the dip tip (disposable thermocouples) in the launder during tapping.

**ISASMELT™ SLAG CHEMISTRY MODIFICATION**

It was established previously the amount of silica in the slag in terms of the silica to iron ratio (SiO$_2$/Fe). At silica to iron ratio of less than 0.77, the magnetite levels get very high. At the opposite extreme, if the silica to iron ratio is more than 0.95, the magnetite level in the slag gets so low that it becomes difficult for the smelting.

The design specification for silica to iron ratio was 0.88, but at this slag composition coarse particles of undissolved silica were regularly observed leaving the ISASMELT™ furnace.

SPCC and Xstrata Technology jointly evaluate modification to the ISASMELT™ slag chemistry in order to improve the ISASMELT™/RHF performance.

In order to reduce the amount of slag generated in the ISASMELT™ furnace, as well as the amount of un-dissolved silica in the RHF slag, the ISASMELT™ furnace target SiO$_2$/Fe was reduced from 0.88 to 0.82, while keeping the SiO$_2$/CaO ratio at the design value of 7.0, and the bath temperature at 1180°C.

**RESULTS**

- The amount of slag was reduced by ~6%, approximately 0.61 metric tons of clean slag is produced per ton of dry and un-fluxed concentrate fed to the ISASMELT™. It is well known that the copper content depends of residence time in the RHF and it is benefit with a less amount of slag.

- The copper content of slag sampled from the RHF slag spout was kept around 0.83 ± 0.4 %.

- The magnetite content in the RHF slag was increased when the silica to iron ratio was reduced, Figure 3 illustrates these results. It was necessary to increase the coal addition in the ISASMELT™ furnace in order to keep a magnetite content below 7.0% in the RHF slag.

- Undissolved silica was not observed in the RHF’s bath, although this condition depends on the type and size of the silica flux too.
Also the matte grade of the ISASMELT™ furnace was increased in order to reach the target and therefore to increase the copper production of the converters. It was noted an increasing of the magnetite content in the RHF slag as shown in the Figure 4.

**ISASMELT™ Bath Temperature and Fluxing Strategy**

A modelling of Al₂O₃-CaO-FeO-SiO₂ liquidus using Factsage was conducted by PYROSEARCH and Xstrata Technology in order to predict the slag liquidus temperature in the Al₂O₃-CaO-FeO-SiO₂ system at oxygen partial pressure of 10⁻⁸.4 atm and at fixed Al₂O₃ of 6 wt % with focus on the range of SiO₂ concentrations from 30 to 50 wt%. The results are shown in Figure 5. All iron oxide is recalculate to FeO for presentation purposes, the compositions in this figure are represented using weight ratios of CaO/(CaO+FeO+SiO₂), FeO/(CaO+FeO+SiO₂) and SiO₂/(CaO+FeO+SiO₂). The CaO/SiO₂ and SiO₂/Fe are also shown for convenience.
Figure 5: Liquidus in the system Al₂O₃-CaO-FeO-SiO₂ at P₀₂ = 10⁻⁸.₄ atm and Al₂O₃ = 6 wt %

Using the diagram showed in the Figure 5, the liquidus temperature of the design chemistry slag composition (SiO₂/Fe = 0.88 and SiO₂/CaO = 7.0) was predicted to be around 1195°C (black circle), with a target matte grade of 62%. If the SiO₂/Fe is reduced to 0.82 the liquidus temperature tends to increase, therefore it is necessary to raise the ratio SiO₂/CaO from 7.0 to 7.5 in order to keep the liquidus temperature close to 1195°C (red circle).

ISASMELT™ furnace bath temperature was progressively increased until 1190°C in order to get a better slag viscosity. At the same time the brick wear rate was carefully recorded. Despite higher operating temperature, the brick wear rate did not increase. This can be attributed to the good process control of the ISASMELT™ furnace.

**RHF SLAG COPPER CONTENT**

By design the copper content of the ISASMELT™ slag will be expected to be less than 0.8 wt% Cu, sufficiently low to be discarded without further treatment. The copper content of the RHF slag (average 0.83 ±0.4 % Cu in the year) was higher than the target (0.8% Cu).

A study of SPCC ISASMELT™ slag phase equilibria was performed by PYROSEARCH for Xstrata Technology, Australia. Granulated SPCC ISASMELT™ slag sample was analyzed using optical and scanning electron microscopy, and compositions of phases were accurately measured with electron probe X-ray microanalyser (EPMA). The main findings are:
Main phases in the sample are glass (liquid slag), iron oxide (most likely spinel), matte globules and some metallic Cu, the latter precipitated from matte during granulation.

- Iron oxide (most likely spinel) was present in the slag before granulation.
- Slag has ~0.3 wt% Cu₂O compared to the bulk ~2.0 wt% (recalculated to Cu₂O and normalized to 100%) – the difference is due to the Cu trapped in matte globules.

The presence of Cu in the slag (physically entrained matte due to high viscosity) is linked to the presence of magnetite. Figure 7 shows a direct correlation between the copper and magnetite contents in the RHFs slag.

When the magnetite content of the RHF slag was less than 7%, it was normal for RHF slag to contain few copper (average 0.7%). When the magnetite content of the slag exceeds 7% the copper content of the slag is variable. The average was 1.1% Cu, but the distribution was broad. These results are illustrated in Figure 8.
Possible causes of high Fe₃O₄ content in the RHF include:

- Periods of high matte grade (exceeding 63% Cu)
- Low bath temperature in the ISASMELT™ furnace when re-melting WHB accretions
- Low effective SiO₂/Fe ratio in the slag (excluding the undissolved silica).

For internal control we take samples of the slag deposits, the copper content of the RHF slag dam weekly surveys results are higher than the copper content of routine slag spout samples. The difference between them is due to the matte carryover from the RHF’s to the pot slag during skimming as consequence of high bath matte height in the RHF’s (mainly by lower matte conversion capacity due to a lack of oxygen and lower matte grade, and in some cases by lower converters availability).

**RHF OPERATING PRACTICE**

It was experienced that the copper loss in RHF’s slag is highly dependent of the following operating conditions:

**RHF Matte Bath Height**

The matte bath depth has a big influence in copper loss. Figure 9 shows a photograph of the RHF slag dam where it was noted the matte presence (white spots) as a consequence of high matte inventories in the RHFs.

Taking a dip measurement is essential to the RHFs operators since this gives them the matte and slag levels contained in the vessel. With this information the operators can organize to dispatch matte for converters or adjust ISASMELT™ furnace feed rate to satisfy supply and demand.
Figure 9: Matte presence in the RHF slag dam site

Figure 10 shows, for one RHF, the frequency of the ISASMELT™ tapping, RHF slag pouring, RHF matte pouring, and RHF bath matte height. In order to avoid matte carryover in the slag, the maximum matte + accretion depth has been set at 1.2 meters that is equivalent to ~6 pots of matte available, considering an accretion height of no more than 0.4 meters.

Figure 10: Operating practice in the RHF

ISASMELT™ tapping alternates between tap holes and during each non-tapping period each RHF normally removes one slag pot, however in some periods two slag pots are removed consecutively.

**Residence Time and Pouring Time**

At 165 tph of concentrate feed rate to the ISASMELT™ furnace, the tapping and pouring rates can be controlled to achieve sufficient settling time in order to decrease the matte suspension loss.

Currently SPCC is evaluating to increase the tapping time and hence to reduce the tapping frequency, in order to increase the ISASMELT™ furnace residence time. But it is important to considerate that the number of tapping cycles should not exceed the number of slag pots in order to maintain good operating rhythm.

Another operating practice to reduce the matte entrained in the RHF slag is to have an adequate pouring slag time. By this reason SPCC in coordination with Xstrata has implemented an auto-skim sequence on the RHF drive, with this tool the RHF change position very slowly to keep a constant slag flow until the hauler pot is full.
RHF Temperature
According to ISASMELT™ slag chemistry, the operating temperature of the slag in the RHF was set between 1180 to 1200°C. These temperatures ensure a good slag viscosity and allow the phases to separate and matte globules settle into the matte layer.
In order to save fuel oil in RHF’s, and considering the ISASMELT™ furnace brick’s length, the ISASMELT™ bath temperature was increased from 1180 to 1190°C.

CONCLUSIONS
With the new ISASMELT™ slag chemistry the amount of slag was reduced by ~6% compared to the design. The copper content in the RHF slag (launder samples) was kept around 0.83% (design target 0.80%). Most of the copper in the slag is entrained matte; the remainder is dissolved in the slag.
Copper content of the RHF slag dam was much higher than the RHF slag launder. The difference was due to the matte carryover from the RHFs to the pot slag during slag pouring. With the new furnaces the copper content depends largely on the operating practices. Operating with high matte bath depth has a big influence in the RHF slag copper loss.

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REFERENCES