HIGH TEMPERATURE PROCESSING SYMPOSIUM 2014
Swinburne University of Technology
3 – 4 February 2014, Melbourne, Australia

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Geoffrey Brooks

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HIGH TEMPERATURE PROCESSING SYMPOSIUM 2014
Swinburne University of Technology
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We wish to thank the main sponsors for their contribution to the success of this symposium
Symposium Program

Day 1 (Monday, 3 February 2014) in EN103

8.30 to 9.00 Registration in Foyer Engineering (EN) Building

9.00 to 9.10 Welcome by Prof Geoffrey Brooks – Pro-Vice Chancellor (Future Manufacturing), Swinburne University of Technology

Session 1 Chaired by: Assoc Prof M Akbar Rhamdhani (Swinburne)

9.10 to 9.40 01 – Keynote: Prof Kenneth S. Coley (McMaster University/Steel Research Centre) - Fundamental Kinetic Studies of Slag Metal Gas Reactions in Support of Process

9.40 to 10.00 02 – Dr Mirco Wegener (CSIRO) - Towards a Slag Droplet Heat Exchanger – Capillary Breakup of Molten Oxide Jets (FULL PAPER)

10.00 to 10.20 03 – Ms Shabnam Sabah (Swinburne University of Technology) - Investigation of Splashing at Different Sampling Positions and Cavity Modes in Oxygen Steelmaking

10.20 to 10.40 04 – Prof Joonho Lee (Korea University) - Surface Tension Measurements of 430 Stainless Steels Using the Electromagnetic Levitation Technique

10.40 to 10.55 Coffee/Tea in EN Building Foyer

Session 2 Chaired by: Assoc Prof Brian Monaghan (Univ of Wollongong)

10.55 to 11.25 05 – Keynote: Assoc Prof Damien P. Giurco (University of Technology, Sydney, Institute for Sustainable Futures) - Minerals, Metals and Innovation in the Circular Economy

11.25 to 11.45 06 – Ms Karolien Vasseur (Umicore Group Research & Development) - Collaboration: The Key Towards a Resource Resilient Society

11.45 to 12.05 07 – Mr Tijl Crivits (The University of Queensland) - Protecting the Future – Investigation of Phase Equilibria and Freeze Linings in Novel High Temperature Recycling Processes

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High Temperature Processing Symposium 2014  
Swinburne University of Technology
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9.20 to 9.40  18 – Mr Quanrong Fan (Fansmelt) – Dynamic Free Lance for Slagmaking and Steelmaking Desulphurisation
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11.15 to 11.35  23 – Mr Lang Shui (The University of Queensland) - Flow Dynamics Study in Bottom Blown Copper Smelting Furnace (FULL PAPER)
11.35 to 11.55  24 – Dr Xiaodong Ma (The University of Queensland) - Phase Equilibria in the CaO-SiO\(_2\)-Al\(_2\)O\(_3\)-MgO System Related to Iron Blast Furnace Slag

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1.55 to 2.15  27 – Mr Zhe Wang (University of Wollongong) - Effect of Sintering Conditions on the Formation of Mineral Phases during Iron Ore Sintering with New Zealand Ironsand
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**Chaired by:** Mr Naoto Sasaki (Nippon Steel & Sumitomo Metal)

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**Close of Symposium**

**Day 3 (Wednesday, 5 February 2014)**

**Post-Symposium Plant Tour: OneSteel Laverton** (total 21 person max)

- **8.15 to 8.30** Convene at ATC Foyer to board a bus. Bus will be arranged by Swinburne
- **8.30 to 9.00** Travel to OneSteel Laverton
- **9.00 to 1.00** OneSteel Laverton site Tour
- **1.00 to 1.30** Return to Swinburne

**Campus Map – Swinburne @ Hawthorn, Melbourne**

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High Temperature Processing Symposium 2014
Swinburne University of Technology 6
Fundamental Kinetic Studies of Slag Metal Gas Reactions in Support of Process
Kenneth S. Coley
McMaster Steel Research Centre, Department of Materials Science and Engineering,
McMaster University, Hamilton, Ontario, Canada

Keywords: Kinetics, Slags, Steelmaking

Abstract

High temperature metallurgical reaction kinetics have been the subject of study for many years [1, 2]. However, for most of that time such studies, whilst presenting a stimulating intellectual challenge to academic researchers, have been considered to offer no more than an insight into the behaviour of industrial processes. However, in recent years hope has been expressed, regarding the emergence of kinetics as a discipline with quantitative application, much as thermodynamics has been for several decades [3]. Indeed, there has been notable recent success in process modelling of real plant data, based on a fundamental kinetic approach [4]. The current paper will discuss two fundamental studies from the author’s laboratory and the way in which they have been applied in modelling process behaviour.

Kinetics of Slag Gas Reactions

Carbon injection into slag has been used in smelting reduction and in slag foaming in the electric arc furnace (EAF). To develop a proper model of such a process it is important to understand the mechanism and possible rate determining steps for reaction between individual carbon particles and slag. A number of researchers have suggested that when a carbon particle reacts with oxidising slag, a CO/CO$_2$ halo forms around the particle [5, 6] requiring individual gas/slag and gas/carbon reactions for reduction to proceed. Given the relatively thin halo and the rapid nature of gas phase mass transport, it is likely that such either the gas/slag, gas/carbon reactions or transport in the slag will be rate determining. It has been reported that for low iron oxide slags the latter controls and for higher iron oxide, one or other of the chemical reactions is rate determining. The gas carbon reaction has been well studied [7] as has the slag gas reaction [8]. However, in the latter case, workers had been previously unable to offer a theoretical explanation that would explain all of the observed phenomena. Barati and Coley [11], employed the isotope exchange technique pioneered in the Metallurgical field by Belton and co-workers [8-10], to develop a data set covering a wide range of slag and gas composition. These workers found, in agreement with previous researchers [8-10], that the rate of reaction could be described by Equation 1 and the apparent rate constant represented by Equation 2.

\[ v = k_a (p_{CO_2} - p_{CO}) \]  
(1)
\[ k_a = k_a^o (a_O)^{-n} \]  
(2)

The value of the parameter n has been found to lie between 0.5 and 1, and it has proved problematic to justify the range of this and effect of basicity and FeO concentration on $k_a^o$. The primary reason for the discrepancy in n is the assumption that reaction must proceeds via...
an adsorbed activated complex of the form \((\text{CO}_2)^2\). This was originally proposed because it fits very well with a value of \(n = 1\), but is contradicted by the fact that \((\text{CO}_2)^2\) is known to be unstable, whereas \((\text{CO}_2)^-\) is more stable. Barati and Coley [12] identified that if the reaction proceeds via the singly charged activated complex the reaction site requires two neighbouring \(\text{Fe}^{2+}\) ions. If this requirement is included in the rate equation, the observed range of values for \(n\) can be explained as can all other observations. Based on this mechanism, Barati and Coley [12] developed Equation 3 to calculate the rate constant for reaction between \(\text{CO}/\text{CO}_2\) and \(\text{FeO-CaO-SiO}_2\) slag.

\[
k_o = 2.67 \times 10^{-4} (C_{\text{Fe}})^2 \frac{1}{r(1+r)^2} \exp\left(\frac{-475.7 - 452.4\Lambda}{RT}\right) \quad [\text{mol} \cdot \text{cm}^{-2} \cdot \text{atm}^{-1} \cdot \text{s}^{-1}] \quad (3)
\]

Where \(r = \text{Fe}^{3+}/\text{Fe}^{2+}\), \(C_{\text{Fe}}\) is the concentration of iron in the slag and \(\Lambda\) is the optical basicity of the slag. The agreement between this equation and experimental measurements is excellent over the entire range of slag composition and temperature employed by Barati and Coley.

Combining Equation 3 with the rate equation of Turkdogan and Vintners for carbon gasification allows the calculation of the rate for a single carbon particle surrounded by a gas bubble. King and co-workers [13, 14] integrated the resulting rate equation over all injected particles to predict the rate of carbon gasification during injection. Figure 1 shows the agreement between the model proposed by King et al and measurements of gasification rate. The agreement is very good but as is shown in the figure, by assuming the carbon to be less reactive than that studied by Turkdogan and Vintners (adjusted carbon reactivity), better agreement is obtained. The gasification model can be combined with the foaming model of Zhang and Fruehan [15] to predict slag foam height [13].

\[\text{Figure 1: Carbon gasification rate as a function of time from King et al. [13, 14]}\]

\[\text{Droplet Swelling in BOF Steelmaking}\]

Recent work from Swinburne University [4], has shown that BOF steelmaking can be quantitatively modelled with remarkable success, when a deep understanding of the kinetics and mechanisms of the various reactions is employed [4]. In this work Dogan et al [4] used...
the bloated droplet model first proposed by Brooks and co-workers [16] to calculate the residence time of metal droplets in the slag.

To be used over a wide range of conditions the bloated droplet model requires a detailed evaluation of swelling kinetics caused by CO formation inside the droplet. Considerable progress in this regard has been made through recent research by Coley and co-workers [17, 18].

Conclusions

Process models based on detailed kinetic analysis of the key phenomena offer the best opportunity for accurate prediction of process behaviour.

References

Towards a Slag Droplet Heat Exchanger – Capillary Breakup of Molten Oxide Jets

Mirco Wegener, Luckman Muhmood, Shouyi Sun, Alex Deev
CSIRO Process Science and Engineering

Keywords: slag, surface tension, jet breakup

Abstract

Molten slag contains a considerable amount of sensible heat which can be recovered provided that a large specific surface area is created to facilitate heat transfer to an ambient gaseous medium. It is preferable to disperse the molten slag into uniformly sized droplets in order to permit a more reliable process design. The basic concept is to distribute a volume of molten material into coherent ligaments or jets which consecutively break into droplets by action of capillary forces. This can be done either radially using centrifugal forces as currently explored in the dry slag granulation process, or vertically by forming cylindrical liquid jets issuing from capillaries or nozzles as proposed in the direct contact droplet heat exchanger (DHX). The latter option is explored in this paper investigating the controlled breakup of molten calcia/alumina jets at 1660°C in a recently commissioned three-zone high temperature furnace.

INTRODUCTION

Molten slags exhibit a great potential in direct heat transfer applications as shown in the following two examples. The utilisation of sensible heat contained in waste metallurgical slag may reduce the energy consumption and hence the CO_2 footprint in the energy-intensive metals industry. Currently, in modern integrated steelmaking processes, blast furnace slag – which is usually tapped at around 1500°C and therefore contains sensible heat – is quenched with water in the wet granulation process in order to produce vitrified granulated blast furnace slag as a feed material for cement production. However, in order to recover the heat, the wet granulation has to be replaced by a dry granulation technology as currently being developed by CSIRO Australia (Jahanshahi et al., 2011; Jahanshahi and Xie, 2012; Xie et al., 2008) and within a research project driven by Siemens VAI, Thyssen Krupp Steel Europe, voestalpine Stahl Austria and the FEhS Building Materials Institute Germany (McDonald, 2012). A stream of molten slag is tapped onto a rotating device which forces the liquid to flow radially and form, ideally, ligaments or, at higher flow rate, sheets at the rim of the rotating device. These ligaments or sheets eventually break up into discrete droplets which then are cooled and solidified by an ambient gas stream and possibly further cooled downstream in a packed-bed heat exchanger (Jahanshahi and Xie, 2012). However, none of the potential processes has been successfully commercialised yet (Barati et al., 2011).

In a second example, Bruckner (1985) proposed a concept – although not realised yet – in which molten slag is considered as a heat transfer medium in processes where the heat is generated from a solar thermal power plant. In this concept, glassy solid slag particles are delivered to a solar receiver where they are transformed to a liquid by concentrated solar radiation. An essential part of the concept is the direct contact droplet heat exchanger (DHX). The DHX is basically a vertical column in which molten slag enters at the top through...
capillaries to form multiple jets which consecutively break into – ideally – uniformly sized droplets. The heat is transferred to a counter-current gas stream, and the droplets solidify and can be fed back to the receiver.

Both examples have in common that a continuous stream of molten slag has to be broken up into discrete droplets by capillary (or surface tension) forces in order to increase the specific surface area available for heat transfer. In the ideal case, the drop size distribution should be controllable via process parameters and be as narrow as possible to facilitate estimations on process design parameters such as fluid dynamics, throughput, and heat transfer.

The instability of a liquid column falling vertically in the gravitational field is a classical problem in fluid dynamics and has been studied analytically and experimentally in a comprehensive manner since the 19th century, at least for low temperature liquids (≤ 500°C). But knowledge is limited concerning the dynamics of droplet and jet formation with consecutive breakup and jet disintegration in high temperature oxide melts. In order to improve the fundamental knowledge and to test the applicability of theoretical predictions, a high temperature test facility with maximum temperatures of 1750°C has been built which allows optical access to a droplet/jet generating device by means of a high-speed camera (Wegener et al., 2014a,b). The present work explores the controlled breakup of molten oxide jets at different flow rates with and without external mechanical vibration at 1660°C. Measurable outcomes are the size distribution of droplets formed by disintegrating jets, the unbroken jet length and the frequency of droplet formation. All of these are required to be able to conceive a suitable design of a potential DHX.

METHODOLOGY

The experimental setup, see Fig. 1, and method has been described in detail elsewhere (Wegener et al., 2014a,b) and is just briefly recalled here. The setup consisted of four main components: an electrically heated three-zone tube furnace with a maximum temperature of 1750°C (Tetlow Kilns & Furnaces), a 99.8% dense high-purity alumina cross tube assembly for optical access and atmosphere control (McDanel Advanced Ceramic Technologies), a graphite droplet and jet generating device (Mersen Oceania), and a Phantom v3.11 high-speed camera (Vision Research). Around 500 g calcia/alumina slag (49/51 wt%) was prepared, premelted twice in a muffle furnace, and finally crushed and placed in a graphite crucible (V ≈ 200 mL). The crucible was equipped with a tapered bottom to facilitate the flow into the capillary section. Here, a knife-edged graphite capillary (ID ≈ 1.12 mm at 1660°C) was used. A hollow graphite stopper housing a B-type thermocouple to measure the slag bath temperature obstructed the entry to the capillary which could be lifted with a linear actuator to control the flow. Additionally, the crucible could be pressurised with argon up to 2 bar to vary the volume flow rate or jet exit velocity. The crucible could be positioned within the vertical alumina tube using a second linear actuator to ensure that the capillary tip and the jet were visible through the quartz glass window. The window is part of a water cooling end cap attached to the horizontal alumina tube with non-circular cross-section which slides completely through the vertical tube to form a cross. It had a circular opening in its centre position to allow the capillary to extend into the observation section. The joints were sealed with a high temperature ceramic adhesive. The alumina cross tube was flushed with ultra-high purity argon from the bottom and via the two end caps at both ends of the horizontal alumina tube. An oxygen probe measured the oxygen partial pressure which was found to be of the order of 10⁻⁸ – 10⁻⁹ atm.
A high-speed camera equipped with a long-distance microscope lens (focal length around 1030 mm) and a CineMag non-volatile storage device with a capacity of 128 GB captured the process of jet forming and breakup. Frame rates up to 10000 fps were easily achievable due to the brightness of the slag at experimental temperature. The field of view in the present investigations was around 75 mm in vertical length and 12 mm in horizontal width. In all cases, the jet breakup occurred within the field of view. The molten slag droplets formed by jet disintegration were caught in a stainless steel cup supported by a graphite stand which in turn rested on a precision balance (Sartorius). The balance read the slag mass flow rate.

![Figure 1: Experimental setup. a) Close-up of high temperature furnace in test stage with balance chamber at the bottom and lifting device at the top. b) Three heating zones with Kanthal Super 1900°C molybdenum disilicide elements. c) Water cooled end cap with quartz window for optical access. d) Furnace during a hot run. e) Schematic of the graphite crucible with capillary and stopper.](image)

A pneumatic turbine vibrator (Cleveland Vibrator Co.) was used to impose a controlled periodic excitation on the jet. The vibrator was mounted outside the hot chamber on one of the three steel rods which held the graphite crucible assembly in position. An ambient temperature calibration using a piezoelectric accelerometer ensured that the vibration was transmitted from the vibration source to the graphite capillary and hence to the jet. Table 1 shows the performed measurements in the present study. The temperature in the slag bath was 1660°C in all cases. The pressure in the crucible was varied between 0.4 and 1.2 bar above ambient pressure. The pneumatic vibrator was only used for the second measurement at 1.2 bar, all other cases were carried out in natural breakup mode (no additional vibration).

![Table 1: Overview of jet breakup experiments at 1660°C. Trials 1 – 5 were in natural breakup mode, hence no external vibration. In Trial 6, a frequency of 280 Hz was applied. The jet length $L_{\text{jet}}$ is the mean value of a sequence and differs consequently slightly from the instantaneous length given in Fig. 2.](image)
RESULTS AND DISCUSSION

Fig. 2 shows snapshots of slag jets issuing from a graphite capillary at 1660°C with increasing driving pressure and thus increasing exit velocities from left to right. In each image, the main droplet is about to detach from the jet. The scale on the left hand side is in mm and allows comparing the jet lengths. At 0.4 bar, the jet velocity is too small to form a proper jet. Instead, dripping mode can be observed resulting in a highly repetitive droplet formation pattern. Hence, the droplet sizes are quite uniform (≈ 5.2 mm) and much larger compared to the higher velocity cases. The droplet size can be roughly estimated with Tate’s law (Tate, 1864) which considers a simple force balance of gravity and surface tension:

\[ d_p = \sqrt[3]{\frac{6\pi D_{cap}}{\rho g}} \]  

with the capillary diameter \( D_{cap} \), surface tension \( \sigma = 0.58 \text{ Nm}^{-1} \) and density \( \rho = 2719 \text{ kgm}^{-3} \) of the slag. Here, Eq. (1) yields \( d_p = 5.27 \text{ mm} \), which is in agreement with the experiments within 1.4%. The droplet formation frequency is around 6.45 Hz which is relatively low and similar to the frequency of droplet formation in dripping mode at 1600°C found in a previous study (Wegener et al., 2014b). During detachment, a thin liquid bridge connects the droplet with the remaining liquid at the capillary which eventually snaps off due to increasing Laplace pressure. The droplet accelerates in gravity while the thread retracts quickly to merge with the hanging liquid reservoir to form the next droplet.

From 0.6 bar onwards, jetting regime is established. Instabilities occur which grow in time and space, and correspondingly, necks and swells appear. The swell diameter grows while the neck diameter diminishes until the jet breaks up. The jet length increases with increasing jet velocity. Moreover, the jet length is not constant in case of natural breakup as the jet retracts after each droplet detachment due to the unbalanced force of surface tension. It was shown that the jet length is normally distributed around a mean value (Leroux et al., 1996; Wegener et al., 2014b). If the jet is only subject to surface tension and inertia forces, the unbroken jet length \( L_{jet} \) can be estimated with the following equation (Grant & Middleman, 1966; Weber, 1931):

\[ \frac{L_{jet}}{d_{jet}} = \ln \left( \frac{R_{jet}}{\varepsilon_0} \right) + \sqrt{We_{jet} + \frac{3}{Re_{jet}}} \]  

with \( \ln(R_{jet}/\varepsilon_0) = 12 \) (Haehnlein, 1931) and the jet diameter \( d_{jet} = 1.12 \text{ mm} \). Reynolds and Weber numbers are listed in Table 1, in which \( Re = d_{jet} \rho v_{jet} \mu^{-1} \) and \( We = d_{jet} \rho (v_{jet})^2 \sigma^{-1} \) with the slag viscosity \( \mu = 0.237 \text{ Pa s} \). The values obtained from Eq. (2) are also given in Table 1. The deviation is displayed in the last column. The agreement is reasonable in Trials 2 – 6, being within 20%. One has to consider that the experimental jet length is distributed and hence not represented by one discrete value, but by a mean value and a standard deviation.

The size of droplets which are formed from disintegrating jets in Trials 2 – 6 are considerably smaller than those formed in the dripping regime (Trial 1), see the corresponding column in Table 1. In the ideal case, the volume of liquid between two necks (i.e within one wavelength \( \lambda \)) forms one droplet. Tyler (1933) showed that in this case the following equation may be applied to estimate the droplet size \( d_p \) from the jet diameter \( d_{jet} \):

\[ d_p = 1.89 d_{jet} \]
Eq. (3) predicts $d_p = 2.12$ mm with $d_{jet} = 1.12$ mm. The values in Table 1 confirm that the droplet size can be predicted with Eq. (3) with a better accuracy if the jet velocity is higher. This reflects the fact that instabilities are convected predominantly downstream at higher Weber numbers and hence grow according to the stability theory which leads in average to Tyler’s ‘one wavelength = one droplet rule’.

**Figure 2:** Breakup of slag jets issuing from a graphite capillary at 1660°C for different driving pressures. The first five cases show natural breakup, whereas the last case displays a jet subject to periodic excitation (pneumatic turbine vibrator, $f = 280$ Hz). The first case exhibits very short jets and a large droplet size, hence dripping mode close to transition mode. The scale on the left hand side is in mm. Note: the curved surface on the bottom left hand side on each image is the oxygen sensor.
However, in natural breakup mode, non-linearities occur which may result in the formation of smaller satellite droplets. Also, the liquid volume corresponding to more than one wavelength may form one droplet from time to time. These phenomena result in droplet sizes being distributed around a mean value and, in the case of satellite droplet formation, the size distribution being bimodal rather than unimodal. One way to enhance the jet disintegration performance in terms of repeatability, predictability and reliability is to apply a mechanical perturbation which overrules the natural perturbations by several orders of magnitude.

In Trial 6, a mechanical vibration was imposed on the jet. The required frequency was predicted based on the wavelength $\lambda$ and jet velocity $v_{\text{jet}}$ measured in Trial 5, according to the equation

$$f = \frac{v_{\text{jet}}}{\lambda}$$

(4)

which yields $f \approx 230$ Hz with $\lambda \approx 6$ mm. In order to benefit from the larger vibration amplitude of the pneumatic turbine vibrator at higher frequencies, a frequency of 280 Hz was chosen. This frequency is subject to some uncertainties since the calibration had to be done under ambient temperature conditions, hence it is assumed that the mechanical vibration imposes the same perturbation on the capillary at experimental temperature. Thus, it was decided to overestimate the frequency rather than to underestimate it.

The result can be seen on the last image in Fig. 2. The jet length is 30% shorter than in the corresponding case without external vibration and can obviously not be predicted by Eq. (2). The jet length distribution is narrower than in Trial 5 and fluctuates $\pm$ 5 mm (Trial 6) instead of $\pm$ 15 mm (Trial 5). The droplet formation is highly repetitive and uniform. In contrast to Trial 5, no satellite droplets were observed throughout the whole recorded sequence. The droplet formation frequency was found to be around 250 Hz which corresponds very well with the expected value.

CONCLUSIONS

High temperature experiments on calcia/alumina slag jets have been performed at 1660°C in a specially designed three-zone furnace in argon atmosphere with optical access to investigate the dynamics of their breakup into droplets. The main scope of this work is to investigate whether a narrow drop size distribution at high droplet formation rates can be achieved from the controlled disintegration of vertical jets to enable further experimental investigations towards the design of a direct contact liquid droplet heat exchanger (DHX).

The jets issued from a graphite capillary at different flow rates. The transition from dripping to jetting was identified at Reynolds numbers around 8 and Weber numbers at around 2. In dripping regime, the droplets were relatively large; the size could be predicted with reasonable accuracy using Tate’s law. The droplet formation was highly repetitive, but the formation frequency was relatively low (approx. 6 droplets per second).

In jetting regime, the jet disintegration was subject to non-linearities which resulted in wider and multimodal drop size distributions due to satellite droplet formation. The unbroken length increased linearly with jet velocity and could be predicted within acceptable error margins. Also, with increasing velocity, the droplet formation rate increased. However, due to the above mentioned irregularities, natural breakup is not a desirable mode in a potential DHX process.

The impact of an external excitation was finally investigated. The mechanical vibration was imposed by a pneumatic turbine vibrator which was mounted on the furnace rig at a
frequency which corresponded to the wavenumber at which the instabilities grow fastest. The results were more than promising and proved the suitability of this approach for a potential DHX: the jet length was relatively constant and was decreased by 30% compared to the case without external vibration. This will reduce the expected height of a potential DHX. The droplet formation rate corresponded to the applied frequency at given jet velocity. Higher throughput seems to be possible if the required pressure differential can be applied at high temperatures to increase the nozzle exit velocity. The droplet size is uniform and was approximately 1.89 times the jet diameter. This enables the calculation of surface area available for heat transfer. The formation of satellite droplets was completely suppressed which resulted in a narrow drop size distribution.

The successful experiments initiated further experimental activities. Currently, a multiple capillary head is being developed in order to investigate the behaviour of multiple jets issuing simultaneously from separate nozzles. This is considered as the next step necessary towards a liquid droplet heat exchanger using molten oxides as heat transfer medium.

**Nomenclature**

- $d_p$: droplet diameter, m
- $D_{cap}$: diameter of capillary, m
- $f$: frequency, Hz
- $g$: gravitational acceleration, m/s$^2$
- $ID$: inner diameter, m
- $L_{cap}$: length of capillary, m
- $L_{jet}$: jet length, m
- $\Delta p$: pressure difference, bar
- $R_{jet}$: jet radius, m
- $v_{jet}$: jet velocity, m/s
- $V$: volume, m$^3$
- $\varepsilon_0$: initial perturbation amplitude, m
- $\lambda$: wavelength, m
- $\mu$: dynamic viscosity, Pa s
- $\rho$: density, kg/m$^3$
- $\sigma$: surface tension, N/m
- $Re_{jet}$: jet Reynolds number, $Re_{jet} = \frac{d_{jet} \rho v_{jet} \mu}{\nu}$
- $We_{jet}$: jet Weber number, $We_{jet} = \frac{d_{jet} \rho (v_{jet})^2 \sigma}{\mu}$
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Investigation of Splashing at Different Sampling Positions and Cavity Modes in Oxygen Steelmaking

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**Keywords:** Steelmaking, Splashing, Penetrating

In oxygen steelmaking, study of splashing is an essential part of understanding and optimizing the process. Various hot models, cold models and plant trials have been carried out previously to estimate the droplet generation rate and amounts of droplets present in the emulsion. Sampling technique has been commonly used in this regard and in most of the cases, samples were collected from one place of the emulsion to estimate the droplet generation rate. A recent comprehensive plant trial [1,2] on improving phosphorus refining (IMPHOS), commissioned by European Union, was carried out in a 6 t Pilot plant BOS converter at the Swerea MEFOS Metallurgical Research Plant in Sweden. A fully automated sampling system was used to collect samples from seven specified positions in every 2 minutes. The sampling lance was kept 0.045 m offset from the centre of the converter (as shown in Figure 1). Critical analysis of previous studies shows that variations were found in the reported droplet amount and in the rate of droplet generation. In the present study, variations in droplet generation rates in different sampling positions have been investigated quantitatively.

![Figure 1: Schematic of BOS converter in IMPHOS study and sampling positions [1]](image)

Molloy [3] described three cavity modes (i.e. dimpling, splashing and penetrating) and stated that splashing was reduced as cavity mode changed from splashing to penetrating. Subagyo et al. [4] proposed a new dimensional number “Blowing number” (N_B) which is a ratio of inertia force to buoyancy and surface tension forces. The Blowing number theory suggests that increase in N_B always results into increase in the generation of droplets. But the theory has not been investigated for penetrating cavity mode. Though there are few studies [5]
which showed the reduction of splashing in top jetting condition as lance got closer to the bath, no works could be found that studies the issue of splashing in different sampling positions, various cavity modes and the theory of Blowing number for a wide range of operating conditions. In the present experimental work, a comprehensive effort has been made to quantify splashing in different Blowing numbers as well as in cavity modes and to show how droplet generation rate is affected by the sampling positions inside the bath.

In the current investigation, a 1/5th cold model of the BOS converter in IMPHOS [1] has been used for a single phase compressed air-water study. A top lance was kept at the centre of the bath. Heat S1845 of the IMPHOS investigation [1] was taken as the target heat number to compare the results with the present work. The geometric and dynamic similarity between the model and the IMPHOS converter were maintained as much as possible. Blowing number similarity criteria was given preference as suggested by Subagyo et al. [4]. Five sample pots were put in five different vertical sampling positions (i.e. 0.024 m, 0.074 m, 0.124 m, 0.174 m and 0.224 m above the bath surface) which were scaled down from the actual sampling positions of IMPHOS study. Also, the radial sampling positions of the sample pots were also varied (i.e. 0.033 m, 0.060 m, 0.090 m, 0.120 m, 0.150 m, and 0.180 m away from the lance). At each radial position, droplets were collected in the vertically positioned sampling pots for duration of 3 seconds to 150 seconds, depending on the droplet generation rate.

Figure 2 shows the distribution of droplets among sample pots which varied radially and vertically. Sample pots which were closest to the bath surface (i.e. 0.024 m and 0.074 mm above bath surface) showed maximum variation in the amount of droplets with the rest of sample pots.

![Figure 2: Droplet distribution among five sample pots](image)

High speed imaging of the cavity showed that sheet like structures were formed and fell into the sample pots closest to the bath surface. That is why; droplets weight collected in the sample pots closest to the bath was quite greater than that of other pots. This conclusion implies that in the calculation of droplet generation rate, droplets collected in the sample pots closest to the bath needs to be avoided as they collects the sheets, not the actual droplets. High droplet generation rate was reported in IMPHOS [1] study. Present analysis showed that due to the sample positions of present study being equivalent to that of IMPHOS, counting droplets collected in the sample pots closest to the bath may have produced an overestimated droplet generation rate.
Figure 3 represents the results of present study and relation proposed between droplet generation rate per volumetric flow of blown gas ($R_B/F_g$) and $N_B$ by Subagyo et al. [4]. Results from this cold modelling study showed that $R_B/F_g$ was dependent on both lance heights and Blowing number. At a constant lance height, as $N_B$ increased, droplet generation rate per volume flow rate of blown gas also increased in general. But clear distinction could be found between higher lance heights (i.e. 0.170 m, 0.160 m and 0.150 m) and lower lance heights (from 0.120 m to downwards). When lance height was lowered to 0.120 m, there was radical reduction in the value of $R_B/F_g$. This was due to the change in cavity modes from splashing to penetrating. The results of current work were also compared with the empirical equation proposed by Subagyo et al.[4]. Figure 3 showed quite distinctively how splashing rate was affected by the occurrence of cavity modes and why it is important of identifying various cavity modes in the study of steelmaking. High $N_B$ does not necessarily indicate increase in splashing. $N_B$ along with cavity mode is required in estimating droplets amount. These are consistent with the findings of Alam et al.’s [6] angle jet experimental work.

![Figure 3: $R_B/F_g$ vs Blowing number](image)

**Reference**

Surface Tension Measurements of 430 Stainless Steels Using the Electromagnetic Levitation Technique

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Keywords: contamination, electromagnetic levitation, oxygen, surface tension, undercooling

430 stainless steel (SUS430) shows a slightly degraded corrosion resistance than 304 stainless steel (SUS304), but a similar mechanical property as SUS304 [1]. However, SUS430 does not contain nickel, and it is considered as a cost-effective anti-corrosion material for general use. Although mechanical properties of SUS430 are well-known, physical properties in molten state have not been studied well.

Surface tension is one of the important thermo-physical properties of liquid steel. Surface tension data is essential to understand various phenomena in refining, casting, and welding processes such as separation of inclusions from steel to slag, spreading of inclusions in slag, nucleation of bubbles and inclusions, growth of bubbles and inclusions, floating by Stokes law, inclusion absorption time, shaping of welding pool. [2-4]

There are several kinds of surface tension measurements techniques; sessile drop method, maximum bubble pressure method, pendent drop method, detachment method, liquid surface contour method, capillary rise method, and levitation method. Most of them are contacting with a crucible or a refractory ceramic material, but the levitation method is a non-contacting method. Eventually, at high temperatures, contamination of liquid steel by the ceramic material is inevitable. Therefore, in order to get a reliable surface tension data, a non-contacting method is preferred.

At high temperatures, three types of non-contacting methods can be applied: (1) electromagnetic levitation, (2) electrostatic levitation, (3) aerodynamic levitation. Among them, only the electromagnetic levitation method can be applied at a constant temperature under different oxygen partial pressures by controlling the gas mixtures. Since the levitation method prevents the heterogeneous nucleation, we may investigate the surface tension of undercooled liquid as well.

In the present study, the surface tension of SUS430 was investigated with the electromagnetic levitation method. Experimental details can be found in ref. 5. For comparison, the surface tension was measured with a contacting method (constrained drop method – an advanced sessile drop method [6]). The experimental results were compared with theoretically and empirically calculated values.

Surface tension was investigated at temperatures in the range of 1,707 ~ 2,000 K under a H₂-He gas mixture using the electromagnetic levitation method. Temperature dependence of the surface tension was obtained as follows.

\[ \sigma(N/m) = 3.158 - 7.769 \times 10^{-4} T(K) \] (1)
The surface tension at 1823K was estimated to be 1.742 N/m from Eq. (1). On the other hand, the experimental result with the constrained drop method was 1.615 N/m.

The oxygen content analysis showed that the former had 7 ppm of oxygen, and the latter 60 ppm. Therefore, it was suspected that the surface tension difference came from the contamination of the sample from the alumina crucible used in the constrained drop method.

Surface tension of binary and ternary alloys can be calculated using Butler’s equation theoretically [7]. If we consider SUS430 as a ternary alloy composed of major Fe, Cr, and Si, the surface tension can be calculated. The calculated value at 1823K was 1.866, which is much higher than the measurements.

Lee et al. reported that the surface tension of Fe-Cr-O alloys at 1823 K as a function of Cr and O content [8].

\[ \sigma = 1.842 - 0.279\ln(1 + K_\text{O}a_\text{O}) \]  

(2)

Where \( K_\text{O} (=140+4.2[\text{wt}\%\text{Cr}]+1.14[\text{wt}\%\text{Cr}]^2) \) is the adsorption coefficient, and \( a_\text{O} \) is the activity of oxygen. At the oxygen content of 7 and 60 ppm, the surface tension was estimated to be 1.800 and 1.660 N/m, respectively. If we consider that the experimental error of the measured values, the agreements between the measurements and the predicted ones using Eq. (2) are acceptable.

In conclusion, the surface tension of SUS430 was successfully investigated using the electromagnetic levitation method. The temperature dependence was obtained as \( \sigma(N/m) = 3.158 - 7.769 \times 10^{-4} T(K) \). For comparison, the surface tension was measured separately with the constrained drop method, and evaluated using a theoretical model and an empirical model. By comparing the experimental and theoretical results, it was concluded that oxygen contamination is crucial in the surface tension measurements.

References

Minerals, metals and innovation in the circular economy

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Keywords: recycling, wealth from waste, resources, futures

Factors underpinning current modes of production and consumption are changing. Ore grades are declining in Australia, requiring more energy for processing and creating more environmental impact. Both resource and energy constraints are driving the need for innovation focussed on doing ‘more with less’. Geographies of production are also changing and this is opening up new opportunities for increased recycling in the circular economy – however these are yet to be systematically evaluated.

This paper provides an overview of the research agenda for understanding required innovation in the way minerals and metals are managed in a circular economy in Australia. It begins with an overview of the Vision 2040: Innovation in mining and minerals [1] developed by multiple stakeholders and which focused on the need for a national minerals strategy and sovereign, transformational technology including that for recycling, and the potential for ‘brand Australia: responsible minerals ’.

It then presents ‘Wealth from Waste’, the name of a new three year research collaboration between CSIRO, UTS, University of Queensland, Swinburne, Yale and Monash exploring ways to harness value from above ground stocks of metals in Australia with a focus on industrial ecology and circular economy, considering (i) the size and value of the available resource (ii) socio-technical systems needed to overcome barriers to industrial ecology and (iii) new business models which would facilitate the harnessing of wealth from waste.

The circular economy has significant overlap with concepts of industrial ecology. Whilst first described by Pearce and Turner in 1990 [2] its prominence has risen recently with its inclusion in China’s Twelfth Five Year Plan as well as via publications from the Ellen Macarthur Foundation in the UK. Circular economy concepts can be considered at several spatial scales, from that of an industrial complex where wastes from one site may provide raw material inputs to another – all the way to the level of a region or national economy. In each case the focus is on circular flows of resources (via reuse and recycling).

Finally illustrative cases of iron, copper, gold and lithium are used to illustrate key questions in the future research agenda. Areas requiring focus include (i) the tension between developing increasingly complex products manufacture which are harder to recycle and simpler designs (ii) a broader conceptualisation of value (including social and environmental dimension) to underpin the economics of recycling in a circular economy and (iii) the need for a transition plan to guide integration between disciplines and sectors to harness opportunity for Australia in the circular economy.

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Collaboration: the key towards a resource resilient society

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Keywords: sustainable development, entrepreneurship, innovation

The global demand for technology materials is continuously increasing as the world’s population grows and high standards of living are sought in developing and transition countries. To secure a reliable and sustainable supply of these metals, innovative solutions need to be developed along the entire value chain. This requires a system-wide, collaborative approach focusing on sustainable mining methods, substitution of critical metals and recovery of metals from secondary sources.

By recovering materials from end of life fractions, Umicore is contributing to the circular economy and the ongoing supply of (critical) metals. Next to being an integral part of the recycling chain, Umicore co-operates with other stakeholders along the value chain. It is part of a larger eco-system that involves the manufacturing industry via the treatment of production wastes and interfaces with the mining and primary smelter industry for eco-efficient treatment of by-products and residues. The complex metallurgy needed to recover metals in low concentrations from intermediates and end-of-life products will be illustrated by means of Umicore’s flowsheet.

To further develop and enlarge symbiotic eco-systems in which every industry can benefit from each other presence, multi-stakeholder partnerships that foster innovation and entrepreneurship are called for. The value of these partnerships for increasing the resource resilience to supply instabilities is recognized on the global as well as regional level. The EU-Japan-US trilateral roundtable on critical raw materials brings together different stakeholders from across the world. In the US, the aspect of cross-sectoral interaction is implemented through the formation of Energy Innovation Hubs, among others. In Europe, a new innovation strategy for raw materials is being implemented through different initiatives, including the European Innovation Partnership (EIP) and a potential Knowledge and Innovation Community (KIC) on raw materials. The primary focus of the KIC is to develop the human capital and entrepreneurs that are key to drive innovation. By doing so, the KIC will contribute to bridging the gap between strategic objectives and the implementation of sustainable and holistic materials solutions by entrepreneurs.
Protecting the future – Investigation of phase equilibria and freeze linings in novel high temperature recycling processes

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Keywords: phase equilibria, freeze lining

Introduction

In pyrometallurgical processes where high temperatures and/or corrosive slag systems are used, excessive deterioration of the refractory lining is often a problem. One of the newer technologies to protect the furnace wall is freeze lining. A freeze lining is formed by cooling down the furnace wall and solidifying part of the slag onto the wall to form a protective layer. Previously, the interface between the bath and freeze lining was mostly assumed to be the primary phase at the liquidus temperature [1-2]. Recent research, though, has demonstrated that this is not always the case [3]. The present research focuses on the determination of the effect of several slag and process parameters on the bath-freeze lining interface.

Further study is undertaken with a Cu-Fe-Si-O slag in an MgO crucible. This slag system is important in copper smelting, particularly in the “direct to blister” process. The MgO crucible was chosen to minimise the limitations introduced by the high solubility in slag of Al₂O₃ crucibles used in previous studies [3]. The liquidus in the multi-component Cu-Fe-Si-Mg-O system has not yet been investigated. In an earlier stage of the research, the liquidus in this system at low MgO concentrations in equilibrium with copper at temperatures between 1100 and 1300°C was characterised. This information will be used to interpret results obtained from the freeze lining experiments.

Procedure

An air-cooled probe is submerged in liquid slag inside an MgO crucible to create a freeze lining. Temperatures in the freeze lining, probe and bath are measured by installing thermocouples in these respective positions. After reaching steady state, the probe with attached freeze lining is taken out of the bath and quenched in water. The quenched freeze lining is then investigated using electron-probe X-ray microanalysis (EPMA). Phase equilibria of the system are determined separately using a high-temperature equilibration/quenching/EPMA technique.

Determination of interface temperature

The thermocouple measurements in the freeze lining, combined with the 1-D thermal steady state model for heat transfer through a freeze lining can be used to estimate the interface temperature between bath and freeze lining. However, from previous research [4], it can be seen that the deviation between the steady state heat transfer model and thermocouple measurements can be up to 30 °C. As the interface temperature is the primary focus of the current research, it is opted to use an additional method to confirm the interface temperature. As mentioned above, the phase equilibria of the model slag system were determined at temperatures between 1100 and 1300 °C. Knowing these phase equilibria, it is possible to determine the steady state temperatures inside the freeze lining by measuring the composition...
of phases in the freeze lining and comparing them to the equilibrium compositions. This can only be done if equilibrium is reached between phases inside the freeze lining. According to the dynamic steady state model proposed by Mehrjadi et al. [4], this should be the case for the bath-freeze lining interface at steady state if no sealing crystal layer is formed.

**Phase equilibria results**

The liquidus surface of the system at 1200 °C is projected onto the ‘Cu₂O’-‘Fe₂O₃’-SiO₂ plane (Figure 1) and the corresponding pseudo-ternary section with preliminary results is given in figure 2. Measured MgO concentrations have been reported next to the projected compositions on the diagram (Figure 2). Similar projections have been constructed for the isothermal liquidus surfaces at 1100, 1150 and 1250 °C.

![Phase equilibria results](image)

**Figure 1:** Sketch of the projection method used in the current study

In regard to the freeze lining experiments, the liquidus surfaces of interest are those of pyroxene and olivine. These MgO-rich phases are expected to form onto the MgO crucible used in the experiments, slowing down further reaction between slag and crucible. From figure 2, we can observe that the maximum amount of MgO in the slag in order to maintain a liquidus temperature of 1200 °C or less in these primary phase fields increases with increasing SiO₂/‘Cu₂O’ ratios. The suitable SiO₂ concentrations range from 0 wt% to approximately 33 wt%, allowing for a variety of slag viscosities to be tested.

**Conclusions**

A method is proposed to accurately determine the interface temperature between bath and freeze lining. Phase equilibria, needed for this method, have been determined in the first stage of the research. Future stages will concentrate on the effect of several slag and process parameters on the interface temperature.
Figure 2: Projection of the measured and estimated 1200 °C isothermal liquidus surfaces in the tridymite, pyroxene, olivine and spinel primary phase fields at copper saturation in the Cu-Fe-Si-Mg-O system.

Acknowledgements

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References

Modelling of Nickel Laterite Smelting to Ferronickel

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Keywords: nickel laterite smelting, ferronickel

Most nickel is produced as the metal, but about a third of the world’s new nickel is ferronickel. World annual production of ferronickel is around 250,000 tonnes, with the two largest producers being BHP Billiton and Société Le Nickel (Cartman, 2010). Most of the world’s accessible nickel reserves are oxidic ores called “laterite” (Sudol, 2005), and are the result of chemical weathering and supergene enrichment of mafic/ultramafic rocks. They vary greatly in depth, nickel grade and mineralogy (Dalvi et al., 2004). The lower layers are called “saprolite” and have nickel contents from 1.8 to 3 wt-%, relatively low iron contents but high magnesia and silica contents and are suited to pyrometallurgical processing (Cartman, 2010).

Laterite is mined by open cut methods, upgraded by screening to remove low-nickel bedrock, then crushed (Figure 1a). It contains about 35 wt-% free water so is dried in a rotary kiln, with the product still containing approximately 10 - 13 wt-% water. Most of this water is chemically bound within such minerals as garnierite \((\text{Mg},\text{Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4\) so 700 to 900°C is needed to remove it. The dried material, with some added coal, passes to rotary kilns where a flame heats the material. The coal volatiles and some of the fixed carbon partially reduce the ore. The remaining fixed carbon acts as the reductant in the following smelting step. Hot calcine is fed to an electric furnace (Figure 1b) where the remaining \(\text{Fe}_3\text{O}_4\) is reduced to \(\text{FeO}\) and the \(\text{NiO}\) and \(\text{CoO}\), together with part of the \(\text{FeO}\), are reduced to molten ferronickel. The gangue oxides form slag. Finally, the molten ferronickel is refined to remove phosphorus and sulphur and, if necessary, to adjust the carbon and silicon contents to meet market specifications Crundwell et al. (2011). The flowsheet described above is commonly referred to as the “RKEF process” (Walker et al., 2009) due to its use of rotary kilns (RK) and electric furnaces (EF). Typical industrial data was given by Warner et al. (2006) and part of this is shown below for several smelters.

Table 1 – Typical industrial data from Warner et al. (2006)

<table>
<thead>
<tr>
<th>Laterite feed</th>
<th>Alloy Ni grade</th>
<th>Slag/alloy mass ratio</th>
<th>Furnace recoveries</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe/Ni</td>
<td>SiO₂/MgO</td>
<td>wt% Ni</td>
</tr>
<tr>
<td>1. Falcondo</td>
<td>10.5</td>
<td>1.6</td>
<td>38.5</td>
</tr>
<tr>
<td>2. Codemin</td>
<td>11.7</td>
<td>1.6</td>
<td>28</td>
</tr>
<tr>
<td>3. Cerro Matoso</td>
<td>7.0</td>
<td>2.8</td>
<td>35</td>
</tr>
<tr>
<td>4. Loma de Niquel</td>
<td>11.5</td>
<td>1.3</td>
<td>22.5</td>
</tr>
<tr>
<td>5. Doniambo</td>
<td>4.8</td>
<td>1.75</td>
<td>25</td>
</tr>
<tr>
<td>6. Pomalaa</td>
<td>6.1</td>
<td>1.6</td>
<td>19</td>
</tr>
<tr>
<td>7. Pamco</td>
<td>6.1</td>
<td>1.6</td>
<td>18.5</td>
</tr>
</tbody>
</table>
The oxides in the feed are NiO, FeO, SiO$_2$ and MgO and the reductant is carbon. The Ellingham Diagram (as shown in Figure 2) shows that at 1500 – 1600°C, under standard state conditions, there is a thermodynamic driving force for the reduction of NiO and FeO by carbon, but that SiO$_2$ and MgO are too stable to be reduced. Preferential reduction of NiO should be possible. However, NiO is not present at unit activity but is dissolved in slag at low activity. The lines representing the equilibrium oxygen potential of the Ni/O$_2$(g)/NiO reaction at low NiO activities are also shown. It is now apparent that FeO reduction to iron is favoured when nickel recovery is high. The recovery of nickel will increase as the iron content of the alloy increases and the FeO content of the slag will decrease. However, nickel recovery also depends on the masses of ferronickel and slag produced and the slag mass is always much greater than the ferronickel mass. Solar et al. (2008) reported that the mass ratio of slag/ferronickel ranges from approximately 10 to 30 so typical nickel recoveries vary from 90 - 95%. Silicon will also be present in ferronickel at very low activity so a little silica reduction to silicon is expected at the higher extents of reduction. The reduction reactions are strongly endothermic so the required energy input will be large, being typically about 500 kWh/tonne of calcine (Warner et al., 2006).
The nickel grade of the ferronickel is a function of customer preferences (Solar et al., 2008) and ranges from 17 wt-% to almost 40 wt-% Ni. They showed that the extent of iron reduction is the best indicator of reducing conditions. Ferronickels from high iron reduction smelters contain significant amounts of carbon, silicon and chromium. Liquidus temperatures range from 1450-1460°C for low carbon alloys to 1250 - 1350°C for high carbon alloys. However, the minimum furnace temperature is set by the slag because it typically has a liquidus temperature above 1550°C. In fact a ferronickel furnace is mainly a producer of slag, which comprises over 90% of the furnace output. Modification of the slag composition through the addition of fluxes would require large amounts of flux and so is rarely economic (Utigard, 1994). It follows that the properties of the slag are determined by the SiO₂/MgO ratio of the laterite ore and the concentration of unreduced FeO.

Typical calcine feeds were taken to contain 2 wt-% total Ni, have Fe/Ni (wt-%/wt-%) ratios of 5 and 10 and have a SiO₂/MgO (wt-%/wt-%) ratio of 1.8. Nickel metallisation was taken as 20% and iron oxides were assumed to comprise 40% Fe⁴⁺ and 60% Fe²⁺ based on the data of Daenuwy and Dalvi (1997). The activity coefficients of all gas species were taken as unity. The activities of iron and nickel in ferronickel alloys were determined by Conard et al. (1978) and showed that the activity coefficient of iron is close to unity and that of nickel is 0.65. The activity coefficients of carbon and silicon in molten ferronickel were estimated using the dilute solution model described by Sigworth and Elliott (1974). A representative activity coefficient of carbon was determined to be 1.3 and that of silicon 0.003. Kojima et al. (1969) determined the activity of FeO in FeO-MgO-SiO₂ slags at 1600°C. A value of unity was taken to be a satisfactory representation for typical ferronickel slags. The activity coefficient of Fe₂O₃ was taken as unity because it would not be present in the final slag. Experimental activity data for SiO₂ in FeO-SiO₂-MgO slags could not be found so FactSage 6.3.1 software using the FToxid solution database for liquid slag and FSstel solution database for the liquid iron was used to calculate values. A value of unity was also taken to be a satisfactory representation of the activity coefficient of SiO₂(cr) for typical ferronickel slags. The activity coefficient of NiO(s) in FeOₓ-MgO-SiO₂ slags at 1500 °C was determined Henao et al. (2001) and an average value for the activity coefficient of NiO(s) of 3.5, independent of the FeOₓ content of the slag, was reported. At 1550 - 1600°C the activity coefficient of NiO was taken as 3. The appropriate temperature for modelling was taken to be 1550°C.

![Graphs](image-url)

**Figure 3:** (a) The recovery of Ni, Co and Fe with carbon (Fe/Ni = 10); (b) the variation of ferronickel composition with carbon (Fe/Ni = 5)

The recoveries of nickel, cobalt and iron are shown in Figure 3(a) for the feed having an Fe/Ni ratio of 10. The recovery of nickel is close to 100% at 20 kg/tonne of carbon, with the cobalt recovery being about 90%. Iron recovery increases almost linearly with the quantity of carbon in calcine. The composition of the ferronickel is shown in Figure 3(b) for a calcine
with Fe/Ni = 5. Alloys containing 35 - 40 wt-% Ni require about 10 kg of carbon per tonne of calcine i.e. 1 wt-% carbon in calcine. Alloys containing 17 - 20 wt-% Ni require about 25 kg per tonne of calcine i.e. about 2.5 wt-% carbon in calcine. These carbon contents are in good agreement with those used in practice (Crundwell et al., 2011).

The carbon and silicon contents of ferronickel are given in Figure 4(a), together with the cobalt content, for the calcine having an Fe/Ni ratio of 5. The cobalt concentration quickly reaches a maximum, then decreases as more iron is reduced into the alloy. There is a steep increase in both silicon and carbon contents at high levels of carbon in calcine. For the calcine having an Fe/Ni ratio of 10 the carbon and silicon contents are negligible. These qualitative trends are consistent with published industrial data (Warner et al., 2006). The smelting of calcines with low Fe/Ni ratios results in significant carbon and silicon contents in the ferronickel because when low grade alloys are produced the FeO content of the slag is much lower than when calcines with high Fe/Ni ratios are smelted. The oxygen partial pressure in the system is a function of the concentration of FeO so the oxygen partial pressure is much lower when low Fe/Ni calcines are smelted to low nickel alloys.

![Figure 4](image-url)  
**Figure 4:** Predicted ferronickel composition, Co, Si and C (Fe/Ni = 5)

Comparison of the model predictions with industrial data is not possible on the basis of the amount of carbon in calcine, because this figure is rarely reported. Solar et al. (2008) used the iron recovery in the ferronickel as a measure of the extent of reduction, and this permits useful comparisons to be made. The numerical key for the smelters is given on the table of industrial data (Table 1). The relationship between nickel grade and iron recovery (Figure 5(a)) is shown and the agreement between the model predictions and the industrial data is seen to be excellent. The predicted carbon content of ferronickels was compared to plant data as shown in Figure 5(b). That for the low iron reduction smelters is in acceptable agreement with the predictions, but that for the high iron recovery smelters is not. This discrepancy has also been found by others using different computational thermodynamics software.

No explanation for this discrepancy can be offered. Whatever the cause, it is common to both carbon and silicon, and is unlikely to be thermodynamic in origin because both concentrations are little affected by the extent of iron reduction i.e. the oxygen partial pressure in the furnace.

Overall, the modelling of the electric furnace smelting of nickel laterite calcines has provided useful insights into the nature of the process, especially the way in which the Fe/Ni ratio of laterite and the target nickel grade of the ferronickel affect process performance.
Figure 5: Comparison of the model’s results with industrial data in Table 1: (a) nickel grade vs iron recovery, (b) carbon content vs iron recovery

References
Monitoring the Operation of Aluminium Smelter Cells using Individual Anode Current Measurements

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Keywords: Aluminum smelting, Individual anode current, Anode effect, Fault detection

In recent years, productivity and flexibility of aluminium smelting are becoming important economic drivers due to the changing cost structure. In modifying operating practices to meet these requirements there is an increase in occurrence of abnormalities, such as anode effect, which impacts control strategy as well as cell performance [1]. Therefore it is important to monitor the cell conditions during operation to detect the anomalies that will adversely affect the efficiency of operation. Monitoring and control in the Hall Heroult process are commonly based on the continuous measurements of cell voltage and line current. They reflect global process behaviour, and are used to regulate average alumina concentration, and to maintain voltage balance as well as overall heat balance in the cell [2]. Nevertheless, the Hall Heroult process is highly distributed and exhibits a strong internal coupling between process parameters. This makes cell control based on the cell voltage and line current measurements difficult to address changes in local cell conditions and to isolate process abnormalities at a localised level, especially for large modern cells, since spatial variations are more significant as cell dimensions increase [3].

Supported by the CSIRO Cluster on Breakthrough Technologies for Aluminium Reduction, the UNSW team investigated an approach to cell monitoring and fault detection based on the measurements of individual anode current, including an instrumentation scheme and analysis tools for different abnormal conditions. The use of individual anode current signals to increase observability of local cell conditions has been proposed in literature (e.g. [4]). Although monitoring individual anode current signals holds a great potential for cell supervision and control, its application in industrial reduction cells has been limited [5], perhaps due to the lack of cost effective instrumentation schemes and analysis tools.

Instrumentation scheme development. A high-speed anode current distribution measurement system was developed to sample all anode currents (at the rate of 10 to 30 samples per second). The system was designed to cope with the harsh environment in the potrooms (high temperature and strong magnetic fields). The individual anode current signals on the anode rods were determined by measuring the voltage drop over a set distance between the bottom of the anode beam and above the cell hood. The voltage drop is amplified and fed into a data acquisition system as differential voltage input. In order to correctly estimate the individual anode current from the measure anode rod voltage drop readings, the anode rod temperatures are measured to calibrate the resistance of the anode rod material at the locations of the voltage drop measurement. All wiring was secured in high temperature wiring looms and held securely in place to limit possible damage during cell operation. The system was successfully trialled at one of our industrial partners’ premises. The data acquired from the operating cell includes real-time individual anode currents, cell voltages, anode rod temperatures at different locations, and event logs during normal operating conditions, certain measurements of bath temperatures, superheat and bath composition analysis.
**Anode current analysis.** To characterize the individual anode current signals during different operating conditions (normal and abnormal conditions), a series of experiments were conducted where deliberate disturbances were introduced to an industrial operating cell. Individual anode current signals were recorded together with other cell measurements. Some interesting observations were obtained. In addition to time domain analysis, frequency domain analysis was carried out to study the “features” of anode current dynamics. Here are some of the highlights:

- **Anode setting.** The current pick up profile over time for a new anode from the time of setting till approximately 12 hours after setting is shown in Fig. 1. The trend has three distinct regions. The first region involves an initial fast uptake of current and cracking of freeze may be occurring which makes more of the anode accessible to the bath and able to carry current. The second region shows a slowdown of the initial current uptake rate and the anode may initially be consumed more at the sides. Region 3 shows the steady uptake of current up to the full current carrying capacity. A frequency response of the anode current at different regions is presented in Fig. 2. Region 3 shows the typical anode current dynamics where the peak at 0.8-1.2 Hz is associated with bubble release at the surface of the anode. The amplitude of the peak is seen to increase as the newly set anode approaches stage 3.

![Figure 1: Anode rod voltage drop readings](image1.png)  
![Figure 2: Frequency response of a newly set anode](image2.png)

- **Anode effect.** An anode effect arises when anodes are passivated by an insulating layer of bubbles produced by carbon side reactions when the alumina concentration at the anode surface is depleted, leading to concentration polarization and the discharge of fluoride ions [6]. An anode effect often starts at a localized level due to local depletion of alumina before it propagates across the cell. Its occurrence is undesirable as it disrupts normal reaction, leading to reduction of current efficiency, increase of energy consumption as well as PFC emissions. An onset of an anode effect is normally detected from a sudden increase in cell voltage [7]. This method, however, only provides a warning when the cell goes into anode effect, leaving little time for remedial actions to be carried out. In noisy cells, voltage noise can sometimes mask the cell voltage increase. In addition, early anode effect detection based on the cell voltage signal may fail as the cell voltage only reflects the overall cell condition. To obtain the anode current signal at the onset of an anode effect, a feeder near anodes 4, 5, 14 and 15 was manually blocked to reduce alumina concentration. The changes in the cell voltage and the current profiles of the anodes located in the vicinity of the blocked feeder as the cell approached AE are shown in Fig. 3. Note that only the anode current of Anode 15 shows a variation before the onset of the AE.
Although a slight increase in cell voltage (4.75 V) is also observed, it only occurred less than one minute prior to the onset of the AE (taken when the cell voltage has reached 21.77 V). On the other hand, a current reduction at Anode 15 is observed at almost two and a half minutes, as marked by the arrow in the figure, before the sudden increase in the cell voltage and the aggressive oscillation of the anode currents. However, a similar anode current redistribution can also be caused by other events such as a slipped anode. The frequency responses for Anodes 15 and its immediate neighbour (Anode 14) at different stages are shown in Fig. 4. In Stage A, both power spectra of Anodes 14 and 15 (Figs. 4(a) and (d) respectively) show significant peaks formed in the frequency range of 0.8 to 1 Hz, similar to the typical response depicted in Figure 2 (Region 3). As the anode current of Anode 15 is reduced in Stage B, the peak in the frequency range of 0.8 to 1 Hz, is seen to reduce significantly, as shown in Fig. 4(e). However, the peak in the spectrum of Anode 14 in Figure 4(b) is founded at a similar frequency and amplitude as in Stage A. Fig. 4(c) and (f) show both responses in Stage C before the cell entered anode effect. The peak in the spectrum of Anode 15 further reduces while the peak of Anode 14 remains, showing anode effect is occurring at Anode 15.

The present work shows that anode current signals can provide rich information about the operation of aluminium smelters and can be used for detection of abnormal operating conditions such as anode effect. It is shown that bubble dynamics is closely related to the local condition within the cell, and is reflected by the frequency response of the individual anode current signals. Some of the results are reported in [8-9].

References
Sulfidising Roast Treatment for the Removal of Chrome Spinels from Murray Basin Ilmenite Concentrates

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Keywords: Ilmenite, Chrome spinel, Murray Basin, Sulfidation, Chromite, H₂S

The Murray Basin region of southeastern Australia represents the remains of a shallow inland sea and contains heavy mineral sand placer deposits typically comprising the primary economic minerals ilmenite (FeTiO₃), altered ilmenite, rutile (TiO₂), and zircon (ZrSiO₄). Rutile and zircon are easily separable from the bulk heavy mineral concentrate and are currently extracted from deposits. The ilmenite component remains largely unexploited due to its wide spectrum of chemical alteration (making a clean separation difficult) and the presence of impurity mineral grains; mainly, chrome spinel (general formula AB₂O₄; A²⁺ = divalent cation e.g. Fe, Mg, Mn; B³⁺ = trivalent cation e.g. Cr, Al, Fe³⁺). The presence of even a minor amount of chromia (Cr₂O₃ <0.05%) in the ilmenite product downgrades its market value. While magnetic separation is usually an effective method to achieve a clean separation between ilmenite and chrome spinel, this procedure is not effective for the Murray Basin material as there is a considerable overlap in the magnetic susceptibility properties of both mineral phases [1]. Pownceby et al. [2] recently suggested a potential method for separating chrome spinels from ilmenite which involved changing the physical properties of the individual chrome spinel grains through a sulphidising roast treatment. The aim of the current work is to analyse the sulfidation treatment of chrome spinel as a new route for chrome spinel removal from the Murray Basin ilmenite concentrates. This study comprises two phases of investigation: (1) a systematic thermodynamic assessment of equilibrium reactions in the Fe-Cr-Ti-O-S system to evaluate the effect of composition, temperature, and partial pressures of sulfur and oxygen, and, (2) selected experimental investigations using natural ilmenite and chromite samples to test the findings from the thermodynamic calculations.

Equilibrium Calculation of Ilmenite (FeTiO₃) and Chromite (FeCr₂O₄) Sulfidation

Equilibrium calculations were carried out using the thermodynamic package FactSage 6.4. A major component of Murray Basin chrome spinels is chromite (FeCr₂O₄) which is a solid solution of FeO and Cr₂O₃ and this mineral phase was used to represent the chrome spinel component. Calculations were carried out to determine: (1) the standard Gibbs free energy (ΔG⁰) of formation of the different oxides and sulfides relevant to the stability of ilmenite and chromite, (2) equilibrium reactions between ilmenite and chromite using different sulfur sources (H₂S or S) with/without carbon addition, and, (3) the phase stability of ilmenite and chromite under different pO₂ and pS₂ conditions.

The ΔG⁰ calculations for the oxide systems showed that chromite was more stable than ilmenite and therefore it is expected that during heating a mixture of ilmenite and chromite, the former will react first. The ΔG⁰ calculation for the sulfide system showed that the sequence of most stable sulfide phases was: Ti₂S₃>MnS>CrS>FeCr₂S₄>Cr₂S₃>FeS>FeS₂. This signifies that Fe will be sulfidised first followed by Cr, Mn, Ti and so on.
Equilibrium reactions using 1 mole of chromite with different amount of H₂S (or S) in the presence/absence of carbon were investigated at temperatures between 450°C to 1300°C. The general reaction products were determined by using the following equation:

\[
\text{FeCr}_2\text{O}_4 + m\text{H}_2\text{S} \text{ (or S)} + n\text{C} = \text{Equilibrium Products (m=1 to 5 and n=0 to 3)}
\]

Figure 1a shows equilibrium calculations for the chromite reaction with H₂S gas and Figure 1b the sulfidation reaction of an ilmenite and chromite mixture with/without the presence of carbon. In the case of chromite sulfidation with H₂S (Figure 1a), it can be seen that the higher the concentration of H₂S gas, the lower the temperature required for the equilibrium reaction to reach completion. The results from sulfidation of an ilmenite and chromite mixture (Figure 1b) showed that ilmenite was less stable at the conditions studied and reacted at lower temperatures than chromite. The addition of carbon with H₂S appeared to be beneficial in helping to dissociate the chromite at lower temperatures.

**Experimental Results**

Experimental investigations on chromite and ilmenite sulfidation were conducted at one isotherm (1100°C) as a means of verifying the calculations. Figure 2 shows a schematic of the experimental apparatus used. For the sulfidation experiments, 1 g of sample (chromite or a 1:1 wt ratio of chromite/ilmenite mixture) was placed in an alumina boat and located at the hot zone of a horizontal tube furnace (Nabertherm RHTV 200-600).

Experimental results are shown in Figure 3. Figure 3a shows back-scattered electron (BSE) image of the chromite sample after reaction at 1100°C for 5 h. Results indicate the
development of a sulfide outer layer (a mixture of Fe(Cr)S and FeCr$_2$S$_4$ type sulfide compounds) on the rims of chromite grains that was continuous and ~5 µm in thickness. The outer sulfide layer was underlain by a darker layer ~15µm in thickness which was depleted in iron. The inner core regions of the chromite grains remained essentially unreacted. For the chromite plus ilmenite sample (Figure 3b), SEM analysis showed that the majority of ilmenite was preferentially sulfidised under these conditions with iron sulfide (Fe$_{1-x}$S) observed to form on the surface and within pores and fractures of the ilmenite grains.

The present results (both thermodynamic and experimental) are at odds with the results previously shown by Pownceby et al. [2] where selective sulfidation of chromite in a Murray Basin ilmenite concentrate occurred under reducing conditions at ~1100ºC in the presence of carbon (i.e. standard ilmenite reduction conditions operating in a Becher-type reduction kiln). This discrepancy suggested that there must be some operating regime with a specific pO$_2$ and pS$_2$ condition that allows for the selective sulfidation of chrome spinel only.

**Figure 3:** Images showing the effects of sulfidation with H$_2$S at 1100°C for 5 h: (a) BSE image from a sectioned sample mount showing internal textures within reacted chromite grains, (b) BSE image showing textures in the ilmenite and chromite mixture (1:1 wt ratio) after reaction.

Therefore, as a part of further analysis, an overlay of predominance phase stability diagrams for the Fe-Cr-O-S and Fe-Ti-O-S systems at 1100°C with changing pO$_2$ and pS$_2$ was developed using FactSage (Figure 4). Results indicate a narrow window (grey area in the figure) in which selective sulfidation of chromite only can potentially be carried out.

**Figure 4:** Predominance diagram showing the Fe-Cr-Ti-S-O system at 1100°C at varying pO$_2$ and pS$_2$ conditions.
Further investigation is now underway under controlled pS\textsubscript{2} and pO\textsubscript{2} conditions (e.g. using a mixture of CO\textsubscript{2}, CO and SO\textsubscript{2}) to confirm the model predictions.

References


Status of Specific Energy Intensity of Copper: Insights from the Review of Sustainability Reports

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Keywords: copper, energy, sustainability reporting, trends

There are a range of major industry factors placing upward pressure on the energy intensity of primary copper production. Copper ore grades are declining, mines are becoming deeper and deposits are becoming more complex. However, at the same time the individual processes employed during mining, mineral processing and metal production are becoming more efficient. Given these competing trends, a good question to ask: has the rate of innovation by engineers and the research community been exceeding the upward pressure on energy intensity created by trends at the mine-sites?

A study recently examined the greenhouse gas emissions, water and energy consumption data available in the annual sustainability reports of copper mining operations (Northey et al., 2013). The results of the study (Figure 1) highlighted the variability between operations within the industry and confirm many of the general trends predicted by environmental life-cycle assessment studies (Norgate and Haque, 2010; Norgate and Jahanshahi, 2010). One of these findings is the significant increases in energy intensity with declining ore grades. The database from the previous the study has been re-analysed to determine whether there is any noticeable trend in the energy intensity of copper production over time (Table 1).

![Figure 1: Reported energy intensity of different copper operations (Northey et al., 2013).](image-url)
Table 1: Reported energy intensity for copper producers. Annual percentage change is relative to the initial year of reporting. Operations that displayed a decrease in energy intensity are shown in red.

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The limited data for individual smelters and refineries indicate that these operations have been successful in decreasing the energy intensity of copper they produce. The exact reasons for these changes are likely very site specific and could be due to a combination of changes in the composition of feed material and increases in unit process efficiency. Based upon this data, the energy intensity of smelters is approximately 7 to 14 gigajoules per tonne of contained copper (GJ/t Cu) and the energy intensity of refining is approximately 2.5 to 3.3 GJ/t Cu.

The reported increase in energy intensity of mine-site operations significantly exceeds the decreases in energy intensity observed in the smelting and refining stages of production. The weighted average annual increase in energy intensity across all the mine-site operations surveyed was 0.74 GJ/t Cu per year (5.0% per year relative to the first year they reported energy data). A large reason for this increase is due to a decline in ore grades at mine-sites through the periods that they reported. The average rate of ore grade decline at these mines was -0.85% per year (Figure 2). The amount material that has to be moved and processed to produce one tonne of copper contained in product will increase as a result of this.

![Figure 2: Change in ore grade at individual mines relative to the first year of reported energy data.](image-url)

This dataset indicates that the energy intensity of copper production is increasing despite the efficiency and optimisation of processes. The trends at the mine site will largely impact upon the energy requirements of mining and concentrating operations. At the same time, further growth in the copper industry will increase the overall energy demands of primary copper smelting and refining. Further innovation is required across all stages of the copper production chain to counteract these trends.

**References**

Removal Behaviour of Magnesium from Aluminium Melt with Chlorine Treatment

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Keywords: Magnesium Removal, Aluminium Melt, Chlorine, Thermodynamics, Kinetics

The consumption of Al materials has increased recently with sophisticated developments in various industries, for example, the decrease in vehicle weight and the high mileage obtained from gasoline in the automobile industry. At the same time, the generation of Al scrap has been increasing steadily. Aluminum recycling has many benefits in terms of economic, energy, and environmental aspects. It can be imagined easily that the amount of CO₂ and the total air emissions are both also reduced in Al scrap recycling, as compared to the primary processes of production.

Magnesium is one of the important alloying elements used in Al alloys. With cast Al alloys, an Mg component is added in amounts ranging from 0.5%–10%. Thus, because an Mg component can be included in Al scrap, it is necessary to control the Mg content for the recycling of Al. Thermodynamic survey shows that Mg can be removed from Al melt by means of chlorination. Chlorine gas fluxing is widely used in Al foundries to perform degassing and refining. Celik and Doutre¹ and Leroy and Pignault² have conducted the research on the refining effect of Cl₂ gas fluxing in molten Al. Fu et al.³,⁴ have reported their experimental results and offered a mathematical model on Ar+Cl₂ mixture fluxing for the removal of Mg from molten Al. In their studies they also discuss the reaction kinetics of Mg removal, as observed using the bubble detection system.

In the present study, experiments with Ar+Cl₂ gas bubbling were carried out and the behavior of the Mg concentration in Al melt was investigated based on thermodynamic and kinetic theory in order to obtain basic information on the removal of Mg from molten Al.

The experiments were carried out in an electric furnace with Kanthal Super heating elements (Korea Furnace Development Co., Korea). Most of the experiments were performed at 1000 K, but some were performed at 1050 K and 1100 K in order to ascertain if there was any temperature dependence. The temperature of the furnace was controlled with an accuracy of ±5 K by a proportional-integral-differential (PID) automatic controller. The one-end-closed reaction tube was made of 99.8% Al₂O₃ (O.D.: 60 mm, I. D.: 50 mm, L: 600 mm, Samwha Ceramic Co., Korea), and the crucible was made of quartz (O.D.: 48 mm, I. D.: 44 mm, L: 550 mm). The top of the reaction tube was closed with a water-cooled jacket and sealed with an O-ring.

A high-purity Al block (99.9%) and Mg metal piece (99.9%) were melted with the desired Mg concentration in the crucible in an inert gas atmosphere. The flowrate of the Ar gas and Cl₂ gas were controlled by a mass flow controller (MFC), and the gases were mixed at the desired volumetric mixing ratios and supplied to the aluminum melt. The melt samples were taken at time intervals using a specially designed sampler made of Pyrex glass. The Mg
concentration was analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Model: IRIS Intrepid, Thermo Elemental).

Fig. 1 presents the changes in Mg concentration during Cl₂ gas bubbling in Al melt. The experiments were carried out at temperatures ranging between 1000 K and 1020 K. The total gas flowrate was 100 sccm, and the mixing ratios of Cl₂ were 10%, 20%, and 40% in Ar. The Mg concentration in the Al melt decreased with time due to the Cl₂ gas bubbling. A greater rate of decreasing Mg was observed with a higher Cl₂ mixing ratio in the bubbling gas.

![Figure 1](image.png)

**Figure 1**: Change of magnesium concentration in aluminum melt during (Ar+Cl₂) bubbling with different Cl₂ mixing ratios.

In order to evaluate the removal rate of Mg in Al melt quantitatively, kinetic consideration was made as well using zero order equations. From temperature dependency values, the activation energy for the removal of Mg in Al melt can be calculated to be 63.1 kJ/mol in the present work. Jung and Sohn⁵ reported 233 kJ/mol for Pb removal from molten copper. Our value of activation energy in the present work is relatively small compared with those values.

In our experiments, the mixed gas of Ar and Cl₂ was introduced into the Al melt through an alumina tube. Gas bubbles were then formed in the Al melt. The Al melt was assumed to come into equilibrium with the gas phase of the Ar and Cl₂ mixture. The thermodynamic calculations using FactSage software were made on the equilibrium in Al-Cl₂ and Al-Mg-Cl₂ systems based on our experimental conditions of 750g of Al, a total gas flowrate 100 sccm, and a temperature of 1000 K. The results show that the mole fraction of each species changed with the Cl₂ content. Below 30% Cl₂, the main favored species were AlCl₃, AlCl, AlCl₂, and Al₂Cl₆, in decreasing order, and above 30% Cl₂, AlCl₃ and Al₂Cl₆ were more favorable than AlCl and AlCl₂. For all the different Cl₂ contents, AlCl₃ was the most favored species of the gaseous product in the bubbles.

Based on our experimental results and thermodynamic calculations, the mechanism of Mg removal in Al melt by Cl₂ gas bubbling was determined to be as follows. Fig. 2 presents a schematic description of Cl₂ gas bubbling in Al melts. A gas mixture of Ar and Cl₂ is injected into the liquid Al melt, and the bubbles then rise to the bath surface, where they react with Al and Mg to form gaseous or liquid reaction products. The reaction product depends on the composition and temperature of the system. Gaseous AlCl₃ was the primary phase in the Al-
Cl$_2$ system, and it was expected to react with Mg to form MgCl$_2$. Consequently, the mechanisms of magnesium removal from the Al melt were suggested by the following reactions,

Direct reaction: \[ Mg(l) + Cl_2(g) = MgCl_2(l) \] (1)

Indirect reaction: \[
\frac{2}{3} Al(l) + Cl_2(g) = \frac{2}{3} AlCl_3(g) \\
\frac{2}{3} AlCl_3(g) + Mg(l) = MgCl_2(l) + \frac{2}{3} Al(l) \] (3)

**Figure 2:** Schematic diagram of magnesium removal in Al-Mg melt by (Ar+Cl$_2$) gas bubbling.

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**References**

Cu Evaporation Kinetics in Liquid Steel

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Keywords: Cu removal, ferrous scrap, tramp element, Cu evaporation

The use of ferrous scrap in the world continues to increase due to a number of reasons including depletion of high quality iron ore, and requirement of reduction of CO₂ gas emission. However, tramp elements in ferrous scrap such as Cu hinder it from being used for source of wide range of steel grades, since they may cause harmful defects in the final products. Therefore, development of a new technology which is effective in removing the tramp elements or nullifying their harmful effects is essential to utilize ferrous scrap more widely. A number of technological attempts have been proposed for copper removal; namely, sulfide flux refining, vacuum distillation, low melting point bath, and chlorination. However, none of them has yet been fully successful for practical application because of various reasons including low efficiency, high cost and adverse effect on the environment.

The present work focuses on the removal of copper from molten steel in the form of gaseous species. This attempt is based on the difference in the vapor pressure of Fe and Cu. One of the advantages of this approach is that no additional by-products, such as slag/flux, are generated, and it is possible to utilize existing steelmaking processes, for instance, vacuum degassing vessels, with minimal modification. The key technical point for the success of this approach is to increase the evaporation rate, fast enough to complete the copper removal within the time allowed.

The evaporation rate of Cu was experimentally investigated by applying levitation melting technique in order to clarify the mechanism of Cu evaporation reaction. Experiments were conducted mainly at 1600°C by varying a number of related factors including flow rate, alloying element, and carrier gas species. The effects of these variables were examined from kinetic and thermodynamic perspectives.

Previously, it was reported that some types of gases may be beneficial in removing Cu in the form of Cu(N₃)₂(g) or CuH₃(g) [1]. Different gases which may provide N and/or H were tested in the present study as shown in Figure 1. Although the fraction of other gases such as N₂, H₂, and NH₃ in Ar was low (below 5%), noticeable effect by the gas types were not observed. Increasing the gas fraction did not change the results significantly [2]. Therefore, it was thought that Cu evaporates as Cu(g).

The removal rate of Cu from molten Fe could be expressed by the following first order rate equation:

\[
\frac{d[\%Cu]}{dt} = - \frac{A}{V} k_{Cu} [\%Cu]
\]  

(1)

where A and V are the surface area (m²) and volume (m³) of a levitated liquid Fe-Cu droplet, respectively; \(k_{Cu}\) (m/s) is an apparent rate constant. The rate constant was determined from
the experimental kinetic data such as shown in Figure 1. The Cu concentration in the droplet quenched after a time $t$ (s) was determined by ICP analysis.

**Figure 1:** Removal of Cu from molten Fe-Cu droplet at 1600°C under different carrier gas

The flow rate of the carrier gas increased the apparent rate constant $k_{Cu}$ to a certain limit. But when the flow rate was higher than 1 L/min the $k_{Cu}$ did not change under the present experimental condition, as shown in Figure 2. Therefore, when the high flow rate is over 1 L/min, it was apparent that the removal of Cu was not controlled by the gas phase mass transfer.

**Figure 2:** Relationship between gas flow rate with $k_{Cu}$

Figure 3 shows the effect of temperature on the removal of Cu from the liquid droplet in the temperature range of 1600 to 1700°C. It can be seen that the decrease of Cu follows a first order kinetic as evidenced by the linear relationship between the logarithm scale of [%Cu] and the reaction time $t$. This implies that Eq. (1) applies to the Cu removal. The activation energy of the reaction was estimated by an Arrhenius type plot as shown in Figure 4. The value of the activation energy obtained was 218 kJ/mol, which is close to the previous reported values, i.e. 227 kJ/mol [3], and 232 kJ/mol [4]. The value also close to the enthalpy of evaporation of Cu, i.e. 307 kJ/mol [5]. Therefore, at high flow rate where the gas phase resistance is eliminated, the Cu evaporation plays a major role in the overall Cu removal rate.
Figure 3: Effect of temperature on Cu removal rate, showing first order reaction

Figure 4: Plot of ln $k_{Cu}$ versus the reciprocal melt temperature

Figure 5 shows the effect of C on the Cu removal rate. Increasing C concentration increased the rate and consequently the rate constant $k_{Cu}$, compared to that with no C ($k_{Cu,0}$). It is interesting to note that activity coefficient of Cu ($\gamma_{Cu}$) increased with increasing C, and that the activity coefficient was directly related to the rate of Cu removal [6]. It is seen in the figure that the activity coefficient ratio ($\gamma_{Cu}/\gamma_{Cu,0}$) calculated by FactSage [9] shown by a full line is in good accordance with the rate constant ratio. A similar observation could be found in the case of Si addition to the molten iron [2]. This suggests that the effect of alloying element on the reaction rate may be estimated by thermodynamic data of molten metallic alloy, which is generally well known.

In summary, the study on the evaporation kinetics of Cu has been conducted by the present authors, in order to develop a recycling process of Cu containing ferrous scrap by evaporation. Fundamental investigations were carried out by employing the levitation melting technique in order to find reaction rate and mechanism, and further to find a major factor enhancing overall removal rate of Cu.
Figure 5: Effect of C on the rate constant $k_{Cu}$, expressed as $k_{Cu}/k_{Cu,0}$ and relationship with activity coefficient ratio $\gamma^°_{Cu}/\gamma^°_{Cu,0}$.

Reference
Metal-Solvated Carbothermal Production of Aluminium

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**Keywords:** Aluminium, carbothermal production, alloy

**Abstract**

Commercial aluminium production by electrolysis of alumina dissolved in cryolite is carried out in Hall-Héroult cells. Several attempts have been made by other investigators to develop alternate routes that are more intense and reduce pollutants [1-4]. At CSIRO Process Science and Engineering, a program investigated the carbothermal reduction of alumina. An experimental study was conducted at the kilogram-scale in a reactor designed to operate up to 2000°C and down to about 10 kPa. Experiments employed a bed of C-Al\(_2\)O\(_3\) pellets contacting a bath containing tin or copper as a solvent metal. The experiments confirmed the feasibility of smelting alumina with high recoveries of aluminium metal to an alloy at temperatures as low as 1750°C and furnace pressures up to about 45 kPa. A key finding was that the method of contacting the charge with the solvent had a significant influence on the extent of undesirable side reactions and loss of aluminium to the gas. The reaction rate was increased with higher temperature, lower reactor pressure and lower concentration of aluminium in the alloy. The amount of aluminium lost to the fume decreased at lower temperatures and higher pressures. Losses were lower with copper than with tin as the solvent.

1. **INTRODUCTION**

The overall reaction for carbothermal reduction is:

\[ \text{Al}_2\text{O}_3 (s) + 3 \text{C} (s) \rightarrow 2 \text{Al} (l) + 3 \text{CO} (g) \]  

For which:

\[ \Delta G = 1342.91 - 0.5822 \, T = -RT \ln \left( \frac{(\gamma_{\text{Al}} x_{\text{Al}})^2 \, p_{\text{CO}}}{a_{\text{Al}_2\text{O}_3} \, \gamma_{\text{C}} \, x_{\text{C}}} \right) \]  

where \( \gamma \) is the activity coefficient, \( x \) is the concentration, \( a \) is the activity and \( p \) is the partial pressure.

The values for Gibbs free energy given in equation 2 were calculated using HSC Chemistry for Windows Ver. 5.1 [5]. This reaction only proceeds above about 2030°C when both \( a_{\text{Al}} \) and \( p_{\text{CO}} \) are at unity. However, the reaction can proceed at lower temperatures if any of \( \gamma_{\text{Al}}, x_{\text{Al}} \) or \( p_{\text{CO}} \) is lowered. In practice, this can be achieved by reducing the pressure in the reaction system, dissolving the aluminium in another metal, and selecting the solvent metal such that there is a substantial reduction in the activity coefficient of aluminium. Additional reduction in \( p_{\text{CO}} \) can also achieved by diluting it with a purge gas. Dissolving the aluminium into a suitable alloy is termed metal solvation. A thermodynamic study of a number of potential
solvent metals was undertaken. Tin, copper and nickel were selected as potential candidates, although only tin and copper were used in the experimental study.

However, there are a number of side reactions that can compete with the production of aluminium and which must be reduced or eliminated in a potential process. The chief of these side products are the carbide (Al₄C₃) and oxycarbide (Al₄O₄C) and the gaseous compounds (Al₉(g) and Al₂O₉(g)).

2. METHODOLOGY

An experimental apparatus was designed that could achieve temperatures up to 2000°C and operating at pressures down to 15 kPa in a leak-tight system. The apparatus is shown in Figure 1. The reactor comprised of a silica tube that contained machined graphite parts for holding the reactants which were insulated by graphite and zirconia felts. The reactor top was sealed by a water-cooled brass flange. The reactor was heated by an induction heater and temperature was controlled using either a type-R thermocouple or a two-colour pyrometer. The reactor was pumped down using an oil-sealed rotary vacuum pump and the pressure was measured by a pressure transducer and controlled by manually operating the control valve.

The starting alloys were pre-melted and generally weighed about 500 g. Alumina and carbon black powder were well mixed in the stoichiometric ratio according to equation 1, and the pellets were extruded after mixing with a binder. The pellets were thoroughly dried before use and were about 3-4 mm in diameter. The pelletised charge ranged from 10-60 g.

After weighing all the graphite parts, metal and reactants, the reactor was loaded, sealed and leak tested. The reactor was purged with argon for the duration of the experiment and then heated at 10-15°C/min to the set temperature. After the meal was melted, the pellets were contacted with the metals by three methods. These were as a floating raft on the surface, by mixing using argon injection through a lance or by being submerged with perforated graphite disc. Reactor pressure was reduced between 1500°C and the set temperature. Progress of the reaction was measured by analysing the product gas stream for CO₂ and CO. The experiment proceeded for various periods or until the reaction was completed, and then the reactor was cooled while purging. After cooling, the reactor was disassembled and all
contents weighed. The alloy, pellet residue and fumes were sampled and analysed for aluminium and solvent metal as well as unreacted alumina. Pellet residues were also qualitatively analysed by XRD to determine the extent of side reactions. The extent and rate of reaction (expressed as the percentage of charge reacted and the percentage of charged reacted per minute respectively) were calculated by integrating the amounts of CO2 and CO generated over time. Examples of temperature, pressure and CO generation over time are shown in Figures 2 and 3.

3. RESULTS AND DISCUSSION

Experiments were performed to examine the types of reactions that occur in the absence of a solvent metal at 15 and 30 kPa reactor pressures at 1800°C. Figure 4 shows $p_{CO}$ against time while superimposed over the thermodynamically expected phase regions. The experiment at 15 kPa is well into the region where $Al_4C_3$ should predominate and this is confirmed in Table 1. At 30 kPa the material is in the region where $Al_4C_3$ and $Al_4O_4C$ can coexist and again the XRD results show this to be the case. Fume losses were also as expected, with 56% of aluminium lost from the charge at 15 kPa and 21% at 30 kPa. These losses to the vapour phase are in broad agreement with thermodynamic calculations.

These experiments were repeated with the pellets in the presence of a solvent metal over a wide range of temperatures and pressures. Two types of experiments were conducted; some with pellets floating on the surface and others in which the pellets were stirred into the molten metal by argon injection. Experiments with a floating pellet raft showed evidence of side reactions occurring in the pellets while in those with stirring the residue essentially remained as $Al_2O_3$ and C. Stirring also significantly suppressed fuming, as did higher reactor pressure as seen in Figure 5.

<table>
<thead>
<tr>
<th>Sample</th>
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<th>Some</th>
<th>Little</th>
<th>None</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLANK-1</td>
<td>Fume $Al_4O_4C$</td>
<td>$Al_4C_3$</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pellet Residue $Al_4C_3$, C</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>BLANK-2</td>
<td>Fume $Al_4O_4C$</td>
<td>$Al_2O_3$, C</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Pellet Residue $Al_4O_4C$</td>
<td>$Al_4C_3$, $Al_2O_3$</td>
<td>C</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2: Typical temperature and pressure trace

Figure 3: Example of CO trace and cumulative CO generation
Subsequent experiments used a perforated graphite disc to physically submerge the charge while allowing the CO gas to escape the bath. These experiments explored a wide range of conditions and the variables investigated included temperature, pressure, alloy composition, solvent metal and alumina type.

Figure 5 compares methods of contacting the solvent metal and the charge over a range of reactor pressures and shows that submerging the charge further suppresses fume rate as compared to stirring the melt and charge, and a floating charge. Figure 6 shows the effect of time on recovery to pellets, metal and fume based on analytical results rather than using the rate of CO generation to track reaction rate.

The experimental results largely agree with what would be expected from thermodynamic modelling. As expected the variable with the greatest effect is temperature. While the carbothermal reaction can occur at lower temperatures, the rate rapidly increases at about 1700-1750°C as seen in Figure 7. The reaction at 1750°C is slow and becomes about five times faster at 1800°C, while there is a 70% improvement when further increased to 1850°C.

Figure 8 shows the effect of pressure. The reaction rate is approximately doubled when the pressure was reduced from 30 kPa to 15 kPa. However, operating at 15 kPa increased the amount of fume about four times and pellet loss of 24% due to dust generation was observed.

Figures 9 and 10 show examples of the effects of alloy starting composition on reaction rate for both tin and copper alloys. Increasing the amount of aluminium in the alloy increases both $\gamma_{\text{Al}}$ and $x_{\text{Al}}$, thereby reducing the driving force of the reaction. Reduction with tin in particular was adversely affected, as the degree of solvation provided by $\gamma_{\text{Al}}$ was not high. For Al-Sn alloys, $\gamma_{\text{Al}}$ is slightly above unity at 2000 K [6]. In Al-Cu alloys, $\gamma_{\text{Al}}$ is well below unity [7]. For example it is about 0.2 at 30 mol% Al at 2000 K. Therefore, while reaction rate decreases in both systems when there is more aluminium in the alloy, the tin alloys are affected to a greater degree.
Figure 5: Comparison of contact method on the rate of aluminium fuming

Figure 6: Effect of run time on the recovery of aluminium to metal and fume at 1800°C and 30 kPa

Figure 7: Effect of temperature on the reduction rate at 45 kPa

Figure 8: Effect of pressure on the reduction rate at 1800°C

Figure 9: Effect of starting alloy composition on the reduction rate at 1800°C with tin
Another consequence of the high activity of aluminium in the tin alloys is the formation of $\text{Al}_4\text{C}_3$ in these alloys between 5 and 10 wt% Al. This is evidenced by loss of aluminium from the starting alloy (reduced to 8 wt% from an initial 10 wt% Al for example). Carbide formation also causes the solidified alloy to stick to the graphite crucible and to be brittle. High aluminium activity also increases fuming of aluminium at higher aluminium levels. In Al-Cu alloys, fume losses were nearly 10% at 35 wt% Cu with some losses beginning to be observed at 20 wt% Cu. Some carbide formation was suspected at 20 and 35% Cu.

Figure 11 contrasts tin and copper alloys with no aluminium in the starting alloy. As mentioned previously, the activity of aluminium in an Al-Cu alloy [7] is much lower than in an Al-Sn alloy [6] of similar aluminium concentration, and consequently the driving force for the reaction in the copper system should be significantly greater. Therefore, the observation that the reduction rate is slower with copper as the solvent contradicts the expected behaviour. A mechanism by which the solvent metal could affect the reaction rate remains unknown.

Most experiments used analytical-grade alumina in the pellets. Towards the end of the experimental work, a sample of Bayer alumina was obtained and used in a number of experiments. Figure 12 shows the reduction rate reduced significantly when Bayer alumina was used as the alumina source. Examination of the two types of alumina showed some morphological differences. Particle sizing showed the $d_{50}$ of the AR-grade alumina was 75 μm while for the Bayer alumina it was 101 μm. Although the Bayer alumina particles were coarser, this is unlikely to have been the sole cause of the reduction in reaction rate.
Microscopy revealed that the Bayer alumina consisted of blocky particles with few internal voids. In contrast, the AR-grade material had particles with a very open structure. It is unclear whether the AR-grade particles are agglomerates or a spongy single particle with large well-connected channels. The dimensions of the sub-grains in the AR-grade alumina were in the order of 3-6 µm and the voids of a similar size or larger, which greatly increased the surface area in this material.

4. SUMMARY

An experimental study of metal-solvated carbothermal production of aluminium showed that aluminium metal can be produced by capturing it in a solvent metal. The experiments showed the importance of the reacting charge contacting the solvent metal efficiently so that side reactions are avoided and fume losses reduced.

The effects of process variables on the reaction rate are largely in line with what is expected thermodynamically. The process requires temperatures above 1750°C and ideally above 1800°C to proceed. Reducing the reactor pressure increases the reaction rate but it should be noted that pressures below about 30 kPa are impractical due to significant losses of aluminium to the gas phase.

Increasing the amount of aluminium in the alloy reduces the reaction rate, particularly in the case of tin as the solvent. There are limitations to the concentration of aluminium that can be captured without carbide formation in carbon saturated system or unacceptable losses to the gas phase. With tin, this upper limit may be less than 5 wt% Al while with a copper solvent it could be above 20 wt% as long as carbide formation can be avoided.

The reduction rate was significantly decreased when Bayer alumina was used instead of analytical-grade alumina. This would have significant practical implications for an industrial process. Lastly, practical solutions for recovering aluminium from alloys at an industrial scale will need to be addressed.

Acknowledgments

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References

CFD Modelling of Dry Slag Granulation Using a Novel Spinning Disc Process

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Keywords: dry granulation, slag, spinning disc, CFD, modelling, simulation

Slags generated in metallurgical industry are high volume by-products or wastes containing a large amount of heat. In blast furnace ironmaking, for example, for every tonne of hot metal produced, about 300 kg of slag is generated. The cooling of molten slag to ambient temperature can release up to 1.8 GJ/t of thermal energy. Blast furnace slags are currently either water granulated or air cooled. Water granulation is commonly adopted to produce glassy granules that can be used for cement production. However, such slag treatment methods have some obvious shortcomings: ie, no heat recovery, air pollution, and consumption of a large amount of fresh water. Therefore, there has been an increasing interest in processing molten slags without using water quenching, so-called dry slag granulation (DSG).

CSIRO is developing a novel DSG process based on a spinning disc technology [1-4]. This process utilises centrifugal force to break up a molten slag stream into droplets, which are quenched by cold air and solidified into glassy granules for cement manufacture. The process is also able to recover the sensible slag heat as hot air. The integrated DSG and heat recovery process has been successfully demonstrated at a pilot plant scale with throughputs of up to 5 t/h (Figure 1).

Figure 1: Photos of (a) the semi-industrial scale (3 m diameter) integrated DSG and heat recovery pilot plant at CSIRO Clayton laboratory and (b) a typical still image from high speed video recording of the slag atomisation by a spinning disc in CSIRO’s DSG process.

CFD models, developed using commercial ANSYS CFX package [5], have been used to simulate the various complex and dynamic physical steps in the DSG process. These steps include: slag spreading on the spinning disc, slag film breakup after leaving the disc, slag droplet formation, droplet collision with walls, air flow and interaction of air with slag droplets/granules as well as droplet quenching and heat exchange. CFD modelling has played a key role in process design, optimisation and scale up. This presentation provides a brief overview of CFD modelling work on slag atomisation by a spinning disc. The work uses two
multiphase CFD models: a steady-state two-dimensional (2D) model for molten slag spreading on the disc [6] and a transient three-dimensional (3D) model for the breakup of the slag film and droplet formation [7]. Moreover, the 2D model was also utilised in a numerical experiment that was designed based on a fractional-factorial approach and dimensional analysis. This produced a dimensionless correlation that can be used for guiding the DSG operation, process optimisation and scale-up with potential applications to a wider variety of atomisation systems using spinning discs [8].

One important objective of the 2D model is to predict the free surface profile of the liquid slag, from which one can estimate the thickness of the slag film at the disc edge prior to it breaking up into droplets. Figure 2 shows typical results from the 2D model, where Figure 2(a) illustrates the predicted free surface profile as indicated by an interface between the liquid slag (red-region) and air (blue-region), while Figure 2(b) and Figure 2(c) depict the predicted flow and temperature fields, respectively. The model is also capable of predicting the formation of a solid slag layer due to heat transfer; this is marked in Figure 2(a) and Figure 2(b). The predicted slag film thickness at the disc edge, and other properties, are used as input to a 3D model to predict the breakup of the thin slag film into ligaments and finally the formation of droplets.

Figure 2: Typical predictions by 2D CFD model: (a) Free surface and solid slag layer profiles, (b) Flow field, and (c) Temperature fields in fluid and solid regions.

Figure 3: Comparison between CFD simulation and experimental observation on liquid slag breakup by a spinning disc, formation of ligaments and droplets, and droplet and granule size distributions (Liquid slag tapping rate: 2 kg min⁻¹, Disc spinning speed: 1780 RPM) [7].

Figure 3(a) illustrates the process of liquid slag film being broken up into ligaments and droplets by a spinning disc as predicted by the 3D model. Also shown for comparison is a high-speed video image obtained from an experiment (Figure 3(b)). Figure 3(c) gives predicted droplet size distribution in comparison with measured granule size distribution.
It can be seen from Figure 3 that the model qualitatively captures key features of the ligament formation and subsequent breakup processes which were observed in the experiment (Figure 3(a) and Figure 3(b)). From this modelling result one can further evaluate the slag droplet size distribution (Figure 3(c)), which is indicative of potential slag-air heat exchange efficiency and quality of the slag granules as well as the quantitative validity of the model.

Furthermore, by performing a parametric numerical experiment with the 2D model and by means of dimensional analysis and a fractional factorial design approach proposed by Box and Behnken’s [9], a dimensionless correlation between the slag film thickness and the important influencing parameters was obtained as [8]

$$\frac{h}{R} = 0.479 \left( \frac{\rho \Omega R^2}{\mu} \right)^{-0.612} \left( \frac{\mu R}{G} \right)^{-0.336}$$

(1)

where, $G$ is the liquid tapping rate ($kg \ s^{-1}$); $\Omega$ the disc spinning speed ($rad \ s^{-1}$); $R$ the disc radius (m); $\mu$ the liquid viscosity ($Pa \ s$); $\rho$ the liquid density ($kg \ m^3$); and $h$ the liquid film thickness at the disc edge (m).

Within the parameter ranges investigated, Eq. (1) can be used to evaluate appropriate operating and design conditions for producing a liquid film of desired thicknesses suitable for atomising different liquids by spinning discs. For instance, Figure 4 shows a relationship between slag tapping rate and disc spinning speed for maintaining different slag film thickness at the disc edge as implied by Eq. (1). This figure indicates that, for example, in order to keep a film thickness at 0.5 mm the disc spinning speed should be set at 1750 RPM to process liquid slag tapped at a rate of 5 kg min$^{-1}$.

![Figure 4](image-url)  
**Figure 4:** Predicted relationship between slag tapping rate and disc spinning speed for maintaining different film thickness (Disc radius: 25 mm, Liquid slag viscosity: 0.7 Pa s, Liquid slag density: 2590 kg m$^{-3}$).

In summary, CFD modelling has played a key role in the design, operation and scale up of CSIRO’s dry slag granulation process. The 2D CFD model can be used to give timely predictions that allow one to explore and select appropriate design and operating conditions for producing a slag film that will ultimately break up into droplets of desired size; and the 3D CFD model can then be applied to predict the size distribution of these droplets. The relatively efficient nature of the 2D model also allows one to perform virtual (numerical) experiments on multiple parameters (i.e. without doing time-consuming and costly experiments in laboratory) so as to establish dimensionless correlations that can be used for...
optimising and scaling up the DSG process. In addition, the 3D model can be extended to simulate liquid film breakup, droplet formation, droplet motion and deformation at the wall during collisions. This potentially can be applied to provide an in-depth understanding of the entire liquid atomisation process that is based on spinning discs.

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References

Estaño, Xi and Tin
43 Years (and Counting) of TSL Smelting

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Top Submerged Lance (TSL) technology was invented in the early 1970’s at CSIRO in Clayton, by a team led by Dr John Floyd. It was initially developed for reduction of tin reverberatory furnace slags and the first commercial furnace at Associated Tin Smelters in Sydney was installed for this purpose in 1978. This plant was also used to develop tin concentrate smelting at commercial scale before closing due to the collapse of the tin price in the late 1980’s. The technology was then adapted and used in a wide variety of non-ferrous applications but has still managed to maintain contact with its origins in tin. To date some 65 commercial TSL plants have been built by Outotec/Ausmelt, which excludes the Isasmelt contribution to TSL plants. In 1989 HMIB constructed and operated a small TSL tin smelter in Arnhem, Holland. This plant had a relatively short lifespan as local regulations forced the closure of the complex which included a lead smelter. Funsur constructed a greenfield TSL tin concentrate smelter in 1996 in Peru which was followed by YTCL in China in 2000. Following a lull of a few years, China Tin commissioned a TSL tin smelter in 2013 which will be followed by Vinto, Bolivia in 2014.

China Tin Project Background

Guangxi China Tin Group Co., Ltd (China Tin) commissioned Outotec in early 2010 to establish an Ausmelt tin smelter to replace the existing three reverberatory furnaces and expand the production as well as address the environmental situation, within its existing operation at Laibin, Guangxi Zhuang Autonomous Region in the People’s Republic of China.

China Tin Design

The TSL furnace system was designed to treat sufficient tin concentrates (roasted cassiterite) to produce 17,500 tonnes per annum of tin contained in crude bullion (~96% Sn), excluding the contribution to the tin production from all recycled and revert materials, and a slag with low levels of contained tin (3% Sn) in a single TSL furnace. The process route used was the typical two stage batch process, shown schematically in Figure 1. The slag is further processed in existing box fuming furnaces to maximise tin recovery. Fume from both the TSL furnace and box fumer was recycled to the TSL furnace along with typical refinery revert materials.

China Tin Hot Commissioning

The plant was commissioned in February-April 2013 and reached its design capacity within six (6) days after the commencement of concentrate smelting. The remainder of the hot commissioning time was spent on process optimisation and operator training. The Acceptance Certificate was signed on site in six (6) weeks acknowledging successful commissioning of the tin smelter and completion of the project. The commissioning of the
China Tin smelter went very well and is a reflection of the maturity of the technology, the well rounded knowledge of the process and engineering solutions to known issues. After the commissioning the plant has continued to operate well with the only real problem being a shortage of concentrates.

![China Tin Process Flowsheet](image.png)

**Figure 1: China Tin Process Flowsheet**

### Vinto Project

Empressa Metalurgica Vinto (Vinto) commissioned Ausmelt to design a TSL furnace to process local concentrates to produce 38,000 tonnes of tin a year. The project is a modernisation of the plant to replace an existing reverberatory furnace. The proposed process is the conventional two stage process represented in Figure 1, with the addition of oxygen enrichment to increase the smelting intensity. The process fuel for this plant is natural gas.

For this project, the reduction stage is increased in duration and intensity to produce a low tin slag suitable for discard without the need of separate treatment in a fuming furnace. The local concentrates contain a significant level of sulphur which will be a challenge to manage as this increases the fuming of tin. The plant is expected to be commissioned in 2014.

### Tin Market

Tin, like copper, was one of the first metals mined and its many qualities such as its shiny finish made it a highly sought after commodity. Today, its main uses include the production of solder and the tin plating of iron and steel products. Tin is also used in the production of bronze, pewter and die-casting alloys and in modern engineering to make tungsten more machineable. 383,500 tonnes of tin was produced in 2011 [www.lme.com]. The combined annual production of the Ausmelt TSL tin furnaces will be 125,500 tonnes when Vinto starts production next year, which is 33% of the world’s production. The tin concentrates fed to all the TSL tin furnaces are all classed as medium grade, containing typically 40-60% tin. These
concentrates make a significant quantity of slag which is easily handled in the TSL system. Higher grade alluvial concentrates are typically smelted in electric or reverberatory furnaces the slag make is small. Tin containing materials with less than 40% tin are less suited to direct smelting due to the large volumes of slag generated. These materials are typically smelted with a source of sulphur and the tin fumed, producing an oxide fume which is subsequently remelted to metal.

A TSL furnace is suited to both the concentrate fuming and resmelting of the fume to metal. Several projects based on tin fuming have progressed to pilot plant and demonstration plant testwork however none have proceeded to commercial scale at this time. It is expected that as the supply of high and medium grade gets tighter the lower grade materials will become economic.
Dynamic Free Lance for Slagmaking and Steelmaking Desulphurization

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**Keywords:** dynamic free lance, injection metallurgy, desulphurization, steelmaking

**Abstract**

The dynamic free lance, discovered accidentally in 2005, is a new type of injection lance with its top-end connected with a flexible joint so that the lance tip could move during the gas injection. Without mechanical driving apparatus, the free lance is capable of injection of reagent into wide space of the bath. The investigation of the free lance indicated that the lance movement caused forceful interaction of the injection gas with the liquid phase, and jet trajectory was changed due to the drag force from the liquid phase. A lance with weight of 15 kg and length of 2 m has been used as the free lance for modeling study, indicating that the heavy free lance for the industry could achieve certain extent of movement for dispersion injection, and this prediction has been proved in 2012 by industrial application of the 9 meters free lance used for the injection modification of end-slag from BOF converter. In 2013, a stationary refractory lance with weight of 2 t for 120 t ladle of steelmaking desulphurization has also been redesigned and converted into the dynamic free lance with initial tests exhibiting the lance movement.

**INTRODUCTION**

The injection desulphurization of molten iron employs the vertically inserted stationary lance to deliver the reagents and carrying gas into the bath, this injection method could sufficiently stir the liquid phase in the bath center, but the mixing power reaching towards the molten iron near the bath wall is doubtful for the uniform desulphurization. The stationary lance injection also causes the lance to shake and the clamps have to be strongly designed to withstand the lance vibration. The dynamic free lance is a different kind of injection lance, which has no clamps to hold it and the whole lance loosely dangles on a mechanical apparatus such as a universal joint so that the lance could freely move during the gas injection. Water modeling has been conducted to study its behavior and characteristics, indicating that the lance movement changed the trajectory of the gas bubbles due to the drag force from the liquid phase, and the extent of the lance movement was proportional to the gas injection rate. Further investigation of the lance with length of 2 m and weight of 15 kg suggested that the heavy refractory lance used for the steelmaking industry could be converted into the free lance to achieve certain extent of movement for efficient desulphurization. The lance movement could also provide visual information about the injection progress.

The dynamic free lance has been used in 2012 for recycle treatment of BOF slag at China Steel Corporation, the stationary refractory lance with length of 9 meters installed at No 2 Station has been converted into the dynamic free lance, which succeeded in its first time blowing with graceful movement in the molten bath for 20 minutes without interruption. In 2013, a stationary refractory lance with weight of 2 t for steelmaking desulphurization of 120 t ladle has also been redesigned and converted into the dynamic free lance with initial tests exhibiting the lance movement.
METHODOLOGY

The stationary lance used currently for the steelmaking industry needs to be clutched by two clamps at its top, an extra clamp on the platform is also used when the lance moves down to the working position for Mg injection as shown in Figure 1. The dynamic free lance has no clamps to hold it and the whole lance loosely dangles on a mechanical apparatus such as universal joint so that the lance could freely swing during the gas injection, the high frequency vibration of the stationary lance has been converted into the free lance with low frequency swing movement. The bending stress experienced by the stationary lance could be reduced on the free lance. The stationary lance transports the reagent into a fixed point of the bath, while the free lance distributes the reagent into wider area of the bath. The dispersion injection of the reagent may be expressed by $C = \frac{B}{S}$, where $B$ is reagent injection rate, $S$ is the injection area covered by the lance tip.

![Figure 1: Schematic of comparison of stationary lance and free lance](image)

DISCUSSION

In 2006 the change of the injection method for steelmaking desulphurization has been conducted by Usiminas at No 1 desulphurization station using the rotating lance with two horizontal nozzles in 65 t ladle [1]. The rotating lance driven by a mechanical apparatus improved the desulphurization rate by 20% and 30% for CaO-Mg and CaC2-Mg respectively, temperature drop reduced by 50 % and less metal splashing. From the desulphurization results of the rotating lance, it is logical to consider that the free lance could achieve the similar results as the rotating lance due to the similarity in the enlargement of the active zone and the dynamic mixing of the injection gas and reagents with the liquid phase. For the free lance tip covering the area of 1.0 m diameter within a ladle of 3.0 m diameter, the active zone occupies about 10% of the volume from the lance tip up to the bath surface, it appears that the active zone of the free lance is not large enough in this case, however, the distance from the injection point of the free lance to the ladle wall could be reduced by 33% in comparison with the stationary lance, which could change the flow pattern of the whole bath for uniform desulphurization. The drag force acted on the jet from the liquid phase for the free lance is comparable to that for the rotating lance, the reagents are always injected in contact with the renewed molten iron, and the contact mechanism is similar in that the injection gas and the reagent particles leaving the nozzle has a added velocity vector perpendicular to the injection direction, this velocity vector is the unique characteristics of the rotating lance and free lance, which is not applicable to the stationary lance.
The industrial application of the dynamic free lance has been conducted for recycle treatment of end slag of BOF at China Steel Corporation [2]. The stationary refractory lance with length of 9 meters installed at No 2 Station has been redesigned and converted into the dynamic free lance. The heavy refractory lance moved smoothly in its first time blowing for 20 minutes without any disruption as shown in Figure 2. The lance was submerged 0.4 - 0.5 m in the bath, and movement range of the lance tip was about 0.6-0.8 m. The slag splashing was reduced significantly by 30-50 %, the active zone of the injection gas within the bath increased by 25-40%, the shaking of the lance frame reduced by 60-80%. The dynamic free lance has been accepted permanently on the Station for the slag treatment since September 2012, breakthrough in the injection metallurgy for the dynamic free lance has been achieved.

![Image](image_url)

**Figure 2:** Images of dynamic free lance for slagmaking injection

**SUMMARY**

The dynamic free lance is a new type of injection lance invented by accident, which expands the active zone and achieves the forced contact of the reagents with the renewed molten bath. The free lance could inject the reagents into wider area of the bath with dispersion injection expressed by $C = B/S$. The prediction that heavy free lance used for the industry could achieve movement has been proved in 2012 by the injection modification of the BOF slag, a set of excellent data implies a breakthrough in injection metallurgy.

In 2013, a stationary refractory lance, with lance weight of 2 t for 120 t ladle of steelmaking desulphurization has also been converted into the dynamic free lance with initial tests exhibiting the lance movement.

**Reference**


Sintering Performance of Titanium Bearing Iron Ores

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Keywords: Iron Ore sintering, Compact sintering, Titanium oxide, Mineralogy

Titanium-bearing iron ores are found in many large deposits around the world and are becoming an important alternative source of iron ore due to shortage of high purity ores. More importantly, in many cases Ti-bearing secondary raw materials are introduced into the blast furnace to protect the hearth and extend the blast furnace operating life. As the refractory material in the blast furnace hearth is the most critical part of the blast furnace, extending the life of this area can extend the operation life of the whole blast furnace. The mechanism by which the blast furnace hearth can be protected by addition of titanium to the burden is via the formation of complex titanium carbo-nitrides. These titanium carbo-nitrides with very high melting point form in the hot area of the blast furnace then precipitate in the cooler area of the hearth, i.e. the area where the most heat is lost, as an additional refractory.

The amount of Ti-bearing ore added to the burden should be controlled to effectively protect the refractory at the hearth while maintaining smooth operation of the furnace. This is very dependent on the condition of the hearth and typically falls between 4-7 kg/tonne of the hot metal, usually added to the sinter mixture rather than as a direct charge to the blast furnace.

The sintering behaviour of titanium-bearing ores has been previously studied in several works [1-4]. However, as sintering behaviour is affected not only by the amount of Ti in the ore but also by the type and composition of ores, different behaviour has been reported in the literature, especially with respect to the structure and composition of sinter products. For instance, while Paananen and Kinnunen [2] showed no difference in the distribution of Ti in different sintered phases, Bristow and Loo [1] claimed that most of the Ti added to the sinter blend will concentrate in glass, with less concentration in magnetite and hematite phases.

In the present work the specific effect of titanium oxide on sintering behaviour of iron ore has been studied by doping pure TiO₂ into a simulated sinter blend. In this regard, different fractions of analytical grade TiO₂ were doped to a sinter blend containing a high-grade hematite ore and sintering was performed under controlled laboratory conditions, using a compact sintering technique developed by CSIRO [5]. The sinter strength and its mineralogical characteristics were studied. To study the strength of sinter, fired compacts were tumbled together for a duration of 8 minutes in a modified Bond Abrasion tester [5]. Then, the tumbled particles were screened to measure the Tumble Index (TI) as the percentage retained above 2.0 mm. The TI values were plotted as a function of sinter temperature (Figure 1) and the temperature where the TI value first reached 80% TI was considered as the melting point of the sinter.

Results of this work showed the considerable effect of TiO₂ on sinter strength as well as on melting point. While doping TiO₂ up to 2.0% improved the sinter strength and reduced the melting point, any addition of TiO₂ beyond that point negatively affected sinter strength and melting point (Figure 2). Similarly, doping up to 2.0% pure TiO₂ to the sinter improved the sinter matrix pore structure and its mineralogy. Figure 3 shows some examples of the sinter
structure of blends with three different TiO$_2$ levels after firing at 1270 °C, clearly showing increased consolidation (volume reduction) and melting with increasing TiO$_2$.

![Graph showing compacted TI of sinter blends doped to different TiO$_2$ levels.](image)

**Figure 1:** Compact TI of sinter blends doped to different TiO$_2$ levels (%)

![Graph showing melting temperature of sinter blends doped to different TiO$_2$ levels.](image)

**Figure 2:** Melting temperature of sinter blends doped to different TiO$_2$ levels

![Images of sinter structures with different TiO$_2$ levels.](image)

**Figure 3:** Sinter structure of blends with different TiO$_2$ levels after firing at 1270 °C

An important microstructural feature of sintering with high TiO$_2$ compositions was formation of perovskite as a discrete phase in the sinter structure. Although some Ti can be taken up by other phases, not all is accommodated in this way. As there is a high fraction of Ca in the sinter blend, perovskite (CaTiO$_3$) is a possible discrete phase for TiO$_2$ to crystallize in. The presence of the perovskite phase was observed in many samples using a scanning electron microscope and Energy Dispersive X-ray Spectroscopy (EDX) analysis.
phase formation could be contributing to the observed trend in the sinter melting point in TiO₂ doped blends (Figure 2).

To evaluate the effect of TiO₂ addition on the melting point of the sinter mixture through the formation of perovskite, the CaO-TiO₂-Fe₂O₃ phase diagram has been employed. Figure 4 shows a projection of the liquidus surface of the ternary phase diagram [6]. This diagram clearly shows that addition of TiO₂ to the sinter mixture (i.e. iron-oxide and CaO) can produce perovskite within a wide range of mixtures. The perovskite in conjunction with other phases in the diagram can produce several liquidus points with relatively low melting temperatures. Two of the most important liquidus points are shown as A and B in Figure 4. Point A is a phase assembly of perovskite, calcium-ferrite (CF) and hematite with a liquidus temperature of 1220 °C. Similarly, Point B is a phase assembly of perovskite, calcium-ferrite and dicalcium-ferrite (C₂F) with a liquidus temperature of 1223 °C. The presence of such phase assemblies with low melting points may explain the reduction in the melting point of sinter mixtures doped with TiO₂. However, such low temperature phase assemblies are present at low TiO₂ fractions and, as shown by the arrow in Figure 4, increasing the TiO₂ level beyond the equilibrium fraction of those liquidus points will increase the melting point (similar to what we observed after doping more than 2.0% TiO₂ in the sinter mixture).

![Figure 4: A projection of the liquidus surface of the CaO-Fe₂O₃-TiO₂ ternary phase diagram (adopted from Kimura and Muan [6]).](image)

**References**

Design of a Novel Metal Halide High Intensity Solar Simulator for Solar Hybrid Reactor Design Optimisation

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Keywords: solar simulator, hybrid, high temperature, reactor design

Abstract

In this paper, the development of a novel high intensity solar simulator for testing a solar/electric hybrid reactor is described. To simulate the solar energy, an array of seven, 6000 W metal halide lamp/reflector modules, were arranged in a circular pattern. The metal halide lamp with its longer arc has a luminous flux range of 380,000 lm to 600,000 lm and an efficacy of 95 to 100 Lm/W, making the metal halide lamp more efficient in converting electrical power to light in this size range compared to Xenon lamp. In addition, metal halide operates at much lower pressures and have a protective encasing outer bulb for added protection. The arc source of the metal halide lamp and the lamp/reflector were modeled through ray tracing modeling using FRED optical software.

Introduction

The utilisation of the energy of the sun is well advanced and concentrated solar thermal (CST) technology is commercially applied in the generation of electrical power. High temperature material processing has not been commercialised and the only limited research that has been conducted, has not utilised reactor designs that have practical scale up applications. In addition the day/night cycle and weather related solar shading poses additional challenges. Therefore the task is to design a high temperature reactor that can utilise concentrated solar energy when available while incorporating a hybrid power source to enable continuous reactor operation.

Optical configurations based on parabolic-shaped mirrors are commercially available for large-scale collection and concentration of solar energy for the generation of electrical power. The total amount of radiated power collected by any of these systems is proportional to the projected area of the mirrors. Their arrangement depends mainly on the concentrating system selected and the latitude of the site [1, 2]. The most common configurations used for concentration of the sun’s energy in solar thermal applications are linear concentrators such as parabolic troughs and Fresnel concentrators, or point concentrators such as the central solar towers and parabolic dishes (Figure 1).

An alternative reliable research tool is required that is capable of providing an artificial source of concentrated energy with a spectral distribution as close as possible to that of natural sun light. A high flux solar simulator will create the constant conditions required for controlled high temperature experimentation. In this study a novel solar simulator will be used to aid the design of hybrid solar reactors for applications involving high temperature material processing.
Solar Simulator

The design objective of this project was to obtain a source of intense but controlled radiative flux to test a prototype solar electric hybrid receiver at high temperatures in a laboratory controlled environment. A solar simulator is a device that provides illumination approximating natural sunlight. Solar simulators have been designed for both non-concentration and concentrating solar thermal applications [3, 4, 5]. A review has revealed that only a handful of research establishments throughout the world have operational high flux solar simulators, some examples include a 20kw unit at the DLR solar research institute Germany [6], a 30 kw, a 50kw and a 75kw unit at PSI research facility in Switzerland [7, 3, 4] and a 45 kw unit at the university of Minnesota USA [8]. At the same time the review has concluded that although many of these facilities possess dish or heliostat concentrators, solar simulators were used as the preferred tool during high temperature material processing experiments.

From a comparison of the lamps used in high intensity solar simulators, the xenon and the metal halide, are seen as the clear choice. Both Petrasch [4] and Kruger [8] have concluded that as the arc size within the lamp increase, the transfer efficiency of radiative energy originating at the arc that reaches the target is reduced. This negatively affects the magnitude and distribution of the radiative flux in the target plane. For this reason even though the metal halide lamp emits a spectral distribution that more closely replicates sunlight, xenon lamps have been chosen over metal halide. However the luminous efficacy, which is described as how efficiently a lamp converts electrical energy into visible light, has in the past been very limiting with little choice but to choose a Xenon lamp. This is no longer the case as seen in Osram’s technical specifications [9] where Xenon lamps that have a power range of 4 kW to 6 kW have a luminous flux range of 155,000 lm to 280,000 lm and an efficacy of 39 to 47 Lm/W. The power equivalent in the metal halide lamp has a luminous flux range of 380,000 lm to 600,000 lm and an efficacy of 95 to 100 Lm/W, making the metal halide lamp more efficient in converting electrical power to light in this size range. In addition xenon lamps operate under very high pressure and dangerous in the event of any exploding bulb. Metal
halide on the other hand operates at much lower pressures and have a protective encasing outer bulb for added protection. According to Osram [9], there is a direct relationship between the electrode gap, lamp voltage, operating pressure and luminous efficacy of a discharge lamp and as a general rule, lamps with small electrode gaps generally have low efficiencies.

In order to concentrate the light emitted by the artificial light source, we utilise the fact that rays originating from a point source can be collected in their entirety on to a target point by placing the source and target points on the foci of an ideal highly reflective ellipsoid of revolution. Unlike other geometric reflector shapes which have a single focal point such as parabolic or spherical where collimated light may be focused, the ellipsoidal reflector has two focal points. Our design uses an array of commonly focused lamps, each comprising of a truncated ellipsoidal reflector close coupled to a metal halide high intensity discharge lamp. An array of seven, 6000 W lamp/reflector modules, are arranged in a circular pattern (see Figure 2).

The design geometry and configuration of the receiver must maximise the power incident on the target while preventing damage to the target zone. The light source or arc gap is significantly larger in a metal halide lamp as compared to xenon which negatively affects the magnitude of the radiative flux at the target plane. At the same time, more recently, researchers at these facilities have found [10] that the temperatures produced by these high intensity fluxes generated by short arc lamps resulted in a shorter life for the reflectors and because the energy at the target is concentrated into a small spot, are difficult to contain thus creating strong thermal gradients resulting in material thermal stress. Efforts are now being made at these facilities, by using optical mixers such as polished tube flux guides, to defocus the rays and produce a preferred more uniform flux density distribution [10].

The metal halide lamps used in our design, because of the longer arc length, will have a uniform flux density distribution without the need for post defocusing equipment. Each of the following elements will affect the intensity of the energy entering the target receiver; the lamp efficiency, design and output; the quality, size and shape of the reflector; the positioning of the lamp within the reflector; the position and orientation of the reflectors; the window material and size covering the aperture; and the emissivity of the target. The initial aim was to match the total energy output of the lamps to the heat generated by the electrical power of the hybrid furnace, in this way the capacity of the furnace is in balance when used in an

Figure 2: Photo of the finished high flux solar simulator
alternating day/night cycle. It was estimated that the effective power of the 42kW from the lamps, after calculating the various losses in focusing the seven beams into the receiver, would produce the equivalent power of a 6kW electric furnace. We expect to generate receiver cavity temperatures in the order of 1200 °C, however this still needs to be confirmed by experimentation.

**Arc Modelling and Optical Characterisation**

Illumination systems depend greatly on the source characteristics. The design of a solar simulator requires the accurate modelling of the source parameters in order to have the fabricated system agree with the design. For an arc source a generic cylinder can be used to model the emission however arc sources tend to be deformed or bowed so the generic source model is a poor representation of the actual arc source. In order to effectively model the simulator design with optical design software, the most crucial parameter is the source model. Many lamp designs have existing ray files that have been determined either by the manufacturer or researchers which accurately model the light source of the arc however there were no ray files available for the 6 kW metal halide lamp used. One method to model the arc and generate a ray set or ray file is to use a single image captured of the arc with the asymmetry fully accounted. The image captured by the camera showed light intensity and colour in each pixel but the overall colour was close to white and as no spectral imaging data was measured, the ray set generated was monochrome, therefore a spectrum was assigned based on the manufacturer’s data. The program generates one ray from each pixel and the brightness of each pixel indicated the power. The rays were created in a disk (volume) source that encompassed only one row, in 3D the source looks like a disk or a compressed cylinder. The rays are then scaled based on their position and rotation around the centroid axis resulting in n data files, each containing a cylindrical volume of rays. The rays were traced until they intercept the next object and then the geometry of the bulb is inserted into the model. The centre of the arc bow is positioned at the focus of the ellipsoidal reflector and ray tracing is performed. Once the lamp/reflector design are entered into the FRED optical software including the orientation of all 7 lamps together with their material properties, a selection is made of the number of rays to be traced through the optical mechanical system whilst encountering various optical interactions. While the definition of the light source used has a significant effect on the accuracy of the simulation of the system, accuracy also increases with the number of rays traced however larger ray numbers result in longer processing times. Over 1 million rays are generally used to produce acceptable accuracies. Although many ray tracing modelling programs are available, FRED optical software was made freely available for a limited time. The initial results of ray tracing for a single reflector are shown in Figure 3. Optical modelling programs are a powerful tool which allows one to create and analyse optical-mechanical systems prior to the actual design and constructions of the system. They are used in the design, positioning and sizing of heliostat reflector fields as well as parabolic dish designs and to optimise solar receivers.

Peak flux intensities and the flux profile as proposed by the model needs to be verified experimentally. These will be applied to a hybrid solar/electric reactor where heat transfer will be measured and modelled, aiming to optimise the receiver design.
Figure 3: Results of ray tracing for a single reflector using FRED optical software (Photon Engineering Tuscon USA)

Acknowledgement

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References

Performance Evaluation of AlB\textsubscript{12} and AlB\textsubscript{2} for the Boron Treatment of Molten Aluminium

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Keywords: Al-B master alloys, AlB\textsubscript{12}, AlB\textsubscript{2}, boron treatment, molten Al, V removal

Aluminium has been used as an alternative to copper for power transmission. However, the presence of impurities especially transition metals deteriorate the electrical conductivity of smelter grade aluminium [1]. Transition metal impurities such as titanium (Ti), zirconium (Zr), vanadium (V) and chromium (Cr) are removed from molten aluminium by the addition of Al-B master alloys, called boron treatment[2-6]. Al-B master alloys contain AlB\textsubscript{12}/AlB\textsubscript{2} phases that provide boron to form transition metal borides during the boron treatment process. Transition metal borides formed are heavy that settled at the bottom of the furnace during holding of molten aluminium. Thereafter, relatively pure aluminium is decanted from the top of the holding furnace. The boron treated aluminium is used for the manufacturing of electrical conductors.

Khaliq et al. investigated the thermodynamics and kinetics of transition metal impurities removal from molten aluminium [7-10]. Thermodynamics modelling predicted the formation of stable transition metal diborides (TiB\textsubscript{2}, ZrB\textsubscript{2}, VB\textsubscript{2} and CrB\textsubscript{2}) in aluminium melt in the temperature ranging from 650°C to 900°C. It was predicted that excess addition of boron will favour the complete removal of transition metal impurities. The formation of VB\textsubscript{2} rings, encapsulating the initially added AlB\textsubscript{12} were revealed during experimental investigation of Al-V-B alloys. Moreover, the formation VB\textsubscript{2} rings in the early stage revealed the reaction was rapid that lead to the increase in electrical conductivity of molten aluminium as reported by previous investigators. It was further reported that the reaction between AlB\textsubscript{12} and V was incomplete due the formation of VB\textsubscript{2} ring [9]. A kinetic plot of V removal and mechanism of VB\textsubscript{2} formation in molten Al-1wt%V-0.412wt% B alloy is shown in Figure 1. The rate of reaction is faster in the early stage that becomes slower with time. It has been shown in literature that the rate of reaction in the early stage is controlled by the mass transfer of V in the liquid phase (up to 10 minutes). However, the second stage of reaction (after 10 minutes) is controlled by the diffusion of boron through product layer (VB\textsubscript{2}) that was formed in the early stage, as shown in Figure 1.

Limited literature is published on the performance of AlB\textsubscript{12} and AlB\textsubscript{2} during the boron treatment of aluminium. This paper describes the performance evaluation of AlB\textsubscript{12} and AlB\textsubscript{2} for the removal of V from molten aluminium. Kinetics experiments on Al-1wt% V alloy were conducted in the resistant pot furnace at 750°C. Samples taken at regular time intervals were analysed using SEM, EDX and ICP-AES techniques. Selected results from this study are presented in this paper.
In this study, pure Al (99.90%), Al-10%V, Al-10%B (AlB$_{12}$) and Al-5%B (AlB$_{2}$) master alloys were used. SEM-SE image of Al-10%B master alloy showed clusters of AlB$_{12}$ in the Al matrix having particles in the range of 1µm to 60 µm. AlB$_{12}$ particles possess irregular morphology. Contrary to AlB$_{12}$, AlB$_{2}$ particles are smaller in size and are elongated. The characterisation detail of Al-B master alloy is given elsewhere [11].

**Figure 3:** Kinetic plot of V removal from Al-1wt% V-0.412wt% B alloy at 750°C, showing the mechanism of VB$_2$ formation [10]

**Figure 4:** SEM images of Al-1wt%V-0.720wt%B boride sludge collected from the bottom of crucible, using (a) Al-10%B (AlB$_{12}$) and (b) Al-5%B (AlB$_{2}$) master alloys, and (c) Plots of V removal and (d) integrated rates with reaction time for AlB$_{12}$ and AlB$_{2}$ based alloys, added to Al-1wt% V alloy at 750°C (5% error bar) [12]
The possible reactions for the formation of VB\(_2\) in molten aluminium using AlB\(_{12}\) and AlB\(_2\) are given in Equations [1] and [2].

\[ 6[V] + AlB_{12(s)} = 6VB_{2(s)} + [Al] \]  \hspace{1cm} [1]  
\[ [V] + AlB_{2(s)} = VB_{2(s)} + [Al] \]  \hspace{1cm} [2]

Where “[ ]” indicates that elements are dissolved in solution with molten aluminium and “(s)” represents that compounds are present in solid state.

The formation of VB\(_2\) was observed by SEM analysis of boride sludge. Figures 2(a) and 2(b) showed the formation of VB\(_2\) in the aluminium matrix. It is evident that the reaction has taken place in the vicinity of AlB\(_{12}\) and AlB\(_2\) that are added as a source of boron in the molten Al-1wt%V alloy. The dissolution of AlB\(_{12}\) provided free boron for reaction with V to form VB\(_2\) in the molten alloy. Simultaneously, the mass transfer of V to the interface of AlB\(_{12}\) took place and, therefore the formation of VB\(_2\) by chemical reaction. The rings of VB\(_2\) are formed in the molten alloy treated with AlB\(_{12}\) or AlB\(_2\) as shown in Figures 2(a) and 2(b). However, rings formed using AlB\(_{12}\) are thicker and denser compared to that of AlB\(_2\). Moreover, smaller VB\(_2\) particles are observed using AlB\(_2\) based Al-B master alloys as shown in Figure 2(b). The presence of partially dissolved AlB\(_{12}\)/AlB\(_2\) particles suggested the reaction is incomplete and suppressed by the rings of VB\(_2\).

The change in the concentration of V with reaction time is shown in Figure 2(c). Samples collected at regular time intervals were dissolved in HCl and analysed for V in solution using ICP-AES technique. The rate of reaction for VB\(_2\) formation is similar for AlB\(_{12}\) and AlB\(_2\) in the early stage (up to 6 minutes). This is represented by similar mass transfer capacity coefficients as shown in Figure 2(d). However, the kinetics behaviour of AlB\(_{12}\) and AlB\(_2\) changed with further reaction. The rate of reaction become slower for AlB\(_{12}\) compared to AlB\(_2\) as shown in Figure 2(c). This is due the depletion of surface area available for further reaction. It was argued that the smaller and elongated particles in AlB\(_2\) provided additional surface area for reaction to form VB\(_2\) in the molten alloy. Therefore, the rate of reaction was faster using AlB\(_2\) based Al-B master alloys.

It was concluded that the rate of transition metals removal from molten aluminium will be faster using AlB\(_2\) compared to AlB\(_{12}\) based Al-B master alloys. However, the settling of borides will take longer due to smaller VB\(_2\) particles formed during reaction. Therefore, it is suggested to use AlB\(_2\) based Al-B master alloys for boron treatment in launders. For boron treatment in holding furnaces, AlB\(_{12}\) based alloys are more economic due to faster settling rate. However, the consumption of Al-B master alloys based on AlB\(_{12}\) will be higher. The chemistry and morphology of phases in Al-B master alloys are important for boron treatment process.

References:


Study of Mechanically-Entrained Copper Droplet in Slags due to Their Interaction with Spinel Solids

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Keywords: metal losses, copper, spinel, methodology development

Slags play an essential role in pyrometallurgical processes acting as collectors for specific groups of metals, for reducing heat losses and for the elimination of unwanted impurities. Decantation is often the last step, allowing the phase separation between slag and matte/metal. Although desirable, a perfect phase separation is impossible and valuable metal losses are inevitable and, consequently, an important issue in metal extraction industries. In order to further optimize these processes, it is essential to gain fundamental knowledge concerning the nature and origin of these losses.

Based on extensive research, it is currently well accepted that metal losses in slags are mainly caused by chemical dissolution in oxidized form and entrainment of droplets [1-3]. The chemical dissolution of metals is intrinsic to pyrometallurgical processes as its occurrence is determined by the thermodynamic equilibrium of the process. Mechanically entrained metal droplets can arise from a variety of sources like charging or tapping, metal precipitation from slag due to temperature fluctuations, gas producing reactions dispersing metal into the slag or attachment to solid particles in the slag [1-3]. The first three main sources have been studied extensively in literature. Concerning the latter, available literature and fundamental knowledge is scarce; nevertheless this phenomenon is industrially relevant as the attachment of Cu-alloy droplets to spinel particles is found to cause metal losses in the slag [4]. The specific and complex nature of the mechanisms responsible for this phenomenon, warrant a fundamental and systematic investigation.

This study focuses on the sticking interaction between spinel particles and copper droplets, which is a common problem in primary and secondary copper smelting. To our knowledge, no systematic evaluation of the specific interactions responsible for the attachment has been performed in literature so far. Therefore, to gather the desired know-how, two complementary methodologies have been developed to study this interaction, as represented in Figure 1.

On the one hand, the interaction of Cu with spinel particles present in the synthetic slag system PbO-Cu₂O-CaO-SiO₂-Al₂O₃-ZnO-FeO is examined. The experimental methodology for the melting experiments is based on the decantation of one bigger Cu droplet through the slag system with a well-chosen synthetic composition in the \(\{Fe, Zn\}_{2+}[Al, Fe]_{3+}O_4\) single-phase region of the slag system. In order to increase the possible interaction, the slag is saturated with alumina, leading to a spinel layer at the interface between the slag system and the alumina crucible. In a first series of experiments, the methodology to study the metal
droplet-solid-slag interaction has been developed, which has been described extensively by De Wilde [5].

Additionally a methodology for high temperature contact angle measurements has been developed in to study the interaction between Cu-droplets with spinel substrates in the absence of a slag system, using contact angle measurements at high temperature. These contact angle measurements under varying atmosphere could yield the important factors that influence the interfacial interactions between the spinel and Cu-alloys.

To perform the contact angle measurements, spinel substrates have been produced using a powder based methodology, using two commercially available spinel powders (MgAl$_2$O$_4$ and ZnFe$_2$O$_4$). Copper alloys have been produced using an inductive microgranulation furnace, resulting in granules which have the right size for contact angle measurements. As oxygen is a very surface active element, it is extremely important to control the oxygen content. Therefore, the granules have been remelted three times under CO atmosphere in a graphite holder to decrease the oxygen level, as was confirmed by a LECO oxygen analyses. At this moment, three types of alloys have been successfully: Cu-Ni, Cu-Pb, and Cu-Ag. In order to perform the contact angle measurements, an adapted confocal scanning laser microscopy set-up is used. This technique allows one to observe in-situ the interaction between the spinel substrates and the copper alloys in time. More detailed information concerning the set-up is described by De Wilde. [6]
Preliminary tests for pure copper droplets in contact with MgAl$_2$O$_4$ spinel at 1200°C under a protective Ar atmosphere, with different interaction times (10, 60 and 120 minutes), did now show any wetting as can be seen in Figure 2.

In order to diminish metal losses in slags, it is essential to gain fundamental knowledge about the mechanisms responsible for the interactions between metal droplets and solid particles in slags. As no specific methodology was present to study the sticking interaction between spinel solids and copper droplets in slags, two complementary methodologies have been developed and will be presented in this work.

References

Flow Dynamics Study in Bottom Blown Copper Smelting Furnace

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Keywords: copper smelting, bottom blowing furnace, mixing time, cold model

Abstract

The first commercial bottom blown oxygen copper smelting furnace has been installed and operated at Dongying Fangyuan Nonferrous Metals (China) for 4 years. This new copper smelting technology shows a number of advantages including high productivity, low slag rate, high copper recovery and energy sufficiency. These advantages are with the flow dynamics of the bottom blown furnace. This paper reports an investigation into a 1:12 bottom blown furnace model set up at the University of Queensland to examine the novel features of the original furnace. In this paper, the mixing time in the bottom blown furnace model was investigated. As a first approximation Ar gas was injected from the bottom of the water bath to study the effects of gas flow rate and bath depth on mixing time. KCl solution, introduced from above the plume, was used as a tracer for continuous measurement of electrical conductivity as a mean to determine the mixing time. The preliminary correlations among mixing time, stirring energy, gas flow rate, and bath depth have been obtained for the bottom blown furnace. It was found that mixing time decreases with increasing gas flow rate and bath depth. The information from the cold model will be useful for design of the oxygen lances for the industrial furnace.

Introduction

Bath smelting is one of major technologies in copper production due to its high smelting efficiency, low energy consumption and reduced dust production. From the aspect of gas blown regime, traditional bath smelting can be categorised into three general types: 1) top submerged blown, including Ausmelt and Isasmelt; 2) top suspended blown, such as Mitsubishi smelting; 3) Submerged side blown, including Noranda smelting and Teniente smelting.

Recently, Fangyuan Nonferrous Metals Co. Ltd. (Dongying City, Shandong Province, China) developed a new bottom blown copper smelting technology [1]. Bottom blown technology was previously applied in steelmaking convertor, refinery and lead smelting furnace. It was first introduced to copper production by Fangyuan. The main facility of this technology is one bottom blown furnace 4.4 m (diameter) × 16.5 m (length) which is horizontal-cylinder shaped, rotatable and with chrome-magnesite brick lining. The bottom blown furnace is equipped with 9 oxygen lances which are aligned in 2 staggered rows: lower row contains 4 lances, 7 ° offset from vertical line; upper row contains 5 lances, 22 ° offset from vertical line, which makes intersection angles between these 2 rows be 15 °. It is shown in Figure 1.
The field production since the start up has shown many advantages such as higher production rate, autogenous smelting and low copper content in slag. All these features show great potential application for the next generation of copper smelting furnaces. However, there is little information about the flow characteristics of bottom blown furnaces. A basic understanding is that this new blowing pattern has created new flow field of molten bath in furnace. This new flow field promotes mass transfer in the furnace which provides better kinematic condition for chemical reactions occurring in bath. Thus production rate is improved [2]. In order to develop a theoretical justification and reveal underlying mechanisms of these observations, this study mainly focuses on mass transfer in this new furnace.

It is noted that bottom blown technology was firstly developed and put into industrial production from 1950s to 1960s. Nowadays, it has become an essential technology widely used in the industry [3]. Bottom blown steelmaking converter and refinery ladle have been most widely studied since the 1960s. Researchers concentrated on studying the flow patterns caused by the rising plume, and attempted to acquire the optimised stirring energy dissipation for the best mixing in bath [4-7]. In the non-ferrous industry, Yu Guang Nonferrous Metals Co. Ltd. (China) built a bottom blown lead smelting furnace in 2002. The advantages were proved to be highly adaptable to feeds, short and intensified smelting process and high SO$_2$ content in waste gas which reduces the cost of acid production [8]. In recent years, Rue [9-11] investigated submerged combustion in glassmaking industry and reported that combustion bubbles would provide high heat transfer and turbulence during rising, which would lead to high mass transfer and homogeneous product composition. Following these studies completed in other industrial vessels, bottom blown copper smelting furnace requires specific investigation. As a first step, a lab scale cold model was set up for investigation of mass transfer phenomena.

**Experimental**

**Furnace set-up**

Following principles of similarity model, a cold model furnace (Figure 2) made of acrylic was developed with size of 1/12 of the prototype. Water and argon were used to simulate the molten bath and air injection, respectively.

The modified Froude Number Fr’ was used to consider the dynamic similarity between the model and the prototype. It requires that Fr’ of model to be equal to that of prototype:
where the modified Froude Number is defined as follows [12]:

\[ Fr'_m = Fr'_p \]  

(1)

Inserting equation (2) into equation (1) yields

\[ \frac{\rho_g u^2}{(\rho_l - \rho_g)gL} \]

(2)

\[ \frac{\rho_{gm} u^2_m}{(\rho_{lm} - \rho_g)gL_m} = \frac{\rho_{gp} u^2_p}{(\rho_{lp} - \rho_g)gL_p} \]

(3)

where \( u \) is the gas flow velocity (m/s), \( \rho_l \) is the density of liquid (kg/m\(^3\)), \( \rho_g \) is the density of gas (kg/m\(^3\)), \( g \) is the gravity constant (m/s\(^2\)), \( L \) is the characteristic length (m), here it equals bath depth. The subscript \( m \) and \( p \) stand for model and prototype, respectively.

Upon re-arranging, the following equation can be obtained:

\[ Q_m = Q_p \sqrt{\left(\frac{d_m}{d_p}\right)^4 \left(\frac{\rho_{lm} - \rho_{gm}}{\rho_{lp} - \rho_{gl}}\right)\left(\frac{L_m}{L_p}\right)\left(\frac{\rho_{gp}}{\rho_{gm}}\right)} \]

(4)

where \( Q \) is the gas volume flow rate (m\(^3\)/s) and \( d \) is the lance inner diameter (m). Equation (4) link the flow rate to be used in the model with that of the prototype.

In the study, a potassium chloride aqueous solution (4 mol/L) was used as tracer. In each experiment, 5 mL of solution was added through a syringe through a thin alumina tube to the top of plume. Electric resistance of the bath was continuously measured using PARSTAT2273 advanced electrochemical system.

The experimental set-up is shown in Figure 3a. The electrodes were made of two platinum wires with diameter of 1 mm and working length of 5mm. The distance between the two platinum wires was 3 mm. The two platinum wires were fixed in the thin Alumina tube using insulating glue.

The mixing time was defined as the period from the moment the tracer was introduced to the solution to the moment at which the fluctuation of electric resistance was within ±5%. This moment corresponded to 95% well mixed bath [13]. The definition of mixing time on the mixing curve is shown in Figure 3b.

Figure 2: Lab scale cold model of bottom blown furnace
Distance adjustment
Since the vessel has a cylindrical shape horizontally, the effect of blowing on the mixing in the horizontal direction is worth investigating. To investigate this, the horizontal distance between the blowing lance and the electrode position was varied while the bath depth and the argon flow rate were fixed at 10 cm and 450 mL/s, respectively. The single blowing lance was placed at four different locations which corresponded to horizontal distance from lance to electrode of 110, 220, 330 and 440 mm, respectively (see Figure 4). The electrode tip was fixed directly above the right-most lance, with different depths from the surface, i.e. 1.5, 5, and 10 cm deep. A 5 mL KCl aqueous solution was injected by syringe via thin alumina tube to the top of plume and electric resistance was continuously monitored. Each experiment was repeated at least 3 times to obtain the mean value of mixing time.

Bath depth adjustment
To investigate the influence of the bath depth on the mixing, the horizontal distance from the blowing lance to the electrode and the gas flow rate were fixed at 110 mm and 450 mL/s respectively, while the bath depth was varied between 7 cm, 10 cm, 13 cm and 16 cm. For each bath depth, electrode was placed at surface (1.5 cm depth), middle (half depth of bath) and bottom, respectively.

Flow rate adjustment
To investigate the influence of gas flow rate on the mixing, different flowrates of 65, 145, 245, 330 and 450 mL/s were used. In these set of experiments, the horizontal distance between the blowing lance and the electrode was fixed at 110 mm, the bath depth was fixed on 10 cm, and electrode depth was fixed at middle bath depth.
Results and Discussion

Influence of horizontal distance on mixing time

![Graph showing mixing time versus distance between blowing lance and electrode](image)

**Figure 5**: Mixing time versus distance between blowing lance and electrode

As shown in Figure 5, the mixing time changed a little with the depth of electrode and the distance between electrode and lance below 220 mm range. This indicates that in this area that mixing effect was independent of distance between lance and electrode and bath depth. This result is in agreement with Iguchi’s [13] result carried out in an upright cylindrical vessel. In this region, the flow turbulence may behave the same way as in the upright cylindrical vessel such as a steelmaking converter. Further investigation is currently being carried out to clarify this.

When the distance between electrode and the lance was increased beyond 220 mm, the mixing time was found to increase with the distance. The mixing time at surface was much higher than those in the middle and at the bottom. These results suggest that mixing occur better at the bottom area. In addition, when distance is greater than 220 mm, the mixing times measured at surface show relatively larger deviation as shown in Figure 5.

Influence of bath depth on mixing time

![Graph showing mixing time versus bath depth](image)

**Figure 6**: Mixing time versus bath depth
As shown in Figure 6, for the same bath depth, there was no significant variation of mixing time at the three different electrode tips. The mixing time was decreased with increasing bath depth. This may suggest that the deeper the bath depth, the better the mixing effect. For obtaining an explicit relationship, the bath depth was correlated with the average value of mixing time measured at the 3 electrode depths. The correlation shows the following dependence:

\[ \tau \propto h^{-1.81} \]  \hspace{2cm} (5)

where \( \tau \) stands for mixing time, and \( h \) stands for bath depth. Equation (5) is an empirical relationship of mixing time and bath depth at 450 mL/s. A more comprehensive relationship with flow rate is discussed in the next section.

**Influence of gas flow rate on mixing time**

The gas flow rate has significant influence on bath mixing time, as shown in Figure 7. Nakanishi [4] conducted similar research in an RH vacuum degassing unit and in a water model of argon stirred ladle to estimate bath mixing time. Firstly, it was shown that the mixing time and stirring energy has a good correlation with energy dissipation rate, \( \dot{\epsilon}_m \), which is defined as follows:

\[ \dot{\epsilon}_m = \frac{P}{m} = \frac{\rho_L g Q h}{m} \]  \hspace{2cm} (6)

where \( \rho_L \) is the density of liquid, \( g \) is the gravity constant, \( Q \) is the gas flow rate, \( h \) is the bath depth, and \( m \) is bath mass. Later Asai [6], and more recently Mazumdar and Guthrie [5] carried out research in steelmaking ladle and found that mixing time also related to the geometry of the bath, including bath depth and radius. In the present study, the bath geometry is different from steelmaking vessel. As mentioned in previous section, during single lance blowing when distance in longitude is greater than 220 mm, the mixing time shows a different pattern. It is possible that mixing at far distance area is dominated by diffusion rather than stirring. Accordingly, it is improper to take entire bath mass for calculating \( \dot{\epsilon}_m \) through Eq. (6) for single lance blowing situation. Additionally, the mass of bath directly affected by the gas plume is difficult to define because the boundary is unclear and can be affected by gas flow rate. Therefore, for simplicity gas flow rate is directly correlated with mixing time. Taking gas flow rate and bath depth into account, the optimised correlation is as follows:

\[ \tau = 37.34 Q^{-0.456} h^{-1.24} \]  \hspace{2cm} (7)

Since bath radius remains unchanged, the first constant is specific for the radius. Curves in Figure 7 show good agreement between the correlation and experimental data.
Conclusion

A lab scale cold model prototype was successfully built for investigating the mixing and mass transfer in the new bottom blown copper smelting furnace. The mixing time in this cold model was measured to examine the characteristics of the new blowing patterns. From the experimental results, the following conclusions can be made:

1) The mixing time increases as distance from blowing lance to electrode increases. Within the 220 mm range, there is only little variation in mixing time with the depth, while at locations greater than 220 mm, the surface area has longer mixing time than the middle and bottom areas. Areas farther than 220 mm are more randomly mixed.

2) When electrode is 110 mm from blowing lance, mixing time decreases with increasing bath depth.

3) The mixing time, the gas flow rate and the bath depth can be correlated as follows:

\[ \tau = 37.34Q^{-0.456}h^{-1.24} \]  \hspace{1cm} (8)

These conclusions provide a better understanding of blowing patterns in the new bottom blown furnace for the copper industry. Further work is required for better understanding and optimisation of field trials and production.

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Reference

Phase Equilibria in the CaO-SiO$_2$-Al$_2$O$_3$-MgO System Related to Iron Blast Furnace Slag

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The blast furnace process (BF) continues to be the principal technique used for ironmaking in the world. The oxide system CaO-SiO$_2$-Al$_2$O$_3$-MgO forms the major components of final slags tapped from BF. Recommended phase diagram sections with different contents of Al$_2$O$_3$ and MgO have been summarised in Slag Atlas [1], which are mainly based on the works reported by Osborn et al. [2] and Cavalier and Sandrea-Deudon. [3] However, it has been demonstrated in recent reviews and measurements of selected slags that significant differences are observed for the phase diagrams in the Al$_2$O$_3$-CaO-MgO-SiO$_2$ system between these recent studies [4-6] and those presented in the early research [2-3].

Recently, with the increasing trend of utilization of low grade ores with high Al$_2$O$_3$ contents, and the injection of coal, the BF operation confronts the new challenge of low gas permeability and formation of health accretion. The final slags can be easily obtained to measure their chemical and physical properties. However, this information may not be enough for the guidance of BF operation as other slags such as bosh slag are also important. To improve the understanding of the reactions in BF, the experimental investigation of slag systems should be traced back to the upstream of final slags including bosh slags and primary slags.

Most of the final BF slags in China has the ratio of CaO/SiO$_2$ around 1.1. Bosh slags usually has a higher CaO/SiO$_2$ ratio than that of final slags. The pseudo-ternary system (CaO+SiO$_2$)-Al$_2$O$_3$-MgO with CaO/SiO$_2$ ratio of 1.1 has been reported by Zhang et al. [7]. In this study, in order to map the slag journey in blast furnace, the pseudo-ternary system (CaO+SiO$_2$)-Al$_2$O$_3$-MgO with CaO/SiO$_2$ ratio of 1.3 was experimentally measured to simulate the BF bosh slags as well as some extreme conditions of the final slag for strong desulphurization.

The experimental technique for phase equilibrium measurements is based on the high temperature equilibration of the synthetic slag samples followed by quenching. The liquid phase is converted into glass on quenching, and crystalline solids are frozen in place. The quenched sample is then mounted, polished, and compositions of the liquid and solid phases are measured by electron probe X-ray microanalysis (EPMA). The accuracy of temperature is controlled within ±2 degrees Celsius, and the accuracy of phase composition measurements is within 1 wt %.

Figure 1 presents the typical microstructures of the slags quenched from primary phase fields of melilite (a), 2CaO·SiO$_2$ (b), spinel (c) and boundary of 2CaO·SiO$_2$ and merwinite (d) respectively. EPMA measurements show that the compositions of spinel (MgO·Al$_2$O$_3$), merwinite (3CaO·MgO·2SiO$_2$) and periclase (MgO) are close to their stoichiometry. Melilite is the solid solution between akermanite (2CaO·MgO·2SiO$_2$) and gehlenite (2CaO·Al$_2$O$_3$·3SiO$_2$). Experimentally determined pseudo-ternary section (CaO+SiO$_2$)-Al$_2$O$_3$-MgO with CaO/SiO$_2$ ratio of 1.3 is shown in Figure 2. Predictions of FactSage 6.2 are also shown in the figure for comparison. It can be seen that FactSage predictions show the similar
trends as the experimental results, but the positions of the isotherms are significantly different. For example, experimentally determined liquidus temperatures in the spinel primary phase field are 50 °C higher than those predicted by FactSage 6.2.

Figure 3 shows experimentally determined pseudo-ternary sections (CaO+SiO₂)-Al₂O₃-MgO with CaO/SiO₂ ratios of 1.3 and 1.1. Clearly the liquidus temperatures are increased with increasing CaO/SiO₂ ratio. This can be illustrated in pseudo-binaries shown in Figure 4.
Figure 4a shows pseudo-binary section (CaO+SiO$_2$)-Al$_2$O$_3$ at 10 wt% MgO. It can be seen that the liquidus temperatures increase with increasing Al$_2$O$_3$ when the Al$_2$O$_3$ in slag is above 12 wt%. Figure 4b shows pseudo-binary section (CaO+SiO$_2$)-MgO at 10 wt% Al$_2$O$_3$. It can be seen that liquidus temperatures at CaO/SiO$_2$ ratio of 1.3 are much higher than those at 1.1 in the composition range studied. At CaO/SiO$_2$ ratio of 1.1 the liquidus temperatures start to increase rapidly when MgO is above 13 wt%. However, at CaO/SiO$_2$ ratio of 1.3 the liquidus temperatures start to increase rapidly when MgO is above 10 wt%.

Assuming a BF final slag has composition of CaO/SiO$_2$ 1.1, 10% MgO and 16% Al$_2$O$_3$, it can be seen from Figure 3 that this slag is located in melilite primary phase field with the liquidus temperature approximately 1410 °C. The composition of the bosh slag corresponding to the above final slag can be estimated to be CaO/SiO$_2$ 1.3, 11% MgO and 12% Al$_2$O$_3$, which is located in merwinite primary phase field with the liquidus temperature approximately 1480 °C.

![Figure 4: Pseudo-binary (CaO+SiO$_2$)-Al$_2$O$_3$ at fixed 10 wt%MgO (a) and (CaO+SiO$_2$)-MgO at fixed 15 wt%Al$_2$O$_3$ (b)](image)

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**References**

ABSTRACT - 25

Induction: A High Temperature Tool for Research and Industry

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Heat is frequently used in research and industry. Heating methods vary according to what is most appropriate for the application. We are familiar with the three methods of heat transfer, namely radiation, conduction and convection. We are also familiar with conventional sources of heat such as combustion, and passing current through an electrical resistance. A process may involve a combination of methods of heat generation and also of heat transfer. Induction heating has a unique combination of heat generation and heat transfer. This uniqueness provides the researcher with a tool that can be used to good advantage.

The Electromagnetic Induction Heating Difference

In induction heating, the source of power is electrical resistive heating. Consequently the load has to be an electrical conductor. It needs to have some resistance to generate heat but not so much that the current cannot flow. Most metals are ideal loads. The key feature however is that the heating current is induced into the load without it requiring physical contact. Consequently the load can be separated from the source of power by an air gap, insulation or a vacuum. Once heated, the load may conduct heat, re- radiate heat and transfer heat to surroundings by convection. There are a number of unique features of induction heating, which include:

- Heat is generated directly within the load (most other forms rely on heat transfer)
- In some cases the only hot object is the load
- It does not rely on physical contact, only electromagnetic coupling.
- Extremely high power densities are possible
- Very precise power control is possible.
- Energy input can be by quantum (Precise power and time)
- The above features provide very close tolerance repeatability
- Lends itself to a signature associated with each heat cycle for QC purposes
- Rapid starts to full power are possible and a similar ability to stop
- Very narrow band and zone heating possible
- Levitation heating is possible
- Depth control of heating within the load is possible by choice of frequency
- Dual frequency (dual depth) control is therefore also possible
- Curie effects can act as a natural temperature limit.
- Suscepting media can be used to control heat in non suscepting media (gluing)

Theoretical performance modelling
With appropriate software, the effects of frequency, power density, field strength, resistivity, cooling etc. can all be modelled in advance. This shortens the time and expense associated with trials.

References
Phase Chemistry Study to Support the Technology Development for the Recycling of Lithium Ion Batteries

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Keywords: manganese, phase diagram, equilibrium, “MnO”-Al₂O₃-CaO-SiO₂ slag system

The use of the lithium ion batteries has significantly increased over the last few years and is expected to increase in the future, mainly due to their application in electrical cars [1]. Recycling of the batteries is essential to safely dispose hazardous materials as well as to recover valuable elements including cobalt, copper, nickel, manganese, lithium and others. A growing amount of used manganese containing materials in the battery cathode [2], will lead to increasing concentrations of manganese present in the high temperature smelter slag. In order to optimise the recycling process of these metals, accurate information is required on the phase equilibria in the Al₂O₃-CaO-Li₂O-“MnO”-SiO₂ system.

The battery smelter slag is a multi-component system containing alumina from the battery cases, silica and lime from fluxes, and manganese and lithium from the electrode materials. The Al₂O₃-CaO-SiO₂ system is well known, therefore a phase equilibria study was performed on the quaternary “MnO”-Al₂O₃-CaO-SiO₂ system. Discrepancies were identified between different studies [3-7] in the “MnO”-Al₂O₃-SiO₂ ternary system. The present study accurately determined the phase equilibria in the ternary system “MnO”-Al₂O₃-SiO₂ at metal saturation. Particular focus was given to the accuracy and reliability of the final results by highlighting the different reaction pathways, mass transfer mechanisms and reaction mechanisms taking place in the system, to enable improved design of kinetic and equilibration experiments and measurements in the “MnO”-Al₂O₃-SiO₂ system. The quaternary system “MnO”-Al₂O₃-CaO-SiO₂ has been studied by different authors [8-10], but no investigations were found at low constant “MnO”-concentrations.

The experimental procedures developed at the Pyrometallurgy Research Centre (PYROSEARCH) at The University of Queensland, were used, which involves equilibration of mixtures at high temperatures, rapid quenching, and accurate measurement of phase compositions using electron probe x-ray microanalyses. First, different reaction pathways in a closed system were analysed, which enable improved design of phase equilibrium experiments and measurements in the “MnO”-Al₂O₃-SiO₂ system. The quaternary system “MnO”-Al₂O₃-CaO-SiO₂ has been studied by different authors [8-10], but no investigations were found at low constant “MnO”-concentrations.

Attention was given to possible reaction pathways in the slag phase as it approaches equilibrium. A typical microstructure of a slag sample treated with an oxidizing atmosphere, i.e. under CO/CO₂ gas mixture, is shown in Figure 2. An unexpected “MnO” concentration profile was observed. A schematic presentation of the “MnO” concentration profiles is presented in Figure 3. This composition profile is unusual since MnO is higher in the area exposed to the gas phase although it is anticipated that manganese vaporization will occur. The following explanation for the observations is proposed. The fully-liquid slag layer
appears to be the result of oxidation of the alloy in the mixture by the gas phase. The following reaction pathway is proposed.

\[
\text{CO}_2 \text{ absorbed at the gas/slag interface provides a source of oxygen, where upon the oxygen is introduced into the liquid slag and transferred by diffusion from the gas/liquid interface into the bulk slag in the form of Mn}^{3+} \text{ and O}^{2-} \text{ due to the excess of oxygen present at the gas/slag interface. The diffusion of oxygen is accompanied the exchange between Mn}^{2+} \text{ and Mn}^{3+} \text{ ions in the slag. When the oxygen arrives at the alloy/slag interface, oxygen is adsorbed at the interface and the oxidation reaction to MnO takes place. The local “MnO” concentration in the slag is increased until all alloy is oxidised, the alloy/slag interface moves deeper into the sample and the thickness of the single liquid slag phase (zone 3) is increased. Simultaneously vaporization to manganese gas occurs at the slag/gas interface, leading to local concentration gradients on the vicinity of the gas/slag interface.}
\]

The work is being extended to the quaternary system “MnO”-Al$_2$O$_3$-CaO-SiO$_2$ which closely resembles the future recycling industrial slags. Experiments are being undertaken in platinum metal envelopes. The slag reacts with the platinum foil and manganese is dissolved in the platinum. It has been previously demonstrated that the concentration of manganese in platinum alloy can be used to determine the oxygen partial pressure. The relationship between the oxygen partial pressure and the amount of Mn dissolved in Pt was investigated by Rao and Gaskell [12], and is shown in Figure 4. The effective oxygen partial pressure in the system will be derived using these Mn activity data in solid Pt alloy by direct
measurement of the Mn concentration in Pt and MnO activity coefficient values in slag taken from FactSage. Example of such “oxygen partial pressure” calibration curve for the MnO in slag of composition 11.6 wt.% Al₂O₃, 30.5 wt.% CaO, 42.4 wt.% SiO₂ and 15.5 wt.% MnO is given in Figure 5.

A comprehensive investigation of phase equilibria in the quaternary “MnO”-Al₂O₃-CaO-SiO₂ system is in progress.

References
Effect of Sintering Conditions on the Formation of Mineral Phases during Iron Ore Sintering with New Zealand Ironsand

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Key words: Sintering, Iron ore, Silicoferrite of calcium and aluminium, New Zealand ironsand, phase composition

Introduction

New Zealand ironsand is a kind of titanomagnetite containing about 60 wt.% iron, 8 wt.% titania and a small amount of other impurities such as silica, phosphorus and lime [1, 2]. Since it is competitive in price, introduction of the ironsand into the ferrous feed can reduce the production cost and potentially increase blast furnace campaign life [3]. An appropriate method of introduction of ironsand is as a component of the sinter as its small size precludes direct charging into the blast furnace. The final commercial sinter mainly contains hematite, magnetite, calcium ferrite and glassy silicate. Their relative proportions depend on different parameters, such as sintering temperature, composition, oxygen partial pressure and sintering time. Many investigators [4-6] have made attempts to investigate how various mineral phases are developed in sinter, but there has been no satisfactory final conclusion until now due to the complexity of raw materials and variation of sintering conditions.

The introduction of ironsand as a component of the sinter further increases the complexity of raw material composition of sintering. The objective of present work is to investigate the effect of sintering conditions including the raw material composition, gas atmosphere, heating temperature and cooling condition on the formation of minerals during iron ore sintering with addition of New Zealand ironsand.

Experimental Procedure

The raw materials for the iron ore sintering with New Zealand ironsand were iron ore blend, limestone, dolomite, silica sand, manganese ore, Cold Return Fines (CRF) and New Zealand ironsand. Each raw material except New Zealand ironsand was crushed and screened to obtain a particle size smaller than 200 µm before use. These materials were mixed in the proportion of BlueScope Steel’s sinter plant practice. 5 wt.% of the ironsand was added into the mixture. 0.3 g of the mixture was then pressed into cylindrical tablets of 5 mm diameter and ~5 mm height. The samples were sintered in a vertical tube furnace at 1250 – 1325 °C in different gas mixtures. After sintering for 4 minutes, the samples were cooled by one of two methods: either rapid cooling by which the sample was directly lifted to the cool top end of the furnace tube, or slow cooling by which the sample was first lifted to a location at 1160°C for 2.5 min before further lifted to the cool top end. During cooling stage, the gas mixture...
was switched to purging air. After sintering, the sintered tablets were mounted in epoxy resin and cut perpendicular to the top surface, and then polished for optical microscopic and scanning electron microscopic (SEM) observations. The composition of mineral phases of specimens was quantitative examined using image analysis software.

Results

The extent of aggregation of samples increased gradually with increase in sintering temperature. Among specimens sintered at 1325 °C, recrystallised secondary iron oxides were ubiquitous. In comparison, even at this high temperature, the contours of the relict New Zealand ironsand particles were still clear, although they were obviously bound with other components, which means New Zealand ironsand is more resistant to assimilation than traditional iron ores during sintering. The content of SFCA phase was significantly affected by temperature. In the temperature range of 1250 – 1300 °C, SFCA formation was enhanced by increasing temperature. Further increasing sintering temperature retarded formation of SFCA. This retarding effect is attributed to conversion of hematite into magnetite making the availability of the former a limitation to formation of SFCA.

The contents of all major phases in the sintered specimens change with basicity following the same trends at different sintering conditions. The content of SFCA increased, while the contents of magnetite and hematite phases decreased correspondingly with increasing the basicity. Increasing the content of CaO (as formed by decomposition of limestone) increases the reaction kinetics of formation of calcium ferrite by solid state reaction at low temperatures; at high temperatures when SFCA is recrystallised from a melt phase, high concentration of CaO in a melt also favours formation of SFCA via thermodynamics and kinetics.

Increasing the partial pressure of O₂ in sintering gas atmosphere significantly increased the content of SFCA in a sinter specimen, shown in Figure 1. This is particularly true for high sintering temperatures. This is because that decomposition of hematite was suppressed by oxygen in the gas phase. Also a slow cooling of sintered specimens in air resulted in huge increase in the SFCA content of a sinter especially for those sintered in a more reducing gas atmosphere. It is also noted that, although a higher pO₂ favoured SFCA formation by solid-state reaction at lower temperatures e.g. 1250°C, the assimilation of original blend particles was better with a more reducing gas atmosphere. According to CaO-Fe₂O₃-FeO phase diagram [7], FeO fluxes calcium ferrite phases to form melt at lower temperatures, which promotes mass transfer and assimilation reactions between solid particles via the melt.

Comparing the microstructure of commercial sinter with that obtained in laboratory, and based on the sintering process occurred in a sinter plant, it can be recognised that although SFCA and SFCA-1 can be formed at low temperatures by solid state reactions, they are most likely to be formed by recrystallization from a silicate melt formed in the heating stage with relatively low oxygen partial pressure during cooling in an oxidising gas atmosphere.
Figure 1: The phase composition of specimens sintered in different gas atmospheres for 4 minutes followed by fast cooling.

References

Characterisation of Coke Analogue

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Keywords: Coke, Coke Reactivity, Coke Carbon, Raman

Industrial coke made from coal, is a complex heterogeneous material, consisting of different carbon types (macerals), inorganic material (minerals) and a highly variable pore structure¹³. This complexity and heterogeneity make it difficult to isolate specific effects such as mineral type on coke reactivity and carbon structure.

Gill, et al.,⁴ and Niekiek, et al.,⁵ found that the mineral cations present in coke affect its reactivity and could be ranked as follows, K₂CO₃ > Na₂CO₃ > CaCO₃ > MgCO₃ = MgO > FeCO₃ > FeS₂ > A1₂O₃ = SiO₂ (little or no change). From the previous works the resulting effect of combination of minerals and porosity on reactivity, and mineral effect on carbon structure were not reported. However, these limitations have the potential to be eliminated or minimised using a coke analogue. Chapman and co-workers⁶,⁷ investigated the dissolution of the analogue in liquid iron and found that the behaviour was similar to those of industrial coke. In addition, Longbottom, et al.,⁸ and Reid, et al.,⁹ investigated the effect of minerals on coke reactivity in CO₂ using the analogue and observed kaolinite, quartz, potash and feldspar reduced the reactivity, as measured by weight loss, whereas lime, gypsum and iron bearing minerals increased reactivity.

In order to fully understand the effect of the mineral phase on the reactivity and carbon structure of the analogue, the porosity of the analogue was first established (using an image analysis technique) to eliminate it as a variable. A pseudo coke reactivity index CRI test similar to the Nippon Steel Corporation method¹⁰ was used to assess the analogue reactivity. Raman analysis technique (Jobin Yvon Horiba 800 Raman spectrum analyser) was employed to characterize the carbon structure of the analogue. Key details of the experiments and findings are given below.

For porosity, the total percentage porosity in the range of 10 – 500 µm for three samples of the analogue and industrial coke are 29 ± 2.3% and 24 ± 4.3% respectively. The standard deviation for the value of coke is likely an underestimate, as it does not adequately represent the inherent variation in a single batch of coke where it is known that there are significant porosity changes in the coke with respect to where the coke was formed (position) in the coke oven. The pore size distribution in the analogue is compared with those of industrial coke¹, as shown in Figure 1. In the analogue, the pore size is more controlled with less variation than that of the industrial coke.

For reactivity, single minerals with 0.2 mol. of cations per 100g of carbonaceous material after firing were added to the analogue mixture. The relative effects of the minerals were
assessed by reacting it with CO₂ at 1100 °C for 2 hours. The fractional weight change (FWC) of the analogue after reaction was calculated using equation [1], and is presented in Figure 2. The mineral effect on the reactivity of the analogue is ranked from kaolinite to magnetite.

\[
FWC = \frac{\text{mass of reacted analogue} - \text{mass of unreacted analogue}}{\text{mass of unreacted analogue}} \quad [1]
\]

To assess the carbon structure, approximately 20 optical images of each analogue were obtained and assessed with respect to its optical features to obtain a true representation of the analogue. A typical example is shown in Figure 3(a). The corresponding Raman data are presented in Figure 3(b). The I(D) and I(G) are intensities of the defective and perfect graphitic structures respectively, while the I(V) is the minimum point between the D and G bands.

Figure 1: Plot of pore size distribution in (a) coke analogue and (b) industrial coke reproduced from Loison, et al.

Figure 2: Plot of Fractional weight change (FWC) in coke analogue with time during its reaction with carbon dioxide gas.
Figure 3: (a) Typical optical image of the base analogue obtained using the Raman optical microscope, showing the textural reflection of the analogue, and (b) Plot showing the carbon structure of the base analogue, where $I(D)$, $I(G)$ and $I(V)$ are key Raman characteristics.

In conclusion, the characterisation of the base coke analogue materials reactivity, porosity and carbon structure with respect to Raman, has been established. The total percentage porosity in the analogue has been shown to be similar to that of industrial coke, and is controllable and reproducible. While its total porosity is similar to that of industrial coke there is less variability with respect to pore size with the majority of the analogues porosity being in the less than 200 µm pore size range.

References
10. ASTM, (D5341-93) Standard test method for measuring coke reactivity index (CRI) and coke strength after reaction (CSR).
Characterisation of products from the pyrolysis of South Australian Radiata Pine

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¹CSIRO Process Science and Engineering

Keywords: Charcoal, biomass, pyrolysis, condensate, bio-oil.

Abstract

Radiata pine grown in sustainably harvested forests in the mid north of South Australia is a potential source of renewable carbon for local smelting operations. The wood must first be converted into charcoal through pyrolysis. By-products from pyrolysis, including condensate, have value which can be used to offset the cost of producing charcoal and improve the economics of charcoal supply. Pine wood logs were collected from the Wirrabara forest which is near Port Pirie in South Australia. Samples of this wood were pyrolysed at 350, 550 and 750 °C using a kg scale rotary furnace. Pyrolysis products including charcoal and condensate were collected and analysed. The condensate was further treated in a centrifuge to separate the organic ‘bio-oil’ fraction from the aqueous pyroligneous acid fraction. The effect of pyrolysis temperature on the properties of the resulting charcoal was in accord with similar work on other wood types. The carbon content and calorific value of the charcoal increased with temperature while the charcoal volatile content decreased. The organic ‘bio-oil’ fraction of the condensate increased slightly with temperature but was quite low at between 5 and 8 %. The carbon content and calorific value of the bio-oil increased with temperature from 57 to 60 % and from 25.7 to 26.1 MJ/kg respectively. The potential value of the bio-oil, based on the measured properties is discussed.

1. INTRODUCTION

There is growing interest in the use of renewable carbon, derived from biomass, in smelting as a way of reducing the net carbon dioxide emissions. In this way carbon can be recycled through the atmosphere on a 3-8 year cycle. The use of coal and coke, based on fossil carbon, depletes resources which were deposited in geological time scales.

Recent work conducted by the Australian CO₂ breakthrough program¹ has focused on the substitution of charcoal for coal and coke in iron and steelmaking. The key feature of the work is understanding the properties of charcoal which are required for specific operations. Mathieson et al. listed likely substitution rates and properties of charcoal necessary for the different processes. For example iron ore sintering requires a charcoal with low reactivity and high density while blast furnace injection requires a charcoal with low ash content, low alkali and medium volatile content. Charcoal properties can be manipulated through the pyrolysis process through careful control of the conditions (temperature, heating rate and biomass feed stock).

¹ The Australian CO₂ breakthrough Program is a collaborative research initiative of BlueScope Steel, Arrium and CSIRO which aims to reduce the net CO₂ emissions from the Australian steel industry. It forms part of the similarly named program of the WorldSteel Association.
Pyrolysis is the anaerobic thermal decomposition of carbonaceous materials. Products from pyrolysis include: solid charcoal, a condensed mixed aqueous and organic liquid phase and a non-condensable gas phase. Although the solid charcoal product is the main interest of the CO₂ break through program, the other products, particularly the condensate also have value which can be used to help offset the cost of charcoal production and hence strengthen the business case of renewable carbon use\(^6\).

Investigations into the life cycle analysis and techno-economics of charcoal use in iron and steel making found that the economics of charcoal use depends on a number of factors such as the value of the pyrolysis fractions such as condensate, particularly the organic fraction called bio-oil\(^7\). This work attempts to help define the value of pyrolysis condensate through a characterization of the aqueous and organic fractions.

2. EXPERIMENTAL

*Materials*

The Radiata Pine wood used in this work was collected from the Wirrabara forest in the mid north of South Australia. This forest is part of the SA forestry plantation reserves. Table 1 shows the proximate and ultimate analysis of this wood while. The wood was supplied as coarse chips of about 5 cm long and 1-2 cm in high.

*Table 1: Proximate and ultimate analysis and gross dry calorific value of Radiata pine wood used in the pyrolysis experiments.*

<table>
<thead>
<tr>
<th>Moisture (% ar)</th>
<th>VM (% db)</th>
<th>ash (% db)</th>
<th>FC (% db)</th>
<th>C (% db)</th>
<th>S (% db)</th>
<th>N (% db)</th>
<th>H (% db)</th>
<th>Cl (% db)</th>
<th>O (diff)</th>
<th>CV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.4</td>
<td>80.3</td>
<td>0.4</td>
<td>19.4</td>
<td>53.3</td>
<td>0.02</td>
<td>0.1</td>
<td>5</td>
<td>0.03</td>
<td>42.2</td>
<td>34.6</td>
</tr>
</tbody>
</table>

ar = as received, db = dry basis, VM = volatile matter, FC = fixed carbon, CV=net dry calorific value

*Equipment and procedure*

Pyrolysis of the pine wood chips took place in a small 18.7 kW rotary furnace. The experimental set up is illustrated in Figure 1. The furnace lining or shell was heated externally and hence material was heated by radiant heat from the inside surface of the shell. A gas port on the back end of the shell allowed the flow of gas into the furnace at controlled rates.

The furnace shell was sealed by bolting a stainless steel end cap to a wide flange. A rotary coupling located at the centre of the end cap allowed the removal of gas from the furnace during pyrolysis operations and while the furnace shell was rotating. A vertical condenser tube (internal diameter 47 mm and length 1230 mm) was connected to the rotary coupling using a brass ‘T’ piece. The condenser was water cooled using 12 mm copper tubing brazed to the outside surface of the column.

During pyrolysis condensate produced from cooling vapours and fumes dripped down the outside of the condenser tube and collected below the ‘T’ piece in a gas tight glass flask. The temperature of the pyrolysing biomass was measured using a large ‘R’ type thermocouple which protruded through the ‘T’ piece into the basket.


Procedure

A batch of pine wood was dried in an oven at 115 °C for at least 24 hours prior to the test. A pyrolysis run started by filling the steel basket with dry biomass. The volume of the basket is about 24 litres. However the low bulk density of the biomass material limited the weight of each batch to 5 kg. The basket was then placed inside the furnace shell which was sealed using the end plate. The condenser and associated tubing and fittings were then assembled.

During operation the furnace was rotated at about 1.5 revs per minute. Nitrogen gas at 4 l/min flowed through the furnace shell, through the basket and out through the T pieces, condenser tube and chimney piece.

Pyrolysis experiments were conducted at three temperatures (350, 550 and 750 °C). For each experiment the furnace was heated at 10 °C/min to 150 °C, then by 1 °C/min until the planned temperature was reached. A dwell time of 180 minutes followed and then the furnace was cooled at 10 °C/min. The retort contents was kept sealed until the furnace temperature had returned to room temperature. Throughout the heating cycle a nitrogen gas stream flowed through the furnace and was removed with the non-condensable gases. At the completion of the test cycle the retort contents were removed and the charcoal was weighed. The total weight of condensate was also weighed. From these two measurements the amount of non-condensable gas was determined by difference. The condensate was further processed by centrifuge to separate the organic fraction, which is called bio-oil from the aqueous fraction which is called pyrolygineous acid.

3. RESULTS

Table 2 shows the mass yields of charcoal, pyrolysis condensate and non-condensable gas from the pyrolysis experiments and the percentage yields. These results show that the charcoal yield decreases with increasing pyrolysis temperature. This result is expected as increasing temperature decreases the volatile content of the resulting charcoal. The condensate yield shows a minimum at the intermediate temperature. The non-condensable gases show a constant value of about 41 % after 550 °C.
Table 2: Yields of charcoal and condensate following pyrolysis at 350, 550 and 750 °C

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Dry wood (kg)</th>
<th>Charcoal</th>
<th>Mass (kg)</th>
<th>Condensate</th>
<th>Gas</th>
<th>Charcoal</th>
<th>Condensate</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>5.0</td>
<td>2.60</td>
<td>1.30</td>
<td>1.10</td>
<td>52</td>
<td>26.0</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>5.0</td>
<td>1.88</td>
<td>1.07</td>
<td>2.05</td>
<td>37.6</td>
<td>21.4</td>
<td>41.0</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>5.0</td>
<td>1.72</td>
<td>1.22</td>
<td>2.06</td>
<td>34.4</td>
<td>24.2</td>
<td>41.2</td>
<td></td>
</tr>
</tbody>
</table>

The proximate and ultimate analysis of the charcoal produced at the three temperatures is shown in Table 3. The fixed carbon and carbon content of the charcoal is shown to increase with increasing pyrolysis temperature. In comparison the hydrogen and oxygen content of the charcoals decrease with increasing temperature. More severe the pyrolysis conditions leave a purer carbon product which contains less volatile components. This will also increase the calorific value of the charcoal, which can be seen in Table 4.

Table 3: Proximate and ultimate analysis of charcoal

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Moisture (% ar)</th>
<th>VM (% db)</th>
<th>Ash (% db)</th>
<th>FC (% db)</th>
<th>C (% db)</th>
<th>S (% db)</th>
<th>N (% db)</th>
<th>H (% db)</th>
<th>Cl (% db)</th>
<th>O (diff)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>1.3</td>
<td>34.2</td>
<td>2.3</td>
<td>63.6</td>
<td>75.8</td>
<td>0.02</td>
<td>0.26</td>
<td>4.3</td>
<td>0.03</td>
<td>17.3</td>
</tr>
<tr>
<td>550</td>
<td>2.1</td>
<td>13.1</td>
<td>6.3</td>
<td>80.6</td>
<td>82.4</td>
<td>0.02</td>
<td>0.44</td>
<td>2.3</td>
<td>0.38</td>
<td>8.5</td>
</tr>
<tr>
<td>750</td>
<td>1.6</td>
<td>1.3</td>
<td>4.2</td>
<td>94.5</td>
<td>91.5</td>
<td>0.02</td>
<td>0.64</td>
<td>1.1</td>
<td>0.18</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 4: The gross dry calorific value of the charcoal produced at 350, 550 and 750 C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Dry gross calorific value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>29.7</td>
</tr>
<tr>
<td>550</td>
<td>31.0</td>
</tr>
<tr>
<td>750</td>
<td>32.7</td>
</tr>
</tbody>
</table>

The separation of the pyrolysis condensate into organic “bio-oil” and aqueous “pyroligneous acid” fractions allowed the relative amounts of the different fractions to be measured. Table 5 shows the mass and percentage of the organic and aqueous phases split from the pyrolysis condensate at the three pyrolysis temperatures. The proportion of organic phase in the condensate increases with increasing pyrolysis temperature. It would seem that at least some of the volatile components which have been driven from the charcoal substrate at higher pyrolysis temperatures have added to the organic condensate fraction. The chemicals that make up the aqueous phase may be released from the decomposing wood at lower temperatures.

Table 5: Fractions of aqueous and organic fractions split from the recovered condensate

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mass of phase (g)</th>
<th>Proportion of phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aqueous</td>
<td>Organic</td>
</tr>
<tr>
<td>350</td>
<td>648</td>
<td>35.5</td>
</tr>
<tr>
<td>550</td>
<td>723</td>
<td>49.7</td>
</tr>
<tr>
<td>750</td>
<td>534</td>
<td>48.6</td>
</tr>
</tbody>
</table>

The ultimate analysis and gross wet calorific value of the aqueous and organic phases at the three temperatures is shown in Tables 6 and 7 respectively. The carbon content of the organic phase has increased slightly with pyrolysis temperature. The calorific value of the organic phase seems to be independent of pyrolysis temperature.
Table 6: Ultimate analysis and calorific value of the aqueous phase at different pyrolysis temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>Cl (%)</th>
<th>S (%)</th>
<th>Gross wet calorific value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>11.2</td>
<td>9.4</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>550</td>
<td>12.7</td>
<td>9.9</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.12</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>750</td>
<td>11.5</td>
<td>7.1</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Table 7: Ultimate analysis and calorific value of the organic phase at different pyrolysis temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>Cl (%)</th>
<th>S (%)</th>
<th>O (diff)</th>
<th>Gross wet calorific value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>57.4</td>
<td>7.5</td>
<td>0.10</td>
<td>0.01</td>
<td>0.04</td>
<td>35.2</td>
<td>25.7</td>
</tr>
<tr>
<td>550</td>
<td>59.1</td>
<td>7.8</td>
<td>0.24</td>
<td>0.01</td>
<td>0.05</td>
<td>32.8</td>
<td>25.7</td>
</tr>
<tr>
<td>750</td>
<td>59.9</td>
<td>7.7</td>
<td>0.25</td>
<td>0.01</td>
<td>0.03</td>
<td>32.1</td>
<td>26.1</td>
</tr>
</tbody>
</table>

4. DISCUSSION

Charcoal properties

Figure 2 shows a graph of charcoal yield plotted against pyrolysis temperature for the results of the present work and a range of literature data. The results of the present work are slightly higher but generally agree with the Blackbutt results and with the Olive wood and low temperatures. At temperatures greater than about 400 °C the results diverge. The main reason for the divergence of charcoal yield at higher temperatures is the heating rate of the biomass/charcoal during pyrolysis. Low biomass heating rates are known to increase charcoal yield due to reactions between the pyrolysis vapours and charcoal which yield a secondary char. Processes which increase contact between char and vapour such as low heating rates and unidirectional pressure will increase charcoal yield.(8)

The charcoal yield from Blackbutt was slightly less than for the Radiata Pine although the heating rate was the same (1 °C/min). The yields from the Mallee and from Purdy (mixed hardwood) were similar and lower than the results for the pine probably due to the faster heating rate of 3 °C/min. The heating rate used by Purdy is not known but would most likely also be about 3° C/min. The lowest charcoal yield was obtained from the pyrolysis of olive wood at 10 C/min.

Figure 2: Graph of charcoal yield plotted against pyrolysis temperature.

Figure 3: Graph of charcoal volatile content plotted against pyrolysis temperature.

Figure 3 shows a graph of charcoal volatile content plotted against pyrolysis temperature. The results of the present work are shown to agree well with the range of literature data. The
differences in charcoal yield seen in Figure 2 at higher temperatures are not seen in the charcoal volatile content shown in Figure 3. This suggests that the charcoal volatile content may be independent of heating rate at least with the heating rate considered in Figure 3 (1-10 °C/min).

**Bio-oil yield and properties**

Williams and Besler\(^{(12)}\) investigated the pyrolysis products of pine wood between 300 and 720 °C at the relatively high heating rates of 5-80 °C/min. The characterisation of pyrolysis condensate products presented in this work is the best comparison with the present work available. Williams and Besler found that the yield of bio-oil increased with pyrolysis temperature. Oil yield was independent of heating rate at low temperatures (300 and 420 °C) but increased with heating at higher temperatures. The proportion of bio-oil in the condensate was independent of temperature at between 24 and 33 %. This level is much higher than in the present work where the oil proportion of the condensate varied between 5 and 8 %. This apparent low proportion of bio-oil in the condensate in this work may be due to the nature of the pyrolysis condenser. The organic fraction tends to coat the internal surfaces of the condenser and becomes sticky. Hence the measured amount of organic phase is likely to be an underestimate of the true amount. The average calorific value of the oil was reported by Williams and Besler\(^{(12)}\) to be 23 MJ/kg and independent of heating rate. This is 9 % less than the value of the present work (26 MJ/kg).

Table 9 shows the ultimate analysis of the bio-oil made at 720 °C from the work of Williams and Besler\(^{(12)}\) at different pyrolysis heating rates. Also included is the results from the present work at 750 °C. The carbon and hydrogen content of the bio-oil increased with heating rate and the oxygen content decreased slightly. There is generally good agreement between the bio-oil composition results of Williams and Besler\(^{(12)}\) and this work. The carbon content shows excellent agreement at about 60 %, the hydrogen content is a bit lower at 7.7 % compared to 9-10 % and the oxygen content is higher at 32 % compared to 27-30 % for Williams and Besler\(^{(12)}\).

**Table 9:** Ultimate analysis of bio-oil at 720 °C from Williams and Besler\(^{(12)}\) and at 750 °C

<table>
<thead>
<tr>
<th>Element</th>
<th>Heating rate (°C/min)</th>
<th>Present work 750 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>59.5</td>
<td>61.3</td>
</tr>
<tr>
<td>H</td>
<td>9.0</td>
<td>9.1</td>
</tr>
<tr>
<td>N</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>S</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>O</td>
<td>29.8</td>
<td>28.0</td>
</tr>
</tbody>
</table>

**Value of bio-oil**

One possible way to calculate the value of bio-oil is as a proportion of the cost of crude oil based on calorific value. This calculation has been expressed as a formulae which is shown as Equation 1, where CV is calorific value. The assumptions used to calculate the value of crude oil are shown in Table 10 and the results using the data in the present work and the results of Williams and Besler\(^{(12)}\) are shown in Table 11.

\[
\text{Value of bio} \times \text{oil (\$/tonne dry wood)} = \text{crude oil price (\$/barrel)} \times \text{barrel crude oil/tonne} \times \text{exchange rate (\$/US) \times bio} \times \text{oil yield (fraction of dry wood)} \times (\text{CV bio} \times \text{oil/CV crude oil}) \tag{1}
\]
**Table 10:** Assumptions used to calculate the value of bio-oil.

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil price ($US/barrel)</td>
<td>95 (13)</td>
</tr>
<tr>
<td>Crude oil calorific value (MJ/kg)</td>
<td>42 (14)</td>
</tr>
<tr>
<td>Exchange rate ($A/$US)</td>
<td>1.08 (15)</td>
</tr>
<tr>
<td>Crude oil (barrels/tonne)</td>
<td>7.42</td>
</tr>
</tbody>
</table>

Table 11 shows that the value of bio-oil increases with pyrolysis temperature from $6/t wood at 350 °C to $10/t wood at 750 °C. This increase is because both the bio-oil yield and CV increases with increasing temperature. The value calculated using the data of Williams and Besler is much greater than the results of the present work because in their work the yield of condensate and in particular the yield of bio-oil was significantly higher.

**Table 11:** Calculated value of bio-oil at different pyrolysis temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Condensate yield (% of dry wood)</th>
<th>Char yield (% of dry wood)</th>
<th>Bio-oil yield (% of condensate)</th>
<th>Bio-oil yield (% of dry wood)</th>
<th>CV bio-oil (MJ/kg)</th>
<th>Bio-oil value ($A/t dry wood)</th>
<th>Bio-oil value ($A/t charcoal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>26.0</td>
<td>52.0</td>
<td>5.2</td>
<td>1.35</td>
<td>25.7</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>550</td>
<td>21.4</td>
<td>37.6</td>
<td>6.4</td>
<td>1.37</td>
<td>25.7</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>750</td>
<td>24.2</td>
<td>34.4</td>
<td>8.3</td>
<td>2.0</td>
<td>26.1</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>(720 °C &amp; 5 °C/min)</td>
<td>50</td>
<td>23.2</td>
<td>26</td>
<td>13.0</td>
<td>23</td>
<td>56</td>
<td>13</td>
</tr>
</tbody>
</table>

5. **CONCLUSIONS**

The effect of pyrolysis temperature on the properties of the resulting charcoal made from Radiata pine wood was in accord with similar work on other wood types. The carbon content and calorific value of the charcoal increased with temperature while the charcoal volatile content decreased. The organic ‘bio-oil’ fraction of the condensate increased slightly with temperature but was quite low at between 5 and 8%. The carbon content and calorific value of the bio-oil increased with temperature from 57 to 60% and from 25.7 to 26.1 MJ/kg respectively. The potential value of the bio-oil was calculated to be between $6 and $10/t dry wood and increased with pyrolysis temperature.

**Acknowledgements**

The authors wish to acknowledge the staff of HRL Technology, in particular Jasmina Karevski who performed the charcoal and pyrolysis condensate analysis. Financial support for the work was provided by the CSIRO Minerals Down Under Flagship through the Sustainable metal production theme. This support is also gratefully acknowledged.

**References**


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2 The volume of 1 barrel of crude oil is 0.159 m$^3$ and the density of crude oil is 0.85 t/m$^3$, therefore one barrel of crude oil has a mass of 0.135 t (0.159 x 0.85), or 7.4 barrels per tonne.
Evaluation of Experimental Data and Models of Iron Blast Furnace Slag Viscosity

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\textsuperscript{2}School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, China

The blast furnace (BF) is widely used all over the world to produce high quality iron with high efficiency and low energy consumption. Blast furnace slag, formed by ore gangue, coke ash and flux, plays an important role in BF operation. In order to have a smooth operation and higher production, the slag should have some characteristics, such as small volume, easy slag-metal separation, good desulphurization capacity, stable composition, good fluidity and so on. Viscosity is one of the important physical properties to obtain the optimum slag composition. If the viscosity is too high, it will be hard for burden to descend and gas to rise. And the separation of slag-metal will slow down which leads to a bad operation and low production. Hence, it is important to control the viscosity of the slags for optimum BF operation. The aim of the present study was to develop an accurate and reliable viscosity model for the iron-making industry. Development of a reliable viscosity model requires accurate viscosity measurements. Although a large number of experimental data of viscosity have been reported, they have to be evaluated before they are used for the optimisation of the viscosity model.

Critical literature review shows that in last 70 years, over 40 publications (not listed here due to the limited space) have reported viscosity measurements of BF slags in the CaO-SiO_{2}-MgO-Al_{2}O_{3} system, which account for over 95% of the total slag weight. More than 3000 viscosity data were reported in this system with significant discrepancies. In order to evaluate the reliable experimental data for further discussion, criteria are established to screen all viscosity data:

1. Presence of solid phase. It is essential that the viscosity data should be reported with or without solid phase. It is generally understood that viscosity would be measured above the liquidus temperature at fully liquid condition. However, it has been found that many viscosity data were reported below slag’s liquidus. FactSage software\textsuperscript{(1)} is applied in the present study for prediction of the liquidus.

2. Linearity of the experimental data. The temperature dependence of the viscosity for a given slag composition can be described by Arrhenius-type equation: \[ \ln \eta = A + \frac{E_a}{RT} \] (after taking logarithm). Where \( \eta \) is the viscosity in Pa-s, \( T \) is the absolute temperature, \( R \) is the gas constant, the temperature-independent parameters \( A \) and \( E_a \) are the pre-exponential factor and the activation energy, respectively. Non-linearity of the viscosity data usually indicates presence of solid phase or other uncertainties.

3. Comparison with the present measurements. An advanced high-temperature viscosity measurement process has been developed at the University of Queensland (UQ) which has considered all possible sources of the uncertainties to minimise the experimental errors.\textsuperscript{(2-4)} Viscosity data of BF slags measured at UQ are used to evaluate the previous data in the same system. The previous data with large difference from the present measurements are not used in the further discussion.
Despite the above three criteria, other factors such as measuring techniques, use of crucible and spindle materials, post-experimental composition analysis and etc. are also considered. After the careful review of the previous experimental data, about 700 viscosity data in blast furnace slag composition range are accepted in the present discussion. Figure 1 shows examples of the comparisons between previous viscosity data [5-8] and the present measurements.

![Figure 1: The comparisons of present data with previous viscosity data (composition close to: 35% SiO₂, 40% CaO, 15% Al₂O₃ and 10% MgO in weight)](image)

Experimental measurement of high temperature viscosity is time- and money-consuming, and also requires considerable expertise. It is difficult to measure the viscosities for a large composition range to cover the current and potential BF slags. Various viscosity models have been proposed by different research groups.

The viscosities were reproduced based on the description of the selected models. Deviations of the predictions from different models and the selected experimental data were also calculated. It should be noted that the present viscosity measurements was used as a “benchmark” in the discussion. The averages of relative deviations between experimental and calculated viscosities are shown in Figure 2. The composition range for the comparison includes CaO 30-50%, SiO₂ 30-45%, MgO 0-15% and Al₂O₃ 10-25%.

![Figure 2: Average relative deviation of different models](image)

With the continuously increased demand of iron ore, the ore quality has been degraded in recent years. For example, Al₂O₃ content in the BF feeds has increased continuously. At the same time, in order to save energy and cost of iron-making, the amount of pulverized coal injection (PCI) is also increased. Therefore, the concentration of Al₂O₃ in final BF slag has exceeded 15%, which is the traditional limit in the iron-making process. It was found that the viscosity increases significantly with the replacement of (CaO+MgO) by Al₂O₃ at constant
SiO$_2$ concentration. Further analysis shows that the increased Al$_2$O$_3$ concentration in BF slag not only increases viscosity directly but also decreases the thermal stability of the slag. MgO was found to be more efficient to decrease the viscosity of BF slags.

References
The Kinetics of Coke Analogue Reactivity

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University of Wollongong, Northfield Ave, Wollongong, NSW 2522, Australia

Keywords: Coke analogue, Coke kinetics, TGA, Rate of reaction

Coke is the fuel and the primary source of CO for the reduction of iron oxide in the blast furnace. It also gives the structure to the furnace to ensure high permeability for high productivity[1]. Coke is a complex heterogeneous composite material containing different forms of carbonaceous materials, mineral components and a pore structure primarily dependent on the volatile matter in the source coal and coking conditions. When exposed to high temperatures and reactive atmospheres, the heterogeneous compositional and structural features, inherent in a coke, make it difficult to isolate the effects of specific component on coke behavior. This limits the progress in coke studies in assessing the impact of minerals on reactivity and reaction kinetics[2, 3]. A coke analogue has been developed using laboratory grade materials (graphite, Bakelite, Novolac and minerals) to address these reactivity issues. Full details of how is produced are given elsewhere[2, 4]. Use of this coke analogue has several advantages. It can be doped with minerals required, while porosity, carbon structure and mineral dispersion can be controlled, reducing heterogeneity issues. This controlled and improved homogeneity offers new possibilities in isolation specific effects of minerals on coke reactivity and coke reactivity kinetics.

As a first step, and the subject of this article, a validation exercise is being undertaken to establish whether the reaction kinetics with CO\(_2\) of a simple coke analogue containing no minerals is similar to that of industrial coke. A pseudo CRI reactivity test is being used, a schematic of which is given in Figure 1.

The TGA reactivity tests were carried out over the temperature range 900°C-1350°C. The system was heated at 10°C/min to the desired temperature under Ar at gas flow rate of 1 L/min. The furnace gas was then switched to CO\(_2\) at a flow rate of 3 L/min. Both gases were
high purity 99.99% cleaned by passing through drierite and ascarite. The Ar was further cleaned with Cu turnings at 300°C. The experiment was run for 2 hours with CO$_2$, then the CO$_2$ was switched off and the sample cooled down under argon. Weight change during the reaction is logged to a PC and the rate of reaction ($R_C$) calculated using Equation 1,

$$R_C = -\frac{1}{W_o} \frac{dW}{dt}$$  \hspace{1cm} (1)$$

where $W$ is the weight of the sample, $W_o$ the initial weight of the sample and $t$ time.

The $R_C$ can also be evaluated as a function of temperature via Equation 2,

$$R_C = k_o e^{\frac{E_a}{RT}}$$ \hspace{1cm} (2)$$

where, $k_o$ is a pre exponential factor, $R$ is the gas constant, $E_a$ the activation energy and $T$ the thermodynamic temperature.

This equation can be rearranged into a linear form for the purpose of plotting rate data.

$$\ln R_C = -\frac{E_a}{R} \frac{1}{T} + \ln k_o$$ \hspace{1cm} (3)$$

By plotting $\ln R_C$ against $1/T$, as given in Figure 2, three zones have been identified as per Walker et al.[5] for carbon gasification. They are,

I. Region I – Chemical reaction controlled region
II. Region II – Chemical reaction + pore diffusion controlled region
III. Region III – Mass transport controlled region

![Figure 2: Plot of ln Rate against 1/T for the coke analogue](image)

Most of the published work on CO$_2$ reactivity with coke has been carried out in the low temperature range (850 to 1150 °C) where chemical reaction controls the rate, though higher temperature and associated reactions mechanisms also have relevance when considering coke reactivity in the blast furnace. A comparison of the current work with that reported in the literature for the low temperature region (region I) are given in Figure 3 [6-9].
The comparison of results is shown in Figure 3 and it clearly shows that both industrial coke and the coke analogue show similar reaction behaviour though the coke analogue has a lower rate than the industrial coke. This might be due to the absence of minerals in the coke analogue. Future studies will focus on the effect of selected minerals on the kinetics of the coke analogue reactivity.

References
Phase Equilibrium Study of ZnO-“FeO”-SiO$_2$ System at Fixed Po$_2$ 10$^{-8}$ atm

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Keywords: phase equilibrium, copper smelting slag, ZnO-“FeO”-SiO$_2$

Abstract

Analysis of quenched copper smelting slag from the bottom blown furnace at Dongying Fangyuan Nonferrous Metals Co., Ltd. (Fangyuan) shows that significant ZnO is present in both liquid and spinel phases. Phase equilibria have been investigated in the system ZnO-Fe$_2$O$_3$-SiO$_2$ in air and system ZnO-“FeO”-SiO$_2$ in equilibrium with metallic iron. These conditions cannot represent copper smelting process in which oxygen partial pressure is around 10$^{-8}$ atm. In the present study phase equilibria in the system ZnO-“FeO”-SiO$_2$ have been carried out at Po$_2$ 10$^{-8}$ atm. A series of experimental difficulties have been overcome to enable the ZnO-containing system to be investigated under reducing conditions controlled by CO-CO$_2$ gas mixture. The experimental approach includes master slag preparation, high-temperature equilibration, quench and electron probe X-ray microanalysis (EPMA). Phase compositions in the quenched samples were measured by EPMA and used for construction of phase diagram. It was found that the isotherms of the system ZnO-“FeO”-SiO$_2$ at Po$_2$ 10$^{-8}$ atm are significantly different from those in air or in equilibrium with metallic iron. Presence of ZnO in copper smelting slag significantly increases the liquidus temperature in spinel primary phase field. The partitioning of ZnO in liquid and spinel is also reported in this paper.

1. INTRODUCTION

Copper is the third major industrial metal in the world. About 19 million tons of copper was produced in 2011, while 80% of the total production was obtained by pyrometallurgy where huge amount of energy, both electricity and fossil fuel are consumed. The first commercial bottom blown oxygen smelting furnace (BBF) at Fangyuan has gained great attention due to its excellent performances with high adaptable to raw materials, high copper recovery rate (98%) and energy efficiency. However, as a new copper smelting technology, the knowledge of thermodynamics and physic-chemistry in this smelting process is limited, and current research is part of the research program outlined to narrow the gap.

It is well known that slag plays a critical role in the high-temperature processing of copper ore, since metal recovery, slag tapping and refractory consumptions are all closely related to the slag composition under the operating conditions. Table 1 shows the compositions of bulk slag, liquid, matte and solid present in a quenched BBF slag. It can be seen that, in addition to the major components “FeO” and SiO$_2$, the concentration of ZnO is also relatively high. Previous works in this system have been focused in air (Po$_2$ equal to 0.21 atm) and at metallic iron saturation (Po$_2$ is estimated to be around 10$^{-12}$ atm). No information can be found relevant to the copper smelting condition in which Po$_2$ is around 10$^{-8}$ atm. The present study is focused on the phase equilibrium studies of ZnO-“FeO”-SiO$_2$ system at Po$_2$ 10$^{-8}$ atm.
Table 1: Compositions (wt%) of phases present in Fangyang copper smelting slag.  

<table>
<thead>
<tr>
<th>Phases</th>
<th>“FeO”</th>
<th>Cu₂O</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>As₂O₃</th>
<th>MgO</th>
<th>S</th>
<th>PbO</th>
<th>ZnO</th>
<th>MoO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk-XRF</td>
<td>62.2</td>
<td>3.2</td>
<td>1</td>
<td>24.2</td>
<td>3.1</td>
<td>0.1</td>
<td>0.6</td>
<td>1.7</td>
<td>0.5</td>
<td>3.1</td>
<td>0.2</td>
</tr>
<tr>
<td>glass</td>
<td>58.4</td>
<td>0.8</td>
<td>1.2</td>
<td>30.5</td>
<td>3.2</td>
<td>0.1</td>
<td>0.7</td>
<td>1.1</td>
<td>0.5</td>
<td>3.3</td>
<td>0.2</td>
</tr>
<tr>
<td>spinel</td>
<td>93.7</td>
<td>0.1</td>
<td>0</td>
<td>0.6</td>
<td>3.4</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
<td>0.1</td>
<td>1.7</td>
<td>0.1</td>
</tr>
<tr>
<td>matte</td>
<td>10.1</td>
<td>68.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>20.3</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>

2. EXPERIMENTAL METHODOLOGY

Experimental procedure applied in present study is similar to that described in previous papers. Briefly, the sample was directly quenched into ice water after equilibration at target oxygen partial pressure and temperature, followed by EPMA to determine the compositions of the phases present in the quenched sample.

Under reducing condition, ZnO is progressively reduced and zinc metal vaporises leaving the condensed phases. Previous attempts to conduct phase equilibrium studies on ZnO-containing systems at controlled Po₂ by gas had been proven to be unsuccessful. The research technique has been developed in present study to reduce the vaporization rate of zinc from the slag during the equilibration. 1) ZnO was introduced into zinc-silicate master slag in air to reduce the activity of ZnO; 2) spinel substrate and iron-silicate master slag were prepared in the same conditions (temperature and Po₂) as the equilibration to shorten the final equilibration time of the zinc-containing slags; 3) equilibration time was adjusted to control the ZnO content in slag.

The quenched samples were sectioned, mounted, polished and carbon-coated using QT150TES (Quorum Technologies) Carbon Coater for EPMA examination. A JXA 8200 Electron Probe Microanalyser with Wavelength Dispersive Detectors was used for microstructure and composition analysis. The analysis was conducted with an accelerating voltage of 15 kV and a probe current of 15 nA. The standards used for analysis were from Charles M. Taylor Co. (Stanford, California): Fe₂O₃ for Fe, CaSiO₃ for Si and ZnO for Zn. The ZAF correction procedure supplied with the electron probe was applied. The average accuracy of the EPMA measurements is within 1 wt pct. Both Fe²⁺ and Fe³⁺ are present in the samples, however, only the metal cation concentrations can be measured using EPMA. For the presentation purpose only, all iron is calculated as “FeO” throughout this paper.

3. RESULTS AND DISCUSSION

(1) Experimental results in “FeO”-SiO₂ system

With an aim to evaluating the experimental methodology applied in current research, a reinvestigation of the “FeO”-SiO₂ system was carried out at the temperature range between 1200-1300°C. The examination of samples indicates the presence of wustite, spinel and tridymite primary phase fields in the phase diagram. The eutectic point between spinel and tridymite primary phase fields was determined to be 1200°C at 33.3 wt% SiO₂ in the present study.

The present results in the system “FeO”-SiO₂ at Po₂ 10⁻⁸ atm are compared with previous studies and FactSage calculations as shown in Figure 1. It can be seen from Figure 1 that the present data are in good agreement with the previous data. Experimentally determined liquidus temperatures in the present and previous studies are higher than those predicted by FactSage 6.2 in wustite and spinel primary phase field.
Figure 1: A comparison among current data, previous results\textsuperscript{10,11} and FactSage 6.2\textsuperscript{12} predictions on “FeO”-SiO\textsubscript{2} system at Po\textsubscript{2} 10\textsuperscript{-8} atm

(2) Experimental results in ZnO-“FeO”-SiO\textsubscript{2} system

The liquidus temperatures in ZnO-SiO\textsubscript{2} binary system have been determined in air by different authors.\textsuperscript{13,14} The eutectic point between tridymite and willemite primary phase fields was reported to be 1448±5 °C at 59 wt% ZnO, and the one between willemite and zincite primary phase fields was reported to be 1502±5 °C at 76.8 wt% ZnO. The previous study in ZnO-“FeO” system was only carried out for sub-solidus under intermediate Po\textsubscript{2} by Hansson et al.\textsuperscript{15}

The liquidus temperatures in the ZnO-“FeO”-SiO\textsubscript{2} system have been experimentally determined at Po\textsubscript{2} 10\textsuperscript{-8} atm between 1200 °C and 1300 °C. The primary phase fields in this system include tridymite, spinel, wustite, willemite and zincite (hypothetically). Both spinel [(Fe\textsuperscript{2+},Zn)O·Fe\textsuperscript{3+}2O\textsubscript{3}] and wustite [(Fe\textsuperscript{2+},Zn)O] are iron oxides. Wustite is stable at higher temperatures and spinel is stable at lower temperatures. The typical microstructures of quenched samples in the present study are presented in Figure 2. Figure 2a shows the liquid was in equilibrium with spinel at 1250 °C; Figure 2b shows the liquid was in equilibrium with tridymite at 1250 °C; Figure 2c shows the liquid was in equilibrium with spinel and tridymite at 1200 °C; and in Figure 2d, the liquid was in equilibrium with tridymite and willemite at 1300 °C.

The phase diagram of ZnO-“FeO”-SiO\textsubscript{2} system at Po\textsubscript{2} 10\textsuperscript{-8} atm is constructed based on the critically evaluation of the experimental data and understanding of phase rules. It can be seen from Figure 3 that the thick solid line represents experimentally determined boundary between spinel and tridymite, while the thick dash lines are hypothetical boundaries. The thin solid lines are experimentally determined isotherms, while thin dash lines are approximate isotherms. If the slag composition given in Table 1 is normalised to three components ZnO, “FeO” and SiO\textsubscript{2} and plotted in Figure 3, it can be seen that this slag is located in the spinel primary phase field with liquidus temperature of 1250°C. The liquidus temperature of this slag increases with increasing ZnO or “FeO” concentration.
Figure 2: Microstructures of quenched samples showing: (a) liquid equilibrated with spinel; (b) liquid equilibrated with tridymite; (c) liquid equilibrated with spinel and tridymite; (d) liquid equilibrated with tridymite and willemite.

Figure 3: Experimental determined ZnO-"FeO"-SiO$_2$ phase diagram at Po$_2$ at 10$^{-8}$ atm.

A comparison on 1250 °C isotherm between current research and FactSage 6.2$^{12}$ predictions is shown in Figure 4. The solid lines are current results and the dash lines are predicted from FactSage 6.2$^{12}$. It can be seen that FactSage predictions show the liquid is in equilibrium with three primary phases: spinel, willemite and tridymite at 1250 °C. Present study shows that the liquid is only in equilibrium with spinel and tridymite at 1250 °C. The fully liquid area is much smaller in the present study as compared to that predicted by FactSage 6.2$^{12}$. 
Further comparisons are also carried out in pseudo-binary systems “FeO”-SiO$_2$ at fixed ZnO (Figure 5) and (“FeO”+SiO$_2$)-ZnO at fixed Fe/SiO$_2$ ratio (Figure 6). It can be seen from Figure 5 that, the liquidus temperatures of the slag with 5 wt% ZnO are generally higher than those of ZnO-free slag in the spinel primary phase field. For example, the liquidus temperature of the slag containing 5 wt% ZnO is 1253 °C at 28 wt% SiO$_2$ (Fe/SiO$_2$ = 2 in weight), which is 30 °C higher than that of ZnO-free slag. Figure 6 presents the comparison between experimental results and FactSage predictions at fixed Fe/SiO$_2$ weight ratio of 2. It can be seen that the willemite primary phase field is not present in the experimentally determined phase diagram. The experimentally determined liquidus temperatures are much higher than those predicted by FactSage in the composition range investigated. The enormous difference between current results and FactSage prediction may due to the lack of experimental data at intermediate Po$_2$ for optimisation of thermodynamical modelling. The data obtained in the present study can be used to improve the thermodynamical modelling.
The partitioning of ZnO between spinel and liquid phases has been reported previously in the system ZnO-“FeO”-Al₂O₃-CaO-SiO₂ at metallic iron saturation⁷,¹⁶-²⁰. It was found that ZnO in spinel is much higher than that in the corresponding liquid. The comparison is made on the partitioning of ZnO between spinel and liquid at iron saturation and Pₒ² 10⁻⁸ atm. It can be seen from Figure 7 that, the solid dots were obtained from current research while the blank dots were extracted from the work under the metallic iron saturation⁷,¹⁶-²⁰. A linear relationship was found between ZnO in spinel phase and liquid phase under Pₒ² at 10⁻⁸ atm as indicated in Figure 7, while the partitioning of ZnO in equilibrium with Fe at different ZnO concentration was found to be limited in some area. Besides, the ZnO solubility in spinel slightly increase with the increase of ZnO concentration in liquid in both conditions, while much lower ZnO goes into spinel phase when Pₒ² is 10⁻⁸ atm compared to that in metallic iron saturation. This difference indicates the reducing condition will help ZnO come into the solid phase, which may be useful information for future ZnO recovery, and will great benefit for the thermodynamic modelling of ZnO-containing systems under Pₒ² at 10⁻⁸ atm. It should be noticed that the difference in Po2 or compositions in spinel phase (ZnO-Al₂O₃, FeO-Al₂O₃, FeO-Fe₂O₃ may co-exist in metallic saturation) may both lead to this phenomenon. Future work will be carried out to answer question.
4. SUMMARY

Phase equilibrium studies have been conducted under $10^{-8}$ atm oxygen partial pressure relevant to copper smelting condition with a temperature range from 1200 to 1300 °C. The liquidus temperature and primary phase fields in the “FeO”-SiO$_2$ and ZnO-“FeO”-SiO$_2$ systems have been experimentally determined. The liquidus temperatures obtained from current study in spinel primary phase field are higher than the predictions by FactSage 6.2. The liquidus temperatures in spinel primary phase field increase with increasing ZnO concentration in slag. ZnO partitioning between spinel phase and liquid phase has been compared at $P_O^2$ between $10^{-8}$ atm and metallic iron saturation. The result shows that ZnO tends to be more enriched in liquid phase under $P_O^2$ $10^{-8}$ atm.

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- Dongying Fangyuan Nonferrous Metals Co., Ltd. for providing the financial support to enable this research to be carried out
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REFERENCES


Effects of fluxing conditions on copper smelting slag cleaning

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Keywords: slag cleaning, copper smelting slag, flux, EPMA analysis

In the copper smelting process, more than two tons of slag is produced with each ton of copper. Copper losses in smelting slags are made up of chemically soluble copper (≈ 30%) and as mechanically entrained matter droplets (≈ 70%). This is the key technical concern for copper industries, because those copper losses in the slag are strongly influencing the economy of the copper extraction process. For a typical copper smelter, a decrease of 0.1 wt% Cu in the slag over a year of operation can save an annual value of over several million dollars. Therefore, it is of great importance to recover copper from copper smelting slag.

Slag cleaning processing can be divided into two types. The first is pyrometallurgical reduction and settling, performed in an electric or fuel-fired slag-cleaning furnace. The second is minerals processing of slow-cooled slag, including crushing, grinding, and froth flotation, to recover Cu from the slag. The former process has the advantage of lower capital and operating costs and feasible treatment of minor elements. During the last few decades, the pyrometallurgical processes used for cleaning copper smelting slags have been extensively investigated. The electric furnace or rotary slag-cleaning furnace are now generally used to perform this task, giving a level of copper in discard slag typically in the range of 0.6 - 1.3 wt%, with most plants reporting copper losses in the discard slag in the range of 0.8 - 1.0 wt% [1-3]. The latter process has the advantage of higher Cu recovery. Copper in the tail slag can be as low as 0.3 wt% when slow cooled in ladles and 0.5–0.6 wt% when cooled in pits. Comparing with an average of 0.8 wt% in an electric furnace final product, its higher operating cost compensated by the lower copper loss. However, the mineral processing requires larger court to handle slags. Since each plant’s situation is different, the options of slag cleaning route would be selected from the perspectives of operating costs and court, copper recovery and minor element deportment.

Bottom blown oxygen copper smelting process has been developed and firstly operated in Dongying, China by Dongying Fangyuan Nonferrous Metals Co., Ltd. (Fangyuan) in commercial scale. The main features of the bottom blown smelting process are that high grade matte (up to 75 wt% Cu) can be produced at relatively low temperatures (1160–1180 °C) with 2–3 wt% Cu remaining in the smelting slag. At present, the recovery of copper from slag is processed by slow cooling, milling and flotation at Fangyuan. Bottom blown oxygen copper smelting technology has demonstrated great potential and will be transferred to other plants around the World. In addition to the flotation process, pyrometallurgical slag cleaning has to be provided as an alternative technology for recovery of copper from slag. Low temperature operation of Fangyuan bottom blown furnace and high Fe/SiO₂ ratio in the slag result in spinel-containing slag [4] which is significantly different from conventional copper smelting slags. Presence of solid phase in the slag clearly influences the separation of the matte from slag. In this study, effects of fluxing conditions on cleaning process of Fangyuan
bottom blown furnace slag have been investigated with the aim of minimizing the copper loss in discarded slag.

The industrial copper smelting slags from Fangyuan were used to mix with single and/or mixture of flux (graphite, SiO$_2$, FeS) for high temperature experiments in Al$_2$O$_3$ crucible at 1200/1250 °C for 30/60 minutes. The experiments were carried out under Ar gas flow followed by water quenching. The quenched sample was then mounted, polished and carbon-coated for analysis. The microstructure and compositions of the phases present in the sample were measured by electron probe X-ray microanalysis (EPMA). The accuracy of temperature was controlled within ±2 degrees Celsius, and the accuracy of phase composition measurements is within 1 wt%. The typical microstructures of the quenched samples are shown in Fig.1 and Fig.2. The compositions of the phases measured by EPMA are listed in Table 1 for as-received slag and treated samples. The bulk composition of as-received slag measured by XRF is also given in Table 1. The Fe/SiO$_2$ ratio in as-received slag is approximately 1.9 and its liquidus temperature was determined to be over 1300 °C by reheated experiments. It can be seen that 2.8 wt% Cu was present in the as-received slag which included 2.2 wt% entrained and 0.6 wt% dissolved Cu. This means that at least 0.6 wt% Cu will be left even all matte droplets can be separated from the slag.

**Effect of carbon and SiO$_2$**

One of the important aims in slag cleaning process is to decrease the liquidus temperature so that solid phase in the slag can be reduced. It has been shown that oxygen partial pressure and Fe/SiO$_2$ ratio can significantly affect the liquidus temperature of copper smelting slag [5]. As can be seen from Fig. 1a that, 2% carbon addition did not remove all solid spinel at 1200 °C for 30 min. Matte droplets still distributed in the slag. Cu content in the slag was decreased from 0.7 wt% to 0.5 wt%. In contrast, when both carbon and SiO$_2$ were added to decrease Po$_2$ and Fe/SiO$_2$ ratio from 1.9 to 1.2, it can be seen from Fig. 1b that all spinel disappeared and the matte was settled on the bottom. In the meantime, the Cu content in the slag was decreased from 0.7 wt% to 0.2 wt%. Ideally, this is the Cu loss in the discarded slag if all matte can be separated from slag. Addition of SiO$_2$ decreases not only liquidus temperature but also copper solubility of the slag.

![Figure 1](image_url)

(a) 2% C, 30 min  
(b) 2% C + 16% SiO$_2$, 60 min

**Figure 1:** Microstructures of the samples quenched from 1200 °C

**Effect of FeS**

Cheap FeS can be obtained as a by-product in some processes. It is expected FeS in slag cleaning process can be 1) reductant; 2) fuel; 3) source of SO$_2$; 4) source of Fe. In the present study 3 and 9 wt% FeS were added into the slag respectively at 1250 °C for 30min. It can be seen from Fig. 2a that, addition of 3 wt% FeS did not have significant effect on slag phase
assemblages. On the other hand, addition of 9% FeS resulted in dissolution of spinel and formation of large matte droplets. Sulphur and iron concentrations in slag are increased. Decrease of the liquidus temperature seems to be a combined effect of $Po_2$ and dissolved FeS. Dendritic solid was formed on cooling indicating that viscosity of the slag was lower. However, dissolved Cu in slag was not significantly decreased and matte grade has been reduced significantly. It is possible that dissolved $Cu_2O$ was reduced but dissolved $Cu_2S$ was increased with FeS. Further study is required to find the optimum condition for use of FeS flux.

![Figure 2](image-url)  
**Figure 2**: Microstructures of the samples quenched from 1250 °C, 30min

![Table 1](image-url)  
<table>
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<th>Sample</th>
<th>Phases</th>
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<th>Al$_2$O$_3$</th>
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<th>MgO</th>
<th>ZnO</th>
<th>S</th>
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**References**