

# MANAGING SLAG COMPOSITION TO PROTECT PYROMETALLURGICAL VESSEL INTEGRITY

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## **ABSTRACT**

*Vale Inco Limited (formerly Inco Limited) operates a multiplicity of pyrometallurgical reactors throughout the world to process copper-nickel sulfide concentrates and nickel laterite ores. Refractory wear in these vessels is an important maintenance cost component and has an impact on vessel productivity. In the late 1970s an in-depth experimental project was conducted at Inco's J. R. Gordon Research Laboratory that aimed at understanding and solving a severe refractory wear problem which was affecting the operation of then recently commissioned nickel laterite smelting furnaces in Sorowako, Indonesia. This work showed that a fundamental understanding of slag-refractory interactions is essential to achieve substantially increased vessel campaign life.*

## INTRODUCTION

In 1977, Inco Limited (today Vale Inco) commissioned two nickel laterite operations, one in Sorowako, Indonesia and the other one in Lake Izabal, Guatemala. Both ore processing plants used the standard drying-reduction kiln-electric furnace route used by ferronickel producers. However, the product at the two Inco locations was a low-iron nickel matte. To achieve this goal, a controlled amount of sulfur was added to the discharge of the reduction kiln to generate in turn sulfur-deficient nickel-iron matte in the electric furnace. This material was converted to low-iron nickel matte that was granulated and shipped to overseas facilities where it was processed to market products. This pyrometallurgical route is still used in the now much larger Sorowako operation. However, the Guatemalan mine-plant relied 100% on thermally generated electric power and was shut down after only a few years of operation due to the huge increase in the price of oil by the end of the 1970s.

The Indonesian and Guatemalan electric furnaces were initially identical. They were round with a diameter of 18 m (inside the furnace steel shell), and were equipped with three 2 m diameter self-baking electrodes to deliver up to 36 MW to the charge. The lining of the steel shells consisted of 95% MgO brick, 685 mm thick, with a thin layer of heat-conducting carbon-containing paste between the brick and the shell. A thin water film ran down the steel shell to keep it cool. The mode of operation at the two locations was also similar: reduction smelting energy requirements were mainly generated in the slag by resistance heating, and furnace product mattes had approximately the same composition. However, due to differences in ore mineralogy, and consequently in furnace slag composition, the Guatemalan furnace was operated at a higher temperature. Slag skimming temperatures in Guatemala and Indonesia were respectively 1570°C and 1520°C. Despite the significantly lower slag temperature, severe electric furnace refractory wear was experienced in Indonesia while the opposite phenomenon, skull formation on the furnace wall, was observed in Guatemala. A program was initiated at Inco's research laboratory to find the cause of this dramatically different slag-refractory interaction and to provide a solution to the problem of rapid refractory wear in the Indonesian electric furnace. This program focused on differences in ore composition at the two locations.

## NICKEL LATERITE ORES

Nickeliferous laterites are ores that have been generated by prolonged weathering of *ultramafic* rocks containing ferromagnesian silicate minerals. Nickel leaches from the upper layers and subsequently precipitates in the lower layers, substituting NiO for MgO and FeO in the lattice of respectively silicate and iron oxide minerals. The chemistry and mineralogy of these ores vary over a very wide range, particularly with respect to Fe/Ni and SiO<sub>2</sub>/MgO weight ratios and chemical and physical H<sub>2</sub>O contents. Nickel is recovered from high iron-containing laterites (limonite, nontronite/smectite) by hydrometallurgical processing, while pyrometallurgy is generally used to extract nickel from low iron-containing saprolites and garnierites.

Sorowako and Lake Izabal are both examples of the pyrometallurgical nickel extraction route. However, at the time of commissioning of these two plants, there were important mineralogical differences between their smelter feeds. The Lake Izabal ore contained a high proportion of serpentine, a hydrated nickel-containing ferromagnesian silicate, with a SiO<sub>2</sub>/MgO wt ratio of about 1.5. In Indonesia, the smelter feed consisted of the higher nickel grade Sorowako West Block ore. The main minerals in this material were olivine and pyroxene, two non-hydrated ferromagnesian silicates, with an overall ore SiO<sub>2</sub>/MgO wt ratio generally above 2. As a result, typical Sorowako slag SiO<sub>2</sub>/MgO wt ratios ranged

from 2.1 to 2.5 with 20–30 wt % FeO, while the Guatemala slags had a  $\text{SiO}_2/\text{MgO}$  wt ratio of about 1.5 with about 20 wt % FeO. Other slag components in both operations were (wt %): 2–3  $\text{Al}_2\text{O}_3$ , <1 CaO, 1–2  $\text{Cr}_2\text{O}_3$  and about 0.6 MnO.

## MELTING CHARACTERISTICS OF SLAGS

### Phase Diagram Information

The phase diagram of the  $\text{SiO}_2$ -FeO-MgO system in equilibrium with metallic Fe [1], shown in Figure 1, provides a starting point to discuss the melting characteristics of the Sorowako and Lake Izabal slags. In fact, these three compounds account for over 90 wt % of each electric furnace slag. Sections of the liquidus of the  $\text{SiO}_2$ -FeO-MgO system at respectively 20, 25 and 30 wt % FeO are presented in Figure 2. Shaded areas show the range of compositions of the slags from the two locations. For this purpose, the compositions of the slags were normalized to 100% based on their  $\text{SiO}_2$ , FeO and MgO wt % contents. The data indicate that:

- Indonesian slags, containing 20–30 wt % FeO, were located close to a eutectic-type liquidus valley with steep surfaces on both sides, while Guatemala slags were located on a very steep portion of the liquidus surface;
- The higher the  $\text{SiO}_2/\text{MgO}$  wt ratio of Indonesian slags, the greater was the impact of variations in FeO content on liquidus temperature, while similar changes in composition had a negligible effect on the liquidus of the Guatemalan slags.
- The higher the FeO content of the Indonesian slag, the higher was the  $\text{SiO}_2/\text{MgO}$  wt ratio at which the liquidus surface became steep.

Phase diagram isothermal sections at temperatures slightly below the apparent liquidus temperature were constructed for both Guatemalan and Indonesian slags. Examination of these isotherms indicated that a high melting point solid olivine, a solid solution of  $2\text{MgO}\cdot\text{SiO}_2$  and  $2\text{FeO}\cdot\text{SiO}_2$ , precipitates out of liquid Guatemalan slag below its liquidus temperature, thus offering a possible explanation for skull formation on the electric furnace refractory lining observed at the Lake Izabal Smelter. In the case of the Sorowako slag, a much lower melting point pyroxene, a solid solution of  $\text{MgO}\cdot\text{SiO}_2$  and  $\text{FeO}\cdot\text{SiO}_2$ , precipitates out below the liquidus temperature of the slag.

The experimental program discussed below explored these initial observations.

## Experimental Measurements

### *Determination of Slag Solidus and Liquidus*

Solidus and liquidus temperatures were determined for monthly composites of Indonesian slag from August 1977 to February 1979 period and also for a granulated slag sample. Similar measurements were done on one monthly composite of Guatemalan slag. The  $\text{SiO}_2/\text{MgO}$  wt ratio of the Indonesian slags varied between 2.1 and 2.45 and the FeO content between 20 and 28 wt %. The Guatemalan slag had a  $\text{SiO}_2/\text{MgO}$  wt ratio of 1.5 and analyzed 20 wt % FeO. Fractions of Sorowako West Block ore and samples of East Block ore were also received.

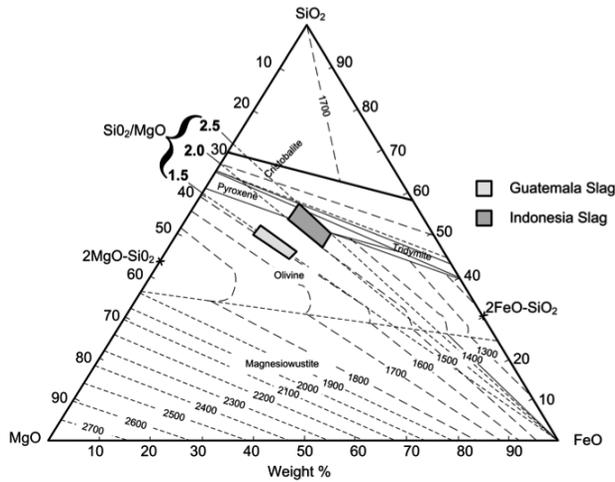


Figure 1: SiO<sub>2</sub>-FeO-MgO phase diagram

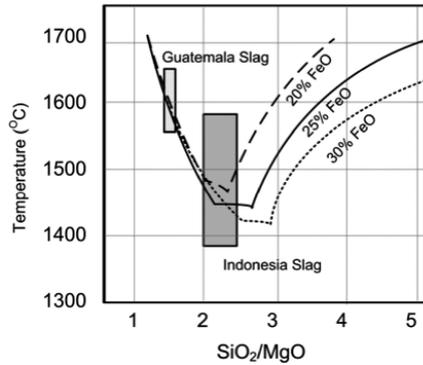


Figure 2: SiO<sub>2</sub>-FeO-MgO system liquidus lines at 20, 25 and 30 wt% FeO

Although a variety of techniques were used in these measurements, hot stage microscopy, under controlled atmospheric conditions, was considered the most reliable method to measure both solidus and liquidus temperatures. Finely pulverized slag was used for this purpose. Individual particles were clearly visible on the thermocouple wire in the microscope field. Some of these particles started to deform at the solidus temperature. As the temperature of the thermocouple junction increased, the entire slag mass deformed. This process continued until a ball of liquid slag with a smooth surface was attained. This temperature was identified as the slag liquidus. However, the apparently fully liquid slags were opaque and, consequently, some solid particles may still have been present in the slag balls. For this reason, the observed liquidus values were probably lower than the actual slag liquidus. Replicate hot stage microscopy measurements with fresh slag gave temperatures varying  $\pm 10^\circ\text{C}$  for the solidus and  $\pm 20^\circ\text{C}$  for the liquidus.

All Indonesian slag samples tested showed liquidus temperatures between 1390 and 1470°C. For slags with 20–25 wt % FeO, the liquidus varied from about 1420°C at 2.4 SiO<sub>2</sub>/MgO wt ratio to 1470°C at 2.1 SiO<sub>2</sub>/MgO wt ratio. These results were consistent with phase diagram trends (see Figure 2). Increasing the FeO content of the slag apparently lowered the liquidus temperature, an observation also in line with phase diagram prediction.

A comparison of the hot stage liquidus data with liquidus temperatures estimated from

the  $\text{SiO}_2\text{-FeO-MgO}$  phase diagram indicated that the measured temperatures were lower by 10–60°C. Two factors may explain this discrepancy: a) the aforementioned opacity of the liquid slags that interfered with a precise determination of the temperature at which the slag was fully molten; and b) the effect of minor elements on the slag melting characteristics that it is ignored when estimating liquidus temperatures using normalized slag compositions.

### Slag Quenching Studies

Slag quenching studies were conducted to investigate the compositions of liquid and solid phases that coexist in equilibrium at selected temperatures. In these experiments, the slag samples were first fully melted and then held for half an hour at temperatures below the liquidus in recrystallized MgO crucibles. The crucibles were then quickly dropped into a pail containing cold water. This technique permitted clear identification of the primary solid crystals that had been in equilibrium with liquid slag at each of the experimental temperatures.

Three equilibration experiments, at 1450, 1500 and 1550°C respectively, were conducted with Guatemalan slag. As predicted from the  $\text{SiO}_2\text{-FeO-MgO}$  phase diagram, the three cooled slags showed well developed and dense primary crystals that microprobe analysis identified as olivine. In all cases, the  $\text{SiO}_2$  content of the olivine was about 40%, and the MgO/FeO wt ratio increased with equilibration temperature. Also, in all cases, the FeO content of the olivine was lower than predicted from the phase diagram. This was most probably due to the effect of minor components ( $\text{Al}_2\text{O}_3$ , CaO, etc.) in the slag. The amount of primary olivine was measured from composite photomicrographs along the entire height of the crucible; it decreased from about 50% at 1450°C to only 12% at 1550°C. These amounts were slightly corrected to account for small quantities of pyroxene that may be indistinguishable from the olivine. Based on this information and the composition of the original slag, the composition of the liquid that had been in equilibrium with the primary olivine was calculated.

The compositions of olivines and liquids from the equilibration tests were used to develop a *laterite slag phase diagram* for slags containing 19–23 wt% FeO (see Figure 3). The error of the slag liquidus line presented in Figure 3 is expected to be not greater than  $\pm 20^\circ\text{C}$ . The diagram shows that actual slag liquidus temperatures are lower than predicted from the  $\text{SiO}_2\text{-FeO-MgO}$  phase diagram at similar FeO content. Also shown in Figure 3 are the hot-stage liquidus temperatures of the Indonesian slags. It was reassuring that a number of the liquidus points generated by this technique fell close to the line generated from the Guatemalan slag quenching experiments.

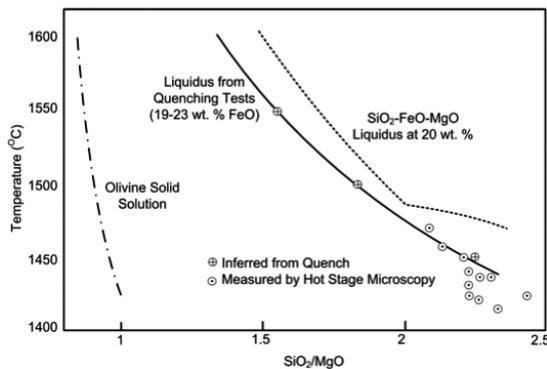


Figure 3: Laterite phase diagram

Quenching experiments were also conducted with an Indonesian slag having a  $\text{SiO}_2/\text{MgO}$  wt ratio of 2.1. Following equilibrations at 1500 and 1550°C, microscopic observation of the quenched slag showed no difference from the as-received granulated sample. No primary crystals were observed, confirming that the slag consisted of a single homogeneous liquid at both equilibration temperatures. However, the slag quenched from 1450°C showed the presence of what appeared to be pyroxene crystals. In addition, a very small amount of primary olivine was observed at the bottom of the crucible.

In one further experiment, the  $\text{SiO}_2/\text{MgO}$  wt ratio of the Indonesian slag used in the quenching studies was lowered to 1.8, while maintaining its FeO content at 21 wt%, by mixing the material with available Sorowako East Block ore. The mixture was homogenized by melting it at 1500°C. Then, the melt was held at 1450°C for half an hour and finally quenched in water. Examination of the cooled material showed that it consisted of 28% primary olivine. The compositions of this olivine and of the slag matrix (liquid at the equilibration temperature) were similar to those observed after equilibrating Guatemalan slag at the same temperature. This provided confirmation for the *laterite phase diagram* presented in Figure 3.

### **Sorowako Electric Furnace Slag Superheat**

The foregoing indicated that:

- In Guatemala, the slag operating temperature of about 1570°C was slightly above the slag liquidus. In addition, upon cooling, the first solid to precipitate out of the 1.5  $\text{SiO}_2/\text{MgO}$  wt ratio slag was high melting olivine. In other words, there were favourable conditions for the formation of a skull on the refractory lining of the Lake Izabal furnace. In fact, skull samples taken at a later time from the wall of the furnace showed that the skull did consist of olivine with a composition in good agreement with the composition predicted from the *laterite phase diagram*. Similar results had previously been obtained by conducting laboratory slag-refractory interaction experiments in miniplant rotating kilns at selected temperatures and controlled atmosphere.
- On the contrary, in Indonesia, the slag operating temperature of 1520°C was substantially higher than the slag liquidus of about 1450°C. In other words, the degree of superheat of the Sorowako furnace slag was too high. This factor combined with high electrode current (close to maximum power input furnace operation) resulted in very high furnace wall heat flux [2] that caused rapid refractory wear.

As discussed earlier, the starting feed to the Sorowako Smelter consisted of West Block ore with a higher Ni grade than East Block ore. The main minerals in West Block ore are non-hydrated Ni containing ferromagnesian silicates, while East Block ore contains 20% to 90% serpentine [3]. Similarly, the Guatemalan ore was highly serpentinized. In the reduction kiln, serpentine dissociates completely at temperatures above 700°C; its lattice structure collapses with 100% elimination of crystalline water. As a result, the Guatemalan calcine was porous, friable and the individual crystals were fine-grained. In contrast, only physical degradation of the un-serpentinized West Block ore occurred in the Sorowako rotary kiln.

These differences in rotary kiln calcine size and mineralogical composition were expected to have an impact on the operation of electric furnaces in a resistive mode. Apparently, the high degree of furnace slag superheat observed in Indonesia was caused by the equilibrium between power input, slag temperature and slow calcine dissolution rate. At maximum power input, a slag temperature well above its liquidus was required to achieve

the desired rate of melting of a calcine that contained very refractory components. In Guatemala, the lower  $\text{SiO}_2/\text{MgO}$  wt ratio of the slag, which required a higher operating temperature, and the nature of the calcine generated from serpentinized ore appeared to lead to a furnace operating equilibrium characterized by a high rate of calcine dissolution at a slag temperature just above its liquidus.

### ***Ore Slag Dissolution Studies***

A series of tests was conducted to investigate in more depth the effect of temperature and ore particle size and mineralogy on slag ore dissolution rate. A slag with a  $\text{SiO}_2/\text{MgO}$  wt ratio of 1.8 was used in preliminary tests. The ore specimens came from respectively East Block and West Block oversize (+ 6"). East Block had a  $\text{SiO}_2/\text{MgO}$  wt ratio of about 1.2, and was completely serpentinized; and West Block had a  $\text{SiO}_2/\text{MgO}$  wt ratio of about 1.0 and was completely unserpentinized. The big pieces were cut into cubes of various sizes. Most of the ore cube dissolution tests were conducted at 1550°C in miniplant rotary kilns, lined with 95% MgO bricks, at constant temperature and controlled atmosphere. At the end of each test, the amount of rock dissolved in the slag was estimated by visual examination of the quenched slag. This methodology generated only qualitative results. However, there was clear indication that the serpentinized rock dissolved 2–10 times faster than the unserpentinized material. As the size of the test cubes decreased, both ores showed faster dissolution rates, but at similar size the serpentinized material always dissolved faster.

A series of slag dissolution tests was also conducted using Sorowako dryer kiln product (DKP) that had previously been calcined in the laboratory at 850°C under reducing conditions. The coarser fractions of this material contained a substantial proportion of refractory olivine. Silica veinlets were also present. In separate tests, calcined as-received DKP, calcined DKP crushed respectively to  $-1/4"$  and  $-1/8"$  and calcined DKP screened to  $-1/8"$  were added to molten Sorowako granulated slag with a  $\text{SiO}_2/\text{MgO}$  wt ratio of 2.4. In each experiment, 100g of calcine was added to 4 kg of molten slag and held in the rotating kiln for a predetermined period. Upon cooling, examination of slag held at 1550°C for 30 minutes following the addition of the test material, indicated that the proportion that had dissolved in the slag was, respectively, ~60% of the calcined DKP, < 90% of the material crushed to  $-1/4"$ , close to 100% of the material crushed to  $-1/8"$ , and 100% of the material screened to  $-1/8"$ . These results provided further evidence of the slow rate of dissolution of olivine containing ore particles in slag. It was also observed that silica was as difficult to dissolve as olivine. Separate tests using Guatemalan slag and Guatemalan rotary kiln calcine showed that the latter material had the fastest slag dissolution rate.

Slag dissolution tests were also done using DKP calcine sintered at a temperature close to the solidus of the material. In fact, sintering of the calcine feed is expected to occur in the charge banks of the electric furnace before contacting the molten slag. The laboratory sinter was not strong, but held together when chunks were preheated in the miniplant rotary kiln flame before being added to the molten slag. Under similar experimental conditions, sintered calcines dissolved faster than the corresponding unsintered calcines, and differences between the dissolution rates of different sintered calcined ores became smaller.

### ***Lowering the $\text{SiO}_2/\text{MgO}$ wt Ratio of the Sorowako Slag***

The test work discussed in the previous sections had indicated that the solution to the rapid refractory wear problem in the Sorowako electric furnaces would require mixing the plant commissioning feed, i.e., West Blok ore, with East Block ore. Although the Ni grade

of the modified feed would be lower, two beneficial effects were expected: an increase in the calcine feed slag dissolution rate; and olivine skull formation on the furnace refractory wall at sufficiently low  $\text{SiO}_2/\text{MgO}$  wt ratio.

The question of how low a  $\text{SiO}_2/\text{MgO}$  wt ratio would be required to achieve the latter objective was investigated by conducting slag-refractory interaction tests in mini-plant rotary kilns lined with MgO refractory. In these tests, granulated Indonesian slag was blended with various amounts of appropriate ore fractions to generate slags with  $\text{SiO}_2/\text{MgO}$  wt ratios from 1.8 to 2.2, while maintaining the FeO content at 23–24%. In all tests, once the slag was molten, it was kept at a temperature just above the corresponding liquidus for a predetermined period. Under these conditions, a refractory protective skull was formed regardless of slag composition. However, the proportion of low melting pyroxene in the buildup increased with increasing slag  $\text{SiO}_2/\text{MgO}$  wt ratio. The conclusion was that formation of skull consisting almost entirely of high melting olivine was only possible at a slag  $\text{SiO}_2/\text{MgO}$  wt ratio  $< 2$ .

### ***Other Laterite Slag Studies***

Various other studies were conducted to provide data leading to an improved operation of the Indonesian electric furnaces, such as measurements of slag heat content and slag electrical conductivity as a function of composition and temperature. The work also included the evaluation of several refractory materials. In addition, feeds of various compositions were smelted in a miniplant 100 kVA electric furnace that had been equipped with wall cooling copper fingers. This test work confirmed that close to 100% olivine skull is formed from slag having a  $\text{SiO}_2/\text{MgO}$  wt ratio  $< 2$ . Thick olivine buildup was observed on the refractory lining just in front of the tips of the copper fingers in the test that generated a slag with a  $\text{SiO}_2/\text{MgO}$  wt ratio of 1.8.

## **CONCLUSIONS**

Following the evaluation of the data generated by this research program, the Indonesian operators decided to start feeding their electric furnaces with a blend of West Block and East Block ores. Starting in 1979, the proportion of east Block ore in the blend increased steadily to reach 60% in 1985. During this period, the Ni grade of the electric furnace feed decreased from 2.1 to 1.9%, and the slag  $\text{SiO}_2/\text{MgO}$  wt ratio decreased from 2.2 to 1.9 [2].

Also, cooling copper finger technology, originally developed by Falconbridge to protect the walls of its nickel laterite smelting electric furnaces in the Dominican Republic, was adopted in Sorowako. Copper coolers were installed in furnaces No. 1 and No. 2 in 1979 [4]. Over the years, there has been continuous improvement in electric furnace copper cooler technology.

Another major development was the implementation of high voltage operation during the period 1987–1990 [4]. In this mode of operation, the electrodes are not submerged in the slag, and an arc is established between the tip of an electrode and the molten bath. A substantial proportion of the energy input is transferred directly to the charge. Consequently, the secondary current is greatly reduced and also the furnace sidewall heat flux.

These positive developments and the installation of new 60/65 MVA transformers in 1989 permitted an increase in furnace power input from the original 30–40 MW level to 50–60 MW and, in turn, achievement of a much greater furnace smelting capacity. In addition, the high voltage mode of operation has permitted operation at a slag  $\text{SiO}_2/\text{MgO}$  wt ratio of slightly over 2. Despite this change in slag composition, furnace campaign life has increased to about 10 years [2].

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