STUDY OF OXYGEN FLASH SMELTING OF NICKEL/COPPER CONCENTRATES

Part II: Miniplant testwork - Kinetics

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Abstract

At its Copper Cliff Smelter, Vale Inco Limited processes a bulk copper-nickel concentrate in two Inco oxygen flash furnaces. Coke supplies a minor proportion of the process heat requirements, limiting the flash furnace matte grade to the target 45% CuNiCo. Coke addition to the furnace offers a potential means of establishing a reducing barrier on the surface of the molten bath. Such a practice would be conducive to producing sulfur deficient (partially metallized) matte. At the same iron content, the iron activity of sulfur deficient matte is higher than that of regular matte. A supernatant coke barrier could, therefore, be expected to lead to higher nickel and cobalt recoveries, reduction or even elimination of magnetite furnace bottom build-up and increased sulfur elimination as SO\textsubscript{2} in the flash furnace. Extensive experiments were conducted in a miniplant flash furnace to investigate the effect on process metallurgy of the suggested modified scheme. The introduction and description of the experimental set up were given in Part 1 of this paper and an early paper published in Yazawa symposium\textsuperscript{1} together with the results and some in depth discussion on metallurgy. This paper intends to discuss the kinetics of the miniplant flash furnace testwork.

Introduction

The design of the experimental set up is based on a miniplant flash furnace that was extensively used in the late 1970s and early 1980s to investigate fundamental aspects of flash smelting and the metallurgy of various possible operating routes\textsuperscript{2}. A vertical section of the miniplant flash furnace is presented in Figure 1. The miniplant flash furnace tests were divided into three series. In series 1 and 2, a supernatant layer of coke was maintained on the surface of the molten bath (See Figure 1). Series 1 differed from series 2 mainly due to the flash smelting O\textsubscript{2}/feed ratio. Series 3 was conducted using a different receiving crucible arrangement (See Figure 2).
The double crucible set-up used in series 3 is shown in Figure 2. This set-up was intended to study the effect of absence of coke layer on the bath surface, and to understand the impact of CO gas oxidation in the furnace freeboard. It was not the desire of this study to recommend any similar facility for any industrial application other than fundamental research.
Kinetics

The oxidation of FeS

As mentioned in Part I, the miniplant flash smelting tests conducted with a supernatant coke layer on the surface of the molten bath were divided into series 1 and series 2, depending on the O₂/feed ratio. Series 3 was conducted using a very different receiving crucible set up (double crucible). The discussion of the degree of FeS oxidation in the furnace freeboard in series 1 and 2 tests, i.e. with a coke layer on the surface of the molten bath, is based on an analysis of the variation of the estimated flash flame FeS/(FeS+FeO+Fe₃O₄) weight ratios and the actual wt%FeS in mattes as a function of the “actual O₂/feed” ratio. The matte wt%FeS was obtained by flash smelting product matte assaying. As already mentioned, the flash flame FeS/(FeS+FeO+Fe₃O₄) weight ratios were derived from actual experimental data by assuming that there was no FeS-Fe₃O₄ reaction on the bath surface in the experiments conducted with a supernatant coke layer.

The flash flame partially oxidized sulfide particles FeS/(Fe₃O₄+FeO+FeS) weight ratio, calculated from the composition of a flash flame particles sample, was plotted in Figure 3 for comparison purposes. The graph shows good agreement between the flame sample FeS/(Fe₃O₄+FeO+FeS) weight ratio and the estimated values for the series 1 and series 2 flash smelting tests.

The data in Figure 3 also show that increasing the “actual O₂/feed ratio” above 0.43 (series 2 tests) did not result in a further decrease of the FeS/(FeS+Fe₃O₄+FeO) weight ratio. In fact, the experimental results indicate that there is a limit to the degree of oxidation of FeS that can be achieved in the freeboard, even in the presence of excess oxygen. This was one of the key findings of this study.

Figure 3 can be divided into two regions, below and above an “actual O₂/feed ratio” of 0.43. In the first region, with O₂/feed ratio lower than 0.43, the FeS/(FeS+FeO+Fe₃O₄) weight ratios in the burner flame share a very similar trend with wt%FeS in matte, both decrease with O₂/feed ratio. As found by other researchers, the burner reaction kinetics produces under-oxidized and over-oxidized particles as a result of size variation of these particles. The small size particles are more likely to be over-oxidized than large size particles. Figure 3 reflects the combination of the under-oxidized and over-oxidized particles, and it represents the overall degree of oxidation of the partially oxidized sulfide mineral particles in the furnace freeboard.

In the second region, the “actual O₂/feed ratio” increases above 0.43. However, both the FeS/(FeS+FeO+Fe₃O₄) weight ratio and wt%FeS in matte no longer decrease with “actual O₂/feed ratio”. The fact is, that as discussed earlier, no further oxidation of FeS is observed for “actual O₂/feed ratios” above 0.43. There are two possible explanations for this phenomenon: (1) A deterioration of kinetic conditions on the suspended particles prevents further oxidation of FeS; (2) The miniplant flashing space restricts the length and size of the burner flame that in turn limits the degree of the sulfide particles oxidation reactions.
above a certain O\textsubscript{2}/feed ratio. A multiphase CFD flash smelting model was used to examine the latter hypothesis.

CFD modeling work

CFD modeling work was conducted utilizing a commercial ANSYS CFX package specifically designed for flash smelting Cu/Ni concentrate\textsuperscript{4}. As described by the commercial package, in the CFD model, flash smelting of Cu-Ni bulk concentrate was simulated by the following simplified reactions:

\[
\begin{align*}
\text{FeS}_2 &= \text{FeS} + \frac{1}{2}\text{S}_2 & 1 \\
2\text{CuFeS}_2 &= \text{Cu}_2\text{S} + 2\text{FeS} + \frac{1}{2}\text{S}_2 & 2 \\
\text{FeS} + 3\text{O}_2 &= \text{FeO} + \text{SO}_2 & 3 \\
3\text{NiFe}_2\text{S}_4 &= \text{Ni}_3\text{S}_2 + 6\text{FeS} + 2\text{S}_2 & 4
\end{align*}
\]

It should be noted that the commercial ANSYS CFX model is based on Jorgensen’s simplified flash smelting modeling work\textsuperscript{5}. To date, only Jorgensen has modeled the flash smelting of nickel concentrate. His model does not consider the decomposition of pentlandite (Equation 4). However, within the objectives of this study, Jorgensen’s model is considered adequate.
Labile sulfur in the above equations is oxidized by \( O_2 \) in the furnace freeboard:

\[
\frac{1}{2}S_2 + O_2 = SO_2
\]

The commercial CFD package permits three-dimensional flash smelting flow modeling, including particle heating, decomposition, and subsequent combustion in the furnace freeboard. The ANSYS CFX model uses Lagrangian particle tracking to describe particle movement for multiphase modeling. Above the ignition temperature, the mass transfer from the particles is limited by diffusion of oxidant and products through the particle boundary layer, as described below for one of the particles reactions:

\[
2CuFeS_2 = Cu_2S + 2FeS + 1/2S_2
\]

The rate of the above reaction is formulated as the rate of \( S_2(g) \) formation

\[
\text{Rate} = (\text{surface area of particle}) \times (Sh) \times (D/d) \times (Cu_2S \text{ concentration})
\]

where

- \( D \) is the diffusivity of \( S_2(g) \)
- \( d \) is the diameter of the particle
- \( (Sh) \) represents Sherwood Number:

\[
(Sh) = 2 + 0.6Re^{0.5}(\nu/D)^{1/3}
\]

Based on stoichiometry of the reaction, the rate of decomposition/production of the species as well as heat is given as:

\[
\begin{align*}
\text{Rate of } CuFeS_2 \text{ decomposition} &= -4 \times \text{Rate} \times WCuFeS_2/WS_2 \\
\text{Rate of } Cu_2S \text{ production} &= 2 \times \text{Rate} \times WCu_2S/WS_2 \\
\text{Rate of FeS production} &= 4 \times \text{Rate} \times WFeS/WS_2 \\
\text{Rate of heat absorption} &= -4 \times 38.98E3 \times 1000/WS_2 \times \text{Rate}/(\text{total particle mass} \times Cp)
\end{align*}
\]

where for example

- \( WFeS \) is the molecular weight of FeS and 39000 is the endothermic heat of reaction in Joules/mole.

The gas reactions are modeled using the standard “Eddy Breakup Model” of combustion in which the combustion rates depend on local turbulence structure and species concentrations. The objective of utilizing the CFD model was to investigate whether the length and size of the burner flame are constrained by the size of the flashing space, thus limiting the degree of oxidation of the sulfide-mineral particles within the burner flame. The \( %SO_2 \) concentrations in the flashing space are calculated by the multiphase CFD modeling work, and compared with the miniplant flash furnace test work observations (without coke) in order to validate the model in a simplified manner. The \( %SO_2 \) values from two miniplant furnace tests (without coke) are estimated from mass balance, as described by Equations 13 to 17.
\[
\frac{(%SO_2,\text{ offgas})}{(SO_2,\text{litre})+(O_2^{\text{unreacted}},\text{litre})} = \frac{(SO_2,\text{litre})}{32(\text{g mol}^{-1}) \times 10^{-3} \times 22.4(\text{litre mole}^{-1})}
\]

in which

\[
(SO_2,\text{litre}) = (O_2^{\text{reacted},S},\text{litre}) = \frac{(\text{feed,kg}) \times %S_{\text{feed}} - (\text{matte,kg}) \times %S_{\text{matte}} - (\text{slag,kg}) \times %S_{\text{slag}}}{16(\text{g mol}^{-1}) \times 10^{-3} \times 22.4(\text{litre mole}^{-1})}
\]

\[
(O_2^{\text{unreacted}},\text{litre}) = (O_2^{\text{input}},\text{litre}) - (O_2^{\text{reacted},S},\text{litre}) - (O_2^{\text{reacted,Fe}},\text{litre})
\]

\[
(O_2^{\text{reacted,Fe}},\text{litre}) = \frac{(\text{matte,kg}) \times %O_{\text{matte}} + (\text{slag},O^{FeO+Fe_3O_4},\text{kg})}{55.85(\text{g mol}^{-1}) \times 3} + \frac{(\text{metallicFe,kg})}{16(\text{g mol}^{-1}) \times 4}
\]

\[
(O_2^{\text{input}},\text{litre}) = \left(\frac{O_2}{\text{feed}},\text{ratio}\right) \times (\text{feed,kg})
\]

For tests conducted without coke, regular mattes were produced. Therefore, metallic Fe in Equation 16 can be ignored. The actual \(O_2/\text{feed}\) ratios for the two tests are 0.345 and 0.242 respectively, and the mass and assays of feed, matte and slag are listed in Table 1. These data are used to calculate the average vol\%\(SO_2\) and other process parameters, using equations 13 to 17 (See Table 2).

Table 1 Mass and assays (without coke)

<table>
<thead>
<tr>
<th>Temp</th>
<th>(O_2/\text{feed}) ratio</th>
<th>Feed</th>
<th>Matte</th>
<th>Matte</th>
<th>Matte</th>
<th>Slag</th>
<th>Slag</th>
<th>Slag</th>
<th>Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>ºC</td>
<td></td>
<td>kg</td>
<td>%S</td>
<td>%O</td>
<td>%S</td>
<td>%metallic Fe</td>
<td>%S</td>
<td>%FeO</td>
<td>%Fe_3O_4</td>
</tr>
<tr>
<td>1340</td>
<td>0.345</td>
<td>15</td>
<td>25.3</td>
<td>3.77</td>
<td>0.48</td>
<td>24.8</td>
<td>0</td>
<td>8.31</td>
<td>0.3</td>
</tr>
<tr>
<td>1273</td>
<td>0.242</td>
<td>15</td>
<td>25.3</td>
<td>5.83</td>
<td>1.59</td>
<td>27.9</td>
<td>0</td>
<td>6.26</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Table 2 Calculation from two test results (without coke)

<table>
<thead>
<tr>
<th>O₂ input</th>
<th>SO₂</th>
<th>O₂ unreacted vol%</th>
<th>Average</th>
<th>Average</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>litre</td>
<td>litre</td>
<td>litre</td>
<td>SO₂</td>
<td>vol%SO₂</td>
<td>O₂/feed</td>
</tr>
<tr>
<td>3623</td>
<td>1985</td>
<td>942</td>
<td>67.8%</td>
<td>67.8%</td>
<td>0.3</td>
</tr>
<tr>
<td>2541</td>
<td>1461</td>
<td>603</td>
<td>70.8%</td>
<td>69.3%</td>
<td>0.3</td>
</tr>
</tbody>
</table>

In Table 2, the average vol%SO₂ and O₂/feed ratio are 69.3% and 0.3 respectively at average 1307ºC. An O₂/feed ratio of 0.3 is equivalent to ~30 m/s burner tip velocity. For the same burner tip velocity and O₂/feed ratio, the CFD modeling suggests 1280ºC temperature at 69%SO₂ inside the receiving crucible (Figures 4 and 5). Although slightly lower, the temperature obtained from the CFD model (1280ºC) is comparable with the test result (1307ºC). Figures 4 and 5 highlight two key issues: (1) The CFD model was validated with respect to temperature at about the same 69vol% SO₂; and (2) the burner flame does not hit the surface of the molten bath at 0.3 actual O₂/feed ratio. The results of further modeling work at 0.45 actual O₂/feed ratio, i.e. 45 m/s burner tip velocity, are compared with the results at 0.3 actual O₂/feed ration, i.e. 30 m/s burner tip velocity, in Figures 6 and 7.

As shown in Figures 6 and 7, the results for 45 m/s and 30 m/s burner tip velocity are very similar, neither flame hits the surface of the molten bath. This confirms that the oxygen-sulfide mineral reaction is not directly affected by the size of flashing space, which leaves the deterioration of kinetics as the only possible explanation for the lack of further oxidation of FeS at actual O₂/feed ratio greater than 0.43, as shown in Figure 3.
Figure 5  Isosurface of SO$_2$ (CFD model)

Figure 6  Gas streamlines (CFD model)
The flash flame reaction

Detailed mineralogical studies conducted on partially oxidized sulfide minerals particles produced in Outokumpu flash smelting\textsuperscript{6,7,8}, show that as oxidation progresses a dense solid magnetite crust ultimately forms on the surface of the particles (See Figure 8). In the earlier stages of oxidation, a porous iron oxide crust is formed. Oxygen can still easily penetrate this crust and reach the molten metal (matte) sulfide core. However, it appears unavoidable to stop further oxidation of the porous iron oxide crust. Eventually, the denser magnetite crust is formed, and oxygen can no longer reach the core melt and, consequently, further oxidation of FeS stops. This is the most probable cause of the deterioration of FeS oxidation kinetics that was observed in the present miniplant flash furnace smelting experiments at $O_2$/feed ratios above 0.43.
Assuming that S concentration on the surface of the particle is negligible, during the progressive oxidation of the partially oxidized sulfide mineral particle crust, its melting temperature would increase from ~1370ºC to above 1580ºC, as suggested by the Fe-O binary phase diagram (Figure 9). Particle fragmentation by high inner vapor pressure may eventually break the dense magnetite crust and permit further FeS oxidation. This phenomenon has been observed in Outokumpu flash furnace flames\(^5,6,7\). Apparently, this did not occur in the present experiments. In the miniplant flash furnace, the particles travel from the bottom end of the flash flame to the surface of the molten bath in an extremely short time.

In the present experiments, at less than 0.43 actual O\(_2\)/feed ratio, the degree of oxidation increases with O\(_2\)/feed ratio, and the rate of reduction by the supernatant coke layer also increases. Apparently, at these lower O\(_2\)/feed ratios, the iron oxides crust that it is formed on the partially oxidized particles is still porous. At 0.43 actual O\(_2\)/feed ratio, the degree of oxidation reaches its limit.

Regardless of the nature of the iron oxides crust, when the partially oxidized sulfide mineral particles hit the surface of the molten bath, the excess magnetite is back reduced by either FeS (experiments with no coke addition) or coke (experiments with a supernatant coke layer). In the latter case, the peak rate of reduction is achieved at 15 mt/m\(^2\)/day specific smelting rate, similar to that of the commercial Inco flash furnace. This demonstrates the key feature of the new operating concept, i.e. production of a sulfur deficient matte, and higher value metals recovery, without any detriment to flash furnace production capacity.
This opens the door for improving metal recovery without requiring furnace geometry modifications, and while maintaining furnace production capacity.

Figure 9  Fe-O binary phase diagram

Flash flame particle samples

A water cooled sampler (See Figure 10) was used to take a sample of partially oxidized sulfide particles from the bottom end of the flash flame during one of the flash smelting tests. The objective was to investigate the actual composition of the material and compare the result with the calculated values of the FeS/(Fe3O4+FeO+FeS) weight ratios. Due to the complexity of the sampling procedure, only one sample of the flash flame partially oxidized particles was successfully taken.

The sampler consisted of a 2.5cm×1.5cm×1.5cm (L×W×H) copper block, with a single loop inner water channel. Two parallel ¼"copper tubes were welded to the copper block, one to each of the single loop water channel openings. Three pieces of vertical thin copper plates were welded as guards on top of the copper block, forming a 2.5cm×1.5cm×1.5cm (L×W×H) container for collecting samples.

Samples of the flash flame partially oxidized sulfide mineral particles were taken at 35 cm from the tip of the burner, as shown in Figure 10. The samples were analyzed by ICP for major elements and by phosphate dichromate titration for Fe2+. Based on these assays, the relative amounts of FeS, FeO and Fe3O4 in the furnace freeboard sample were estimated. These are given in Table 3. Also included in the table are the values of the bath FeS, FeO
and Fe$_3$O$_4$ estimated from matte and slag assays. The matte from the test in which the freeboard sampling was conducted analyzed 43%CuNiCo. The results clearly show that FeS and Fe$_3$O$_4$ react on the surface of the bath to form FeO. In fact, the increase in FeO corresponds reasonably well to the decrease in FeS and Fe$_3$O$_4$ according to reaction 2 (See Part I). It should be noted that a well established bath surface was about 40-60 cm below the tip of the burner depending on the total amount of feed smelted.

![Diagram of burner flame sample location](image)

**Figure 10** Burner flame sample location

| Table 3 Mass fraction of Fe$_3$O$_4$, FeO and FeS in burner flame and bath surface |
|---------------------------------|-----|-----|-----|
| No coke                         | Fe$_3$O$_4$ | FeO | FeS |
| Flame (35 cm below the tip of the burner) | 42.0% | 21.8% | 36.3% |
| Bath surface                    | 14.6% | 56.1% | 29.3% |

It should be noted though, that the composition of the concentrate used in the test in which the burner flame was sampled was slightly different from that of the concentrate used in series 1 to 3 tests (Table 4). The former contained 23.6%CuNiCo and had a Ni/Cu weight ratio of 1.3, while the latter contained 22%CuNiCo and had a Ni/Cu weight ratio of 0.82. At the same O$_2$/feed ratio, the concentrate used in the burner flame sampling test would yield a relatively lower FeS/(Fe$_3$O$_4$+FeO+FeS) weight ratio than the other concentrate.

<p>| Table 4 Composition of the concentrate used in the burner sampling tests |</p>
<table>
<thead>
<tr>
<th>%Ni</th>
<th>%Cu</th>
<th>%Co</th>
<th>%S</th>
<th>%Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.20%</td>
<td>9.98%</td>
<td>0.38%</td>
<td>34.42%</td>
<td>38.13%</td>
</tr>
</tbody>
</table>

XRD and SEM analyses confirmed the presence of magnetite and iron sulfide in the flash burner flame sample (See Figure 11). Also present in the figure are unreacted solid SiO₂ particles, clearly separated from sulfides and iron oxides, indicating that the slagging reaction does not take place in the furnace freeboard.

**Figure 11** SEM analysis of the burner flame sample

The effect of CO gas

In the tests with a coke layer on the surface of the molten bath, one possible argument is that reaction of CO with O₂ in the furnace freeboard may take place which, if indeed occurs, could lower the amount of O₂ available for the oxidation of sulfides, thus resulting in production of lower grade matte at a given O₂/feed ratio. However, the observations made in this study do not support this view. A comparison between two tests conducted at the same temperature, and at the same O₂/feed ratio and with the same percent coke addition (See Table 5) illustrates this matter. In the first test, the coke was mixed with the feed and, consequently, added through the burner. In the second test, the coke was added in one batch directly to the crucible. The grade of the matte produced in the first test was significantly lower than in the second test. This observation shows that the CO generated in the coke reduction reactions that take place on the surface of the molten bath has a much lower effect, if any, on matte grade as compared to coke added to the flash flame. Before the main gas cleaning system, CO gas was expected to react with O₂ that did not participate sulfide minerals oxygen reactions. This O₂ could also come from air infiltration through the refractory lid, the offgas port and the burner port.
Table 5 Coke addition to burner and directly to the crucible

<table>
<thead>
<tr>
<th></th>
<th>Temp</th>
<th>O₂/feed</th>
<th>MG S deficiency</th>
<th>%Coke/feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>coke to burner</td>
<td>1365</td>
<td>0.345</td>
<td>50.9</td>
<td>4.5%</td>
</tr>
<tr>
<td>coke to crucible</td>
<td>1360</td>
<td>0.345</td>
<td>55.2</td>
<td>9%</td>
</tr>
</tbody>
</table>

Reduction in the coke layer

Another key finding of the miniplant flash furnace test work is that the coke reduction mechanism of the flash flame products is very similar to that observed in the graphite rod matte reduction experiments⁹. This indicates that the supernatant coke layer in a flash smelting system reduces Fe₃O₄ before the formation of slag, thus explaining the fast rate of reduction observed in the miniplant flash smelting experiments.

In the miniplant flash furnace test work, the overall rate of reduction and the degree of back reduction are mainly related to two parameters, namely the degree of oxidation of the particles in the flash flame and the operating temperature. The rate of oxygen removal during the miniplant flash smelting test can be estimated from reactants and products masses and assays, bath surface area, and flash smelting time. The estimated rate is acceptable for the purpose of this study. As the partially oxidized sulfide mineral particles percolate through the coke layer, a portion of Fe₃O₄ is reduced to FeO and ultimately metallic Fe, while the remainder reports to the molten slag and matte. The results of series 1 and 2 tests suggest that the rate of oxygen reduction increases with the oxygen input and, consequently, the degree of oxidation, as shown in Figure 12. This is more evident in Figure 13, in which the data show that the reduction rate for series 2 is significantly higher than for series 1 at the same temperature. The bath surface area was used for calculating the rate.

In reality, with no reduction in feed rate, increasing O₂/feed ratio in the current Inco flash furnaces would be restricted by both O₂ supply (pressure and flow) and the capacity of gas cleaning. With more coke addition, the required O₂ for the combustion of CO gas in the furnace freeboard and uptake⁹ would also increase. These issues require more study.

The activation energies for series 2 and 3 were obtained from the data presented in Figures 14 and 15 and Table 6. The value for series 2, i.e. 161 kJ/mole, is comparable with that of graphite-matte reduction (181 kJ/mole)¹⁰, suggesting that, in this series of tests, the dominant reduction mechanism is very similar to that of graphite reduction of matte. For series 3, the activation energy value, i.e. 303 kJ/mole, is comparable with that of graphite-slag reduction (286 kJ/mole)⁹, indicating that the reduction in series 3 is primarily between slag and submerged coke in the bottom section of the annular space between the two receiving crucibles. The different reduction mechanism of series 2 as compared with series 3 highlights one of the key features of the new operating concept for the Inco flash furnace, which takes advantage of the fast rate of reduction of matte (Fe₃O₄)¹¹ as the partially oxidized sulfide particles percolate through a supernatant coke layer.
Figure 12  Rate of O removal for series 1 and 2 tests vs actual O\textsubscript{2}/feed ratio

Figure 13  Rate of O removal vs temperature for series 1 and series 2
In series 2, the partially oxidized sulfide minerals containing $\text{Fe}_3\text{O}_4$ are continuously supplied to the coke layer. One of the reduction products, metallic Fe, is dissolved into the
matte as this material sinks through the coke layer into the molten bath. The continuous percolation of the partially oxidized sulfide mineral particles through the coke layer provides effective contact with coke.

<table>
<thead>
<tr>
<th>E</th>
<th>Miniplant test</th>
<th>Bench scale graphite reduction test</th>
</tr>
</thead>
<tbody>
<tr>
<td>kJ/mole</td>
<td>Series 2 (R²=0.94)</td>
<td>Graphite-matte (R²=0.966)</td>
</tr>
<tr>
<td></td>
<td>161</td>
<td>181</td>
</tr>
<tr>
<td>kJ/mole</td>
<td>Series 3 (R²=0.998)</td>
<td>Graphite-slag (R²=0.999)</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>286</td>
</tr>
</tbody>
</table>

In series 3, with a large portion of the molten bath not covered by coke, and, consequently, exposed to the partially oxidized sulfide mineral particles, more FeS is oxidized on the bath surface by Fe₃O₄ to produce FeO and SO₂. FeO reacts with SiO₂ to form fayalite silicate slag (2FeO·SiO₂) which, together with some Fe₃O₄, join the slag layer. As already discussed, slag FeO and Fe₃O₄ react with submerged coke to produce metallic iron. The continuous supply of fresh slag to the annular area filled by coke provides fresh reactant to react with coke. The rate of mass transfer of oxygen to the reaction sites should not be a critical factor in determining the overall rate of reduction. Therefore, the rate of chemical reaction (the Boudouard reaction) is the rate controlling factor, thus resulting in the series 3 high activation energy value. During these tests, the reduction of matte oxygen may take place at the same time but with much less significance mainly due to the good kinetic condition for slag reduction as a result of large surface area provided by the submerged coke and the higher oxygen content of the slag.

In the commercial Inco flash furnace, the degree of oxidation of the sulfide feed is a direct function of the actual O₂/feed wt ratio. This ratio also has a major impact on the furnace heat balance. The endothermic coke reduction reactions may result in lower liquid matte and slag temperature. However, the open bath surface with a supernatant coke layer would result in increased freeboard combustion of CO that would in turn increase the furnace freeboard temperature and the overall furnace heat balance. In general, greater temperature differential between the flashing zone (freeboard) and the molten bath (below the coke layer) is expected. In fact, a thick layer of “coke checker” in the Kivcet furnace results in ~1400°C flashing zone temperature and only ~900°C Pb bullion temperature⁰¹,⁰². This issue requires further consideration.
The reactivity of the coke used in the miniplant flash smelting tests was compared with the reactivity of graphite used in the crucible and X-ray tests using a TGA technique. TGA tests were conducted in air at 1350ºC, and both coke and graphite samples were comminuted to –100 mesh. Grade 5 argon gas was used during preheating. At 1350ºC, air was introduced to replace argon. The detailed test conditions are listed in Table 7. The results are presented in Figure 16.

![Oxidation in air at 1350C](image)

**Figure 16  TGA test results on coke and graphite**

The data suggest that the reactivity of graphite is slightly higher than that of coke. Therefore, it is expected that the absolute value of the rate of reduction of the partially oxidized sulfide particles by coke in series 2 would not be that different from the rate of reduction of matte observed in the crucible experiments.

<table>
<thead>
<tr>
<th></th>
<th>Air rate</th>
<th>Weight</th>
<th>Temp</th>
<th>Heating rate before 1350°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>coke</td>
<td>170 ml/h</td>
<td>93.4 mg</td>
<td>1350 ºC</td>
<td>60 ºC/min</td>
</tr>
<tr>
<td>graphite</td>
<td>170 ml/h</td>
<td>93.2 mg</td>
<td>1350 ºC</td>
<td>60 ºC/min</td>
</tr>
</tbody>
</table>

The thickness of the coke layer

The rate of reduction and the respective thickness of the coke layer (after tests) are plotted against temperature in Figure 17. The large variation of the coke layer thickness could be
the combined results of the variation of the duration of each test, the total O\textsubscript{2}/feed ratio and the flash smelting temperature.

The data in Figure 17 show that temperature is the sole parameter determining the rate of reduction. Up to a certain level, the thickness of the coke layer appears to be of no significant importance. This observation suggests that the rate of reduction is faster than the rate of percolation of the partially oxidized sulfide particles through the coke layer. Since in none of the tests there was sign of liquid accumulation on top of the coke layer, the percolation rate appears to be faster than the equivalent smelting rate. Therefore, the rate of reduction should be considered faster than the equivalent smelting rate. In other words, indications are that the new operating concept would permit achieving the desired metallurgical goals of producing sulfur deficient matte at the same specific smelting rate as that of commercial Inco flash furnace.

![Figure 17](image)

**Figure 17** Rate of reduction and the final thickness of coke versus temperature

**Conclusion**

(1) With a supernatant coke layer (series 2 tests), the activation energy for the reduction of the partially oxidized sulfide particles is comparable with that for graphite-matte
reduction, suggesting that a similar reduction mechanism prevails, i.e. coke reduction of Fe$_3$O$_4$. On the other hand, with the coke packed in the annular space of the double receiving crucible system (series 3), the value of the reduction activation energy is comparable with that of graphite-slag reduction, indicating that in series 3 the reduction reaction is primarily between slag and submerged coke. These observations highlight the merits of the new flash furnace operating concept that takes advantage of the fast rate of reduction of matte, by reducing the partially oxidized sulfide mineral particles as they percolate through the coke layer prior to the formation of slag.

(2) The rate of reduction of the partially oxidized sulfide particles depends almost exclusively on temperature.

(3) The peak reduction rate is achieved at 15 mt/m$^2$/day specific smelting rate, the same as in the commercial Inco flash furnace. This clearly demonstrates the key feature of the new operating concept. Providing a supernatant coke layer on the molten bath allows maximizing the rate of reduction of the percolating partially oxidized sulfide particles, and matching the flash furnace equivalent smelting rate so that the desired sulfur deficient matte is produced with no reduction in the feed rate.

(4) The CFD model work confirmed that the burner flame is not constrained by the size of the flashing space. Therefore, the oxygen-sulfide mineral reaction in the miniplant flash furnace is not directly affected by the size of flashing space. At greater than 0.43 actual O$_2$/feed ratio, the deterioration of mass transfer rate limits further oxidation of FeS in the furnace freeboard.

(5) TGA test results indicate that the reactivity of the graphite used is slightly higher than that of the coke. Therefore, the absolute value of the rate of reduction of the partially oxidized sulfide particles by coke and the rate of reduction of matte by graphite are expected to be similar.

Acknowledgement

The authors would like to acknowledge Vale Inco Ltd., Dr. C. M. Diaz, Dr. T. Warner, and Dr. R. Yeo for their support and help.
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