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Effects of slag chemistry and temperature on wetting and penetration of refractories by slags

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An *in situ* gravimetric technique based on wetting and capillary action principles has been used to investigate the wetting and penetration of synthesized alumina samples and commercial magnesia spinel refractories by $CaO-SiO_2-Al_2O_3-Fe_2O_3$ slags. Synthetic slags of $40CaO-40SiO_2-20Al_2O_3$ (in weight per cent) with 0 to 9 weight per cent Fe_2O_3 were used and the experiments were conducted at temperatures 1370 to 1470ºC under argon. The contact time between the sample and the slag was 30 minutes.

The results show that the wetting and penetration are enhanced by the iron oxide addition in the slags. Addition of Fe_2O_3 from 0 to 9 weight per cent resulted in a significant increase in the slag penetration into the magnesia spinel refractory by a factor of about 7 and a moderate increase in the synthesized alumina by about 60 per cent. The addition of Fe_2O_3 enhanced the wetting ($\gamma \bullet \cos\theta$, where γ is the surface tension of the slag and θ the contact angle between the slag and the refractory) by 5 to 18 per cent.

An increase in temperature from 1370ºC to 1470ºC resulted in a significant increase in the penetration of a 6 weight per cent Fe_2O_3 slag in the alumina and magnesia samples by a factor of 4 to 5 and a decrease in wetting by approximately 30 per cent.

Keywords: refractories, slag penetration, wetting.

Background

Refractory wear due to slag attack is a major concern for the pyrometallurgical industry[1-2]. In order to extend the service life of the refractories, it is essential to develop a good understanding of the interactions between refractories and molten slags, which involve the wetting and penetration of the refractory by molten slag, slag-refractory reactions, refractory wear and structural failure.

In this study, the effect of slag chemistry (Fe_2O_3 content in the slag) and the test temperature on wetting and penetration of refractories by a typical blast furnace slag were investigated. A commercial refractory (magnesia spinel) was used in the slag test. For comparison, synthesized single oxide (alumina) samples with controlled porosity and pore size similar to that of the commercial refractory were prepared and tested under identical conditions.

Experimental

A new *in situ* gravimetric technique has been recently developed at CSIRO Minerals for studying dynamic slag-refractory interactions based on wetting and capillary effect[3,4]. The experimental arrangement is schematically shown in Figure 1. A cylindrical sample was suspended above a molten slag bath. The test started by raising the molten slag bath to contact the sample. The apparent weight changes detected by the balance were logged to a PC at multiple readings per second. The *in situ* gravimetric data

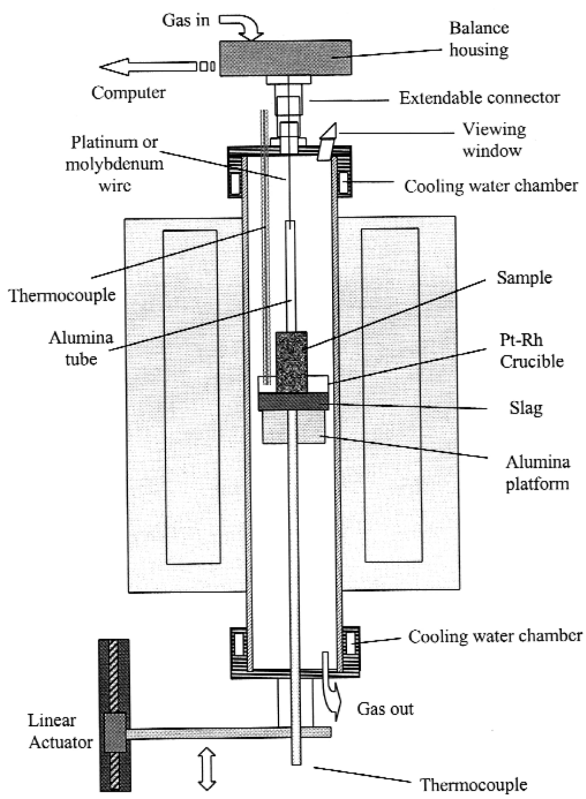

Figure 1. Experimental arrangement

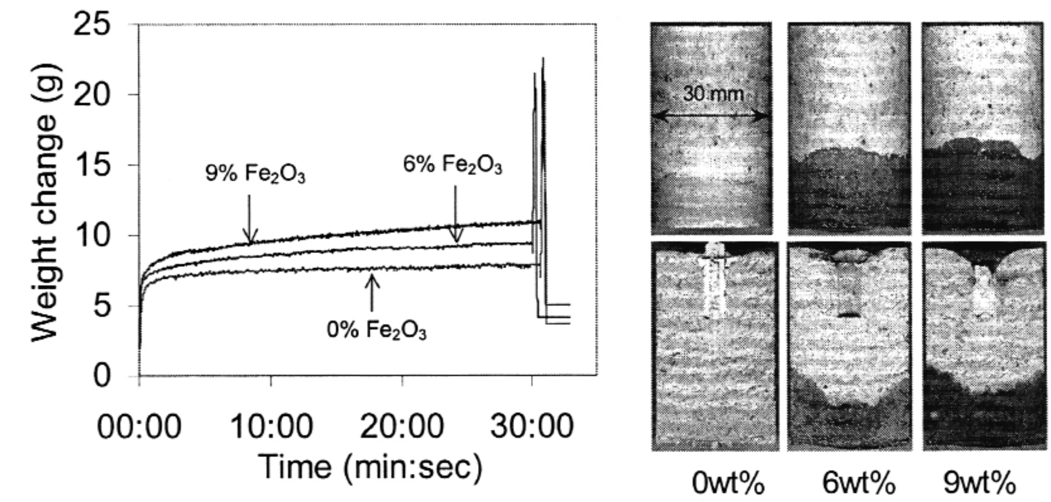

Figure 2. Effects of the slag Fe_2O_3 content on wetting and penetration for the synthesized alumina samples. Upper three photos show the outside of the alumina samples and the lower three show the cross sections

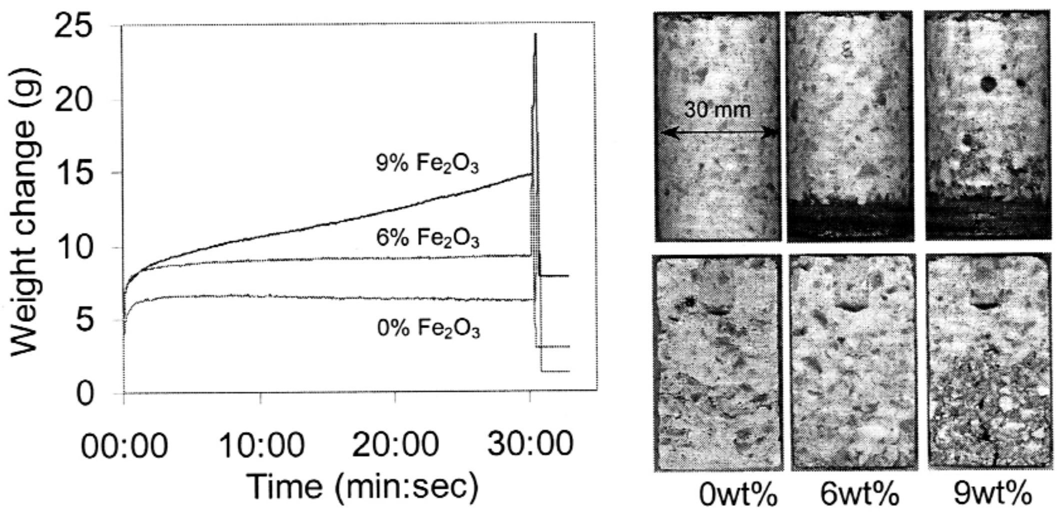

Figure 3. Effects of the Fe_2O_3 content in the slag on wetting and penetration for magnesia spinel refractory. Upper three photos show the outside of the refractory and the lower three show the sectioned refractory

provide information on the interactive process from initial contact and wetting, slag penetration and, if any, refractory dissolution, through to refractory failure[3,4].

Magnesia spinel bonded refractory ($92MgO$-$6.5Al_2O_3$ in weight per cent) used in the tests had an apparent porosity around 17 to 18 per cent and median pore size of 7 to 8 µm. Cylindrical samples ($\Phi30 \times 59$ mm) were core drilled from a virgin brick. Synthetic alumina samples of $\Phi30 \times 43$ mm were prepared in the laboratory from high purity fused alumina granules. By controlling the particle size distribution, compact pressure and firing temperature, the synthesized alumina samples had apparent porosities from 17 to 19 per cent and median pore size between 7 and 8 µm, similar to those of the commercial refractory. Samples selected for slag tests were based on their similarities in apparent porosity and pore distribution, which were assessed from water penetration tests carried out at room temperature to ensure consistent properties so that the slag test results could be compared.

Synthetic slags of $40CaO$-$40SiO_2$-$20Al_2O_3$ (weight per cent) with varying Fe_2O_3 from 0 to 9 weight per cent were prepared from analytical reagent grade chemicals in oxide powder forms ($CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3). The mixtures were pelletized and premelted in platinum-rhodium crucibles in air in a muffle furnace. Slag tests were conducted at temperatures from 1370°C to 1470°C under argon. The contact time between the sample and the slag was 30 minutes in all tests.

Effects of iron oxide content

The effects of the iron oxide content on the wetting and penetration were investigated at 1370°C with the slags containing 0, 6 and 9 weight per cent Fe_2O_3. The *in situ* gravimetric curves and sectioned samples after the tests are shown in Figures 2 and 3 for the alumina samples and the magnesia refractory, respectively.

The results show that wetting and penetration are influenced by the iron oxide content in the slag for both the alumina sample and the magnesia refractory. For the synthesized alumina samples, the sectioned samples showed more slag penetration in the surface region due to extensive slag creeping at the sample surface (slag creeps up onto the refractory sample surface due to the effect of interfacial tension between the molten slag, the gas and the refractory sample surface). In contrast, slag creeping at the

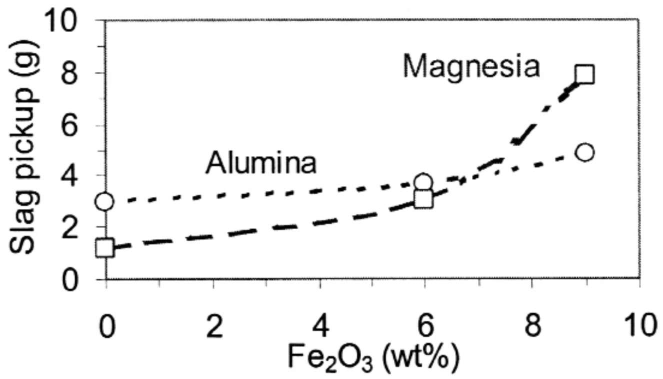

Figure 4. Effect of Fe_2O_3 on slag penetration into synthesized alumina sample and commercial magnesia refractory

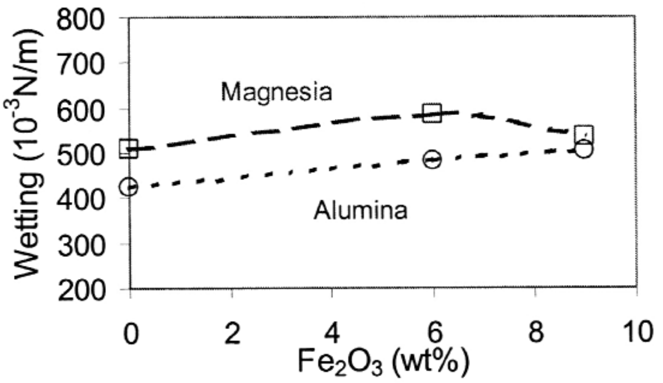

Figure 5. Effect of Fe_2O_3 on the wetting of the slags on synthesized alumina sample and commercial magnesia refractory

surface of the magnesia samples was limited to about 10 mm in height and did not contribute significantly to the slag penetration.

For both the alumina and the magnesia samples, there was little dissolution during the 30-minutes experiments. Thus the sample-free hanging weight measured at the end of the tests gives the amount of the slag penetrated into the samples. The difference between the sample-free hanging weight and the sample 'apparent' weight before the break (prior to the spike) could be used to estimate the wettability ($\gamma \cos \theta$, where γ is the surface tension of the slag and θ the contact angle between the slag and the refractory sample). The results are shown in Figures 4 and 5.

Figure 4 shows that the Fe_2O_3 in the slag has a greater effect on the slag penetration in the magnesia refractory than in the synthetic alumina samples. The slag wets the magnesia sample better than the alumina sample and the addition of iron oxide enhanced (in terms of a broad trend) the wetting of the slag on both the alumina and magnesia samples as shown in Figure 5.

The low iron oxide slags penetrated more into the alumina sample than into the magnesia refractory. The reason might be due to the higher porosity in the alumina sample or some reactions between the penetrating slag and refractory grains.

An increase in wetting accelerates slag penetration as observed with the alumina sample. The significant effect of iron oxide content (particularly from 6 to 9 weight per cent) on slag penetration in the magnesia spinel refractory, however, cannot be attributed to the wetting since there is no dramatic increase in the wetting. The reactions between penetrating slag and refractory grains may play an important role, as will be discussed later.

Effects of temperature

The effects of the temperature on the wetting and penetration were studied with the slag containing 6 weight per cent Fe_2O_3 at temperatures 1370°C, 1420°C and 1470°C. The test results are shown in Figures 6 and 7 for the synthesized alumina sample and the commercial magnesia spinel refractory, respectively.

The results showed that temperature has a significant effect on slag penetration into both the synthetic alumina sample and the magnesia refractory. At 1470°C, the penetrated slag reached the top of the samples in about 20 to 25 minutes, which was shown by the levelling-off of the *in situ* gravimetric curves (Figures 6 and 7) and confirmed by the sectioned samples after the tests.

At higher temperatures, limited dissolution of the samples occurred around the meniscus at the bottom slag-sample contact and the 'necking', commonly referred to as slag line

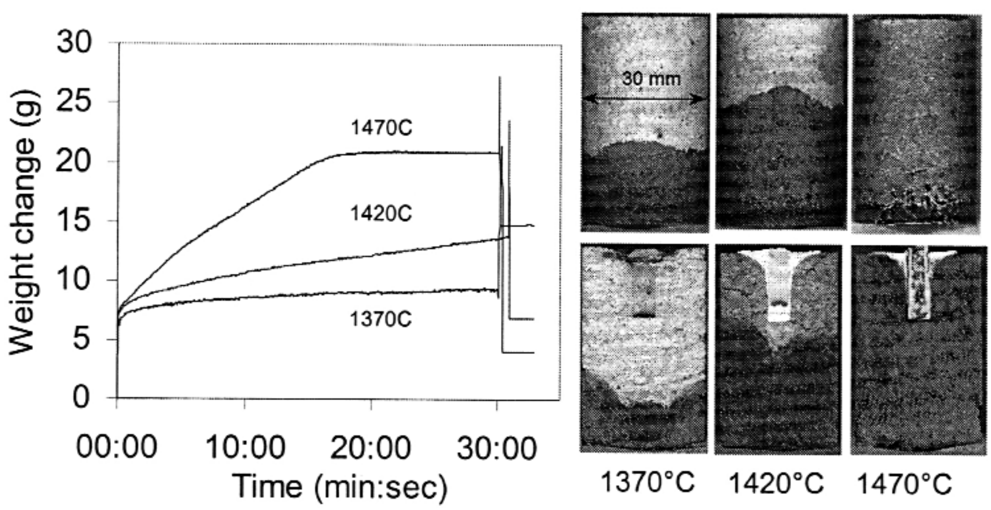

Fig 6. Effect of the temperature on the wetting and penetration of synthesized alumina samples by the 6 weight per cent Fe_2O_3 slag. Upper three photos show the outside of the alumina samples and the lower three show the cross sections

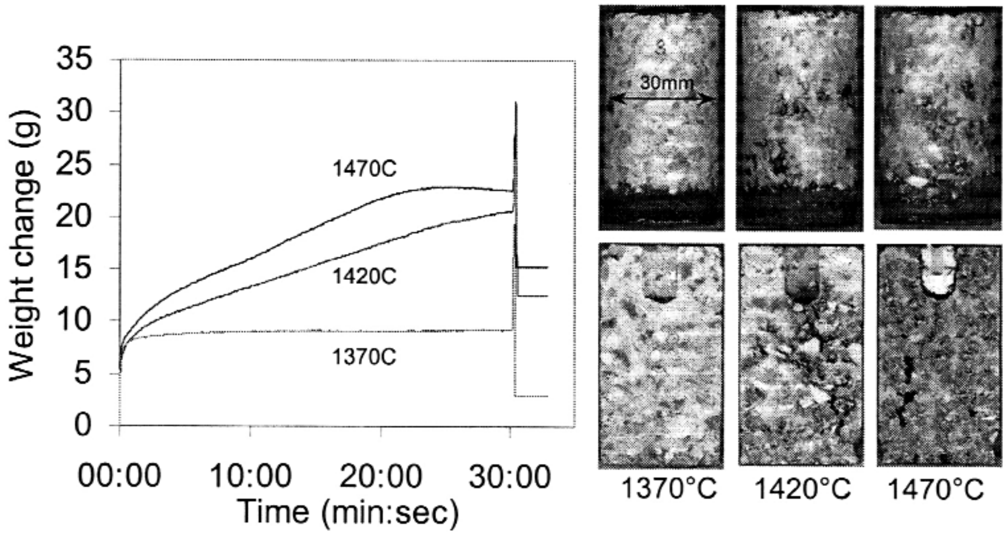

Fig 7. Effect of the temperature on the wetting and penetration of commercial magnesia refractory by the 6 weight per cent Fe_2O_3 slag. Upper three photos show the outside of refractory and the lower three show the sectioned refractory

wear, was visible, particularly on the magnesia sample (Figure 7). The extensive slag creeping occurred again on the alumina samples (Figure 6) but not on the magnesia samples (Figure 7).

The amount of slag penetration and the wetting at different temperatures were estimated from the sample-free hanging weight and the sample 'apparent' weight before the break. No correction was made for the very limited dissolution of the magnesia spinel sample at 1470ºC. The results are shown in Figures 8 and 9.

Figure 8 shows that an increase in temperature from 1370ºC to 1470ºC results in an increase in the slag penetration by a factor of 4 to 5. The effect of temperature on the magnesia sample was shown clearly at 1420ºC. In comparison, the effect on slag penetration into the alumina sample was less significant at 1420ºC and was dramatic at 1470ºC, particularly when taking into account that the penetration reached the top of the alumina sample even earlier than the magnesia sample, as shown in Figures 6 and 7.

The estimated wetting (Figure 9) shows a trend of decreasing wetting with increasing temperature for both the alumina and magnesia samples (higher value for the alumina sample at 1420ºC may be regarded as still within the experimental scatter). Therefore, the observed 4–5 folds increase in the slag penetration over the temperature range could not be attributed to the wetting. As mentioned earlier, limited dissolution at 1470ºC from the magnesia spinel sample was not corrected and might introduce a small error. Nevertheless, the results should be reliable in indicating the range of the wetting values and the effect of temperature.

The rate of liquid rise in a capillary is described by the following well-known equation[5-6]

$$h\frac{dh}{dt} = \frac{r^2}{8\eta}\left(\frac{2\gamma\cos\theta}{r} - \rho g h\right)$$

where h is the height of liquid rise in the capillary of radius r, g the gravitational acceleration, and η and ρ are the viscosity and density of the liquid, respectively. Although the equation is not quantitatively applicable to the penetration of molten slag into a porous refractory with a complex three-dimensional pore structure[3], it nevertheless shows in principle the key factors governing the rate of slag penetration. In addition to the influence from the structural properties of the refractory (e.g. pore size and porosity), the wetting ($\gamma \cos \theta$) and the viscosity (η) of the slag play a key role on the rate of slag penetration, which increases with an increase in wetting and a decrease in viscosity.

The experimental results showed that temperature had a significant effect on the slag penetration. Data analysis showed a broad trend of decreasing wetting with increasing temperature for the present slag-refractory systems. Accordingly, the increase in the slag penetration must be due to the effect of temperature on slag viscosity and possible reactions with refractory grains. An increase in temperature could reduce the viscosity of the slag and thus result in a faster slag penetration. The variation in the slag viscosity over the temperature range (1370~1470ºC) used in the present study, however, is unlikely to have been large enough for the 4–5 fold increase in the slag penetration observed.

Therefore, the observed effect of temperature must be due to the reactions between the penetrated slags and the refractory grains, which caused changes to the composition of the penetrated slag and hence its liquidus temperature inside the pores. The variation in the slag liquidus temperature could lead to the precipitation of solids, which may cause a rapid increase in the slag viscosity and blocking (or partially blocking) the pores. This might have been the reason for a slow slag penetration at relatively lower temperatures. A higher temperature would have broadened the slag liquidus region and thus, reduced the effect caused by a slag-refractory reaction. Hence a much faster slag penetration was observed.

Similar mechanisms may also play a part when the starting composition of the penetrating slags varies as shown by the results for iron oxide series tests (Figure 4). The addition of the iron oxide in the slag may cause a decrease in the slag liquidus temperature; hence a similar effect to that of the test temperature. The observed strong effect of the iron oxide on the slag penetration into the magnesia refractory is due to the preferential reaction between the iron oxide and the periclase grains inside the refractory pores.

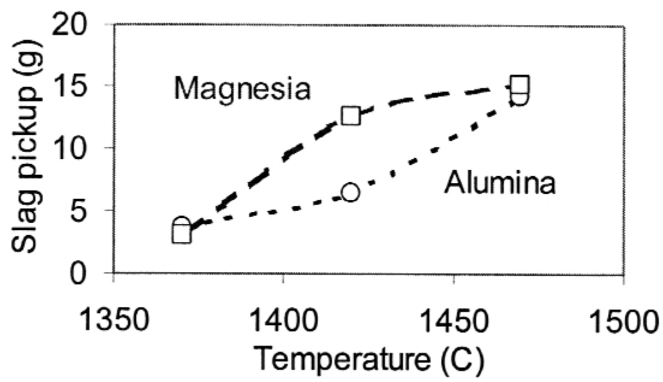

Figure 8. Effect of temperature on slag penetration into the synthesized alumina sample and commercial magnesia refractory

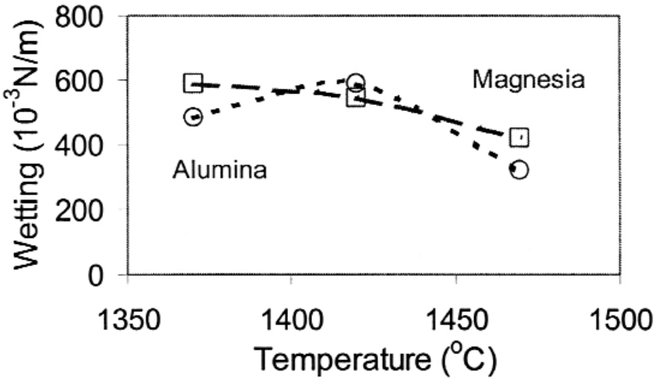

Figure 9. Effect of temperature on the wetting of the slags on the synthesized alumina sample and commercial magnesia refractory

Summary

The effects of iron oxide content in the slag and temperature on the wetting and penetration of synthesized alumina sample and commercial magnesia spinel refractory by a blast furnace-type slag were studied using the new *in situ* gravimetric technique.

Addition of Fe_2O_3 from 0 to 9 weight per cent increased the slag penetration in 30 minutes by about 60 per cent for the synthesized alumina and by a factor of 7 for the magnesia spinel refractory. The addition of Fe_2O_3 enhanced the wetting by 18 per cent and 5 per cent, respectively.

An increase in temperature from 1370°C to 1470°C resulted in an increase in the penetration of a 6 weight per cent Fe_2O_3 slag in the alumina and magnesia samples by a factor of approximately 4 to 5. However, an increase in temperature decreases the wetting by about 34 per cent for the alumina samples and approximately 29 per cent for the magnesia samples.

Analysis of the results suggests the slag-refractory reactions inside the refractory pores may play an important role in suppressing the slag penetration, particularly at lower temperatures close to the slag liquidus temperature.

Acknowledgement

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