

## DISSOLUTION OF LIME INTO SYNTHETIC COAL ASH SLAGS.

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### ABSTRACT

One of the alternate processes presently being investigated to produce electrical power from coal is Integrated Gasification Combined Cycle (IGCC). The ash that remains when the coal is gasified in this process, is removed by granulating the molten ash at 1400 - 1500°C. To reduce the melting temperature of the coal ash to this level, a flux, usually limestone, is added with the coal to the gasifier. The rate of dissolution of the flux is uncertain.

This paper reports the investigation of the rate of lime dissolution into synthetic coal ashes, consisting of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO. Results previously reported have shown that the free dissolution of fine particles (50-200µm) is mass transfer controlled. To investigate forced dissolution, a high temperature viscometer was used to rotate a cylinder of lime in the molten slag for a given period. At temperatures between 1450°C and 1650°C, reaction products of 3CaO.SiO<sub>2</sub>/3CaO.Al<sub>2</sub>O<sub>3</sub>, 2CaO.SiO<sub>2</sub>/3CaO.Al<sub>2</sub>O<sub>3</sub>/12CaO.7Al<sub>2</sub>O<sub>3</sub> form around the lime pellet. The concentration gradient involved in the mass transfer was defined, and initial studies of the diffusion coefficients were completed.

### INTRODUCTION

Entrained flow gasifiers partially combust coal at elevated temperatures and pressures to create a product gas consisting of carbon monoxide and hydrogen, which is combusted in a gas turbine to produce electrical power. The ash that remains after this combustion, must melt to allow the resulting slag (molten ash) to run down the walls of the gasifier and is tapped from the base of the gasifier. The minimum temperature experienced by the ash within the gasifier is usually between 1400 and 1500°C. The ash must therefore be molten at these temperatures for the ash to be efficiently removed from the gasifier.

Coals with high ash fusion temperatures require the addition of a flux with the coal to lower the melting point of the ash. The alternative, increasing the operating temperature lowers the process efficiency, which is undesirable. Usually this flux is CaCO<sub>3</sub>, which, when exposed to the atmosphere within the gasifier breaks down into CaO and CO<sub>2</sub>. The flux reduces the viscosity of the resulting slag (depending on the ash being considered).

This paper considers the dissolution process of lime into synthetic coal ash slags, that consist of silica, alumina and lime for forced dissolution and silica, alumina, lime and ironoxide for free dissolution. Our preliminary results have shown that for no convection, dissolution from small lime particles in a synthetic ash is mass transfer controlled and a dicalcium silicate layer formed around the lime particles.<sup>(1)</sup>

Matsushima<sup>(2)</sup> et al. investigated the forced dissolution rate of lime in SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO and SiO<sub>2</sub>-FeO-CaO slags and found a 2CaO.SiO<sub>2</sub> layer around the solid lime, though he suggested that the layer did not sit next to the lime but was separated by a slag layer. Matsushima determined a boundary layer size by an equation using dimensionless numbers, (determined for the dissolution of steel) and by determining the mass transfer constant  $k = \frac{D}{\sigma}$  by a mass transport equation and assuming  $D = 5.5 \cdot 10^{-6}$  cm<sup>2</sup>/s. Samaddar et al.<sup>(3)</sup> investigated the dissolution of alumina, mullite, anorthite and silica in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> melts with a similar technique as used here. Cooper et al.<sup>(4)</sup> also used this technique to study sapphire dissolution and Taira et al.<sup>(5)</sup> studied dissolution of alumina in similar slags, while Gudenau et al.<sup>(6)</sup> and Olsson et al.<sup>(7)</sup> studied the dissolution of carbon into hot metal baths.

### METHOD

#### Free Dissolution.

Small particles of lime, with average diameters of 275, 500 and 750 µm were mixed into synthetic coal ash mixtures: 60SiO<sub>2</sub>-30Al<sub>2</sub>O<sub>3</sub>-6Fe<sub>2</sub>O<sub>3</sub>-4CaO(wt%). The mixtures of ash and lime were

placed in a platinum crucible and heated in a vertical tube furnace to 1400, 1500 or 1600°C for a defined time in an argon atmosphere. At the end of the experiment, the melt was removed from the furnace and quenched.<sup>(1)</sup> The regions around the lime particles were studied quantitatively under the Scanning Electron Microscope using EDAX to establish concentration profiles, and the amount of unreacted lime determined by an oxalic titration method.<sup>(8)</sup>

#### Forced Dissolution.

Cylindrical pellets of lime were produced by pressing powdered lime in a die and then sintering the pellets in a muffle furnace for two hours at 1550°C. Samples of slag were premelted from reagent grade oxides, producing a homogeneous melt prior to dissolution experiments. Each slag sample was produced in a molybdenum crucible liner, ensuring no dissolution of carbon from the outer graphite crucible occurred. The slag compositions selected are based on coal ash silica to alumina ratios (2 to 3.35). The range of lime content in slag (15 to 25 wt%), was chosen to ensure the melt would be completely fluid at temperatures used in this set of experiments.

At the beginning of each dissolution experiment, a pellet was suspended on a molybdenum rod above a melt in a vertical tube furnace, refer Figure 1, allowing the pellet to heat to approximately the same temperature as the melt. The furnace atmosphere was kept at a mildly reducing composition by the graphite crucible, which reacted with any oxygen entrained into the furnace with the nitrogen purge gas. Each melt was maintained at temperature for at least thirty minutes to allow the melt to equilibrate. The pellet was then lowered into the melt and rotated at the desired speed for a given period of time. To remove the pellet at the end of a test, a molybdenum cradle containing the crucible the pellet still in position in the melt, was lifted out of the furnace into a cooling tube. Nitrogen was directed onto the crucible to cool it as quickly as possible, as shown in Figure 2. This required three to five minutes.

The frozen melt in the crucible was sectioned through the vertical axis of the pellet and polished before the concentration profile around the lime pellet was determined using a Scanning Electron Microscope. The change in size of the pellet was also measured.

The thickness of the boundary layer was determined by fitting an exponential equation to the lime concentration profile. The boundary layer size is assumed to be the distance from the lime source to the point where the lime concentration does not change (within 1%). The diffusion coefficient for lime dissolving into SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/CaO slags was determined from equation 1:

$$-j = \frac{dx}{dt} = \frac{D(C_i - C_\infty)}{\sigma(1 - V_i C_i)} \quad \text{eqn 1}^{(9)}$$

Where  $j$  is the flux of lime,  $x$  the amount of lime (in cm) removed from the lime pellet,  $t$  the time of dissolution,  $D$  the lime diffusion coefficient,  $\sigma$  the boundary layer size,  $C_i$  the saturation lime concentration at experimental temperature,  $C_\infty$  the bulk slag lime concentration and  $V_i$  a volume fraction, or  $\frac{\rho_s}{\rho_l}$  (the ratio of the density of the solid and liquid phases).

## RESULTS

### Free Dissolution

A 3CaO·Al<sub>2</sub>O<sub>3</sub> + 2CaO·SiO<sub>2</sub> layer (reaction zone) was found to form around the lime particles, with no separation of the layer from the lime by slag, after which the lime concentration falls to the bulk slag concentration. Figure 3 shows the lime concentration outside the crystalline phases does not fall evenly as it is affected by dissolution of lime from adjacent particles. Using the model of a shrinking particle in a fluid with changing concentration, the rate of mass transfer through the melt was found to be the rate limiting step in the dissolution process, as shown in Figure 4.<sup>(1)</sup>

### Forced Dissolution

A typical concentration profile in the slag around the pellet is shown in Figure 5. The figure shows a reaction zone followed by an area that exhibits a concentration profile typical of diffusion control. The reaction zone is a combination of 2CaO·SiO<sub>2</sub> and 3CaO·SiO<sub>2</sub>. The corresponding alumina phase: 3CaO·Al<sub>2</sub>O<sub>3</sub>, on the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram, is only seen at the end of the reaction zone, though it is believed to occur throughout the reaction zone in fine defined ribbons around the alumino-silicate crystals. This behaviour of the two types of crystals forming an unhomogeneous layer around the lime is shown in maps of the reaction zone from the Scanning Electron Microscope, Figure 6. The brighter the points appears on the image, the higher the concentration

of that species. The aluminium concentration in this region is higher than can be completely accounted for in the compound  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ . Some  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  is also being created in this region, though no discrete particles can be determined as it is finely divided amongst the other tricalcium-aluminate crystals.

Other samples showed very little evidence of  $3\text{CaO}\cdot\text{SiO}_2$  in the reaction zone, consisting mainly of  $2\text{CaO}\cdot\text{SiO}_2$ , as shown in Figure 7. This figure also shows the existence of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ , again with some  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ , to account for the alumina content found, at the interface of the lime pellet and the reaction zone. To produce these compounds the alumina concentration rises well above the bulk slag alumina concentration. This indicates that these phases are crystalline.

The diffusion coefficients calculated from the concentration profile of lime from the end of the "reaction zone" to the bulk slag concentration are given in Table 1. The diffusion coefficient calculated from the forced diffusion experiments are variable. Work is continuing on this area. These initial experiments appear to indicate that temperature may have a greater effect on the size of the reaction zone than the speed of rotation. The size of the boundary layer appears to be affected by both the change in temperature and the speed of rotation. The size of the boundary layer should theoretically decrease with increasing rotational speed, while increasing temperature will decrease the viscosity, affecting the boundary layer size. The results shown are inconclusive and further work is required.

#### CONCLUSIONS

- The rate limiting step of dissolution of lime into molten ash is the mass transport of the lime into the slag, for both forced and free dissolution.
- A crystalline layer of  $2\text{CaO}\cdot\text{SiO}_2$  or  $3\text{CaO}\cdot\text{SiO}_2$  interspersed with  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  form around a lime particle dissolving into molten ash.
- The driving force for the mass transport step appears to be the difference between the CaO concentration at the reaction zone and the bulk slag.

#### ACKNOWLEDGMENTS

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#### REFERENCES

1. Wang S. M. et al. Experimental Studies and Computer Simulation of Dissolution of Lime Particles into Coal Ash Slags. Australian Symposium on Combustion and the Fourth Flame Days, University of Adelaide, South Australia, November 9-10, 1995.
2. Matsushima, M., et al. A Fundamental Study on the Dissolution Rate of Solid Lime into Liquid Slag. Transactions ISIJ, Vol 17, 1977, p442 - 449.
3. Samaddar B. N. et al. Dissolution in Ceramic Systems: 11, Dissolution of Alumina, Mullite, Anorthite and Silica in a Calcium-Aluminum-Silicate Slag. Journal of the American Ceramic Society, Vol. 47, 1964, p249 - 254.
4. Cooper A. R. et al. Dissolution in Ceramic Systems: 1, Molecular Diffusion, Natural Convection, and Forced Convection Studies of Sapphire Dissolution in Calcium Aluminium Silicate. Journal of the American Ceramic Society, Vol 47 (1) 1964, p 37 - 43.
5. Taira, S. et al. Kinetic Behaviour of Dissolution of Sintered Alumina into  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  Slags, ISIJ International Vol 33, (1) 1993 p116 - 123.
6. Gudenau et al. Dissolution of Carbon Brocks in Hot Metal Baths (Auflösung sverhalten von Kohlenstoffsteinen im Roheisenbad. Stahl Eisen Vol. 111 (2), 1991 p89 - 94.
7. Olsson, R.G. et al. Rate of Dissolution of Carbon in Molten FeO-C alloys. Transactions of the Metallurgical Society of AIME, Vol236, 1966 p426 - 429.
8. Russell, R.O. Journal of Metals, 19 (8), 1967. P104.

#### FIGURES

Table 1: Diffusion Coefficient Estimates from equation 1.

$\text{SiO}_2/\text{Al}_2\text{O}_3$	CaO %	Rotational Speed rpm	Temperature °C	Reaction layer thickness mm	Boundary layer thickness mm	Diffusion coefficient. $\text{cm}^2/\text{s}\cdot 10^{15}$
3.35	25	83.25	1550	0.0544	7.2484	6.9
3.35	25	83.5	1450	0.056	5.39	11.4
3.35	25	37.15	1450	1.328	5.8	6.89
3.35	25	20	1450	0.0587	2.35	2.04
3.35	25	110	1450	0.0267	0.518	0.326
2.25	15	83.5	1550	0.039	0.933	0.784
2.25	20	74	1450	0.384	9.539	6.5
2.25	20	74	1650	0.190	4.7664	8.5

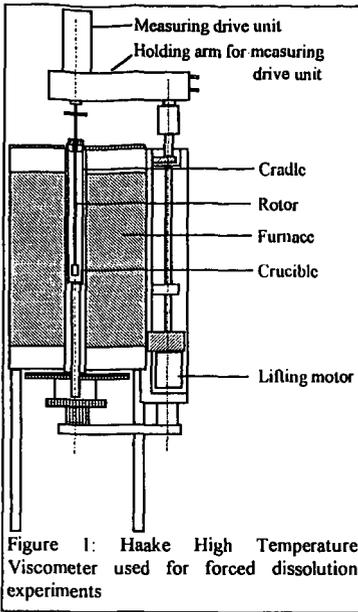


Figure 1: Haake High Temperature Viscometer used for forced dissolution experiments

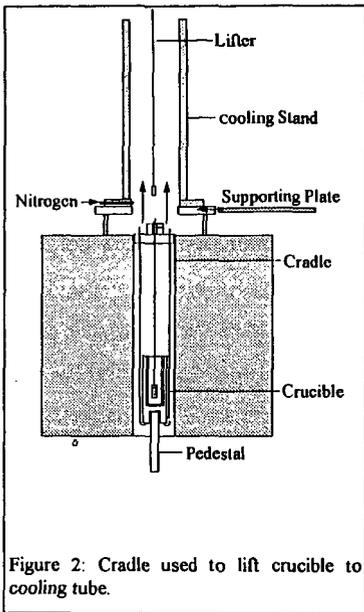


Figure 2: Cradle used to lift crucible to cooling tube.

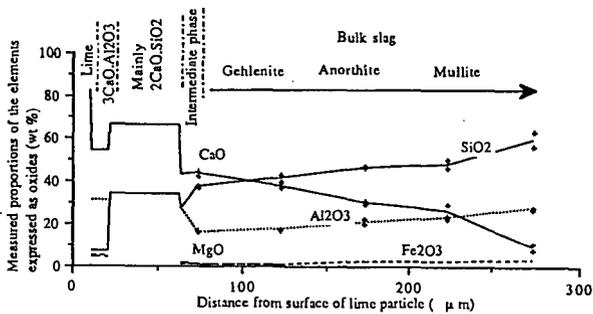


Figure 3: Free Dissolution Concentration Profile around a 750 μm lime particle in slag at 1500°C

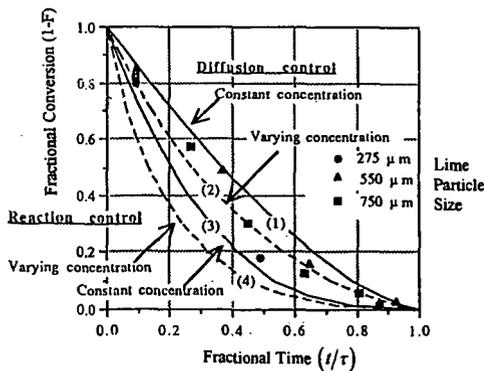


Figure 4: Free Dissolution Experiments: Comparison of Experimental Results with Theoretical Curves for Dissolution Rates Controlled by Diffusion and Reaction Kinetics.

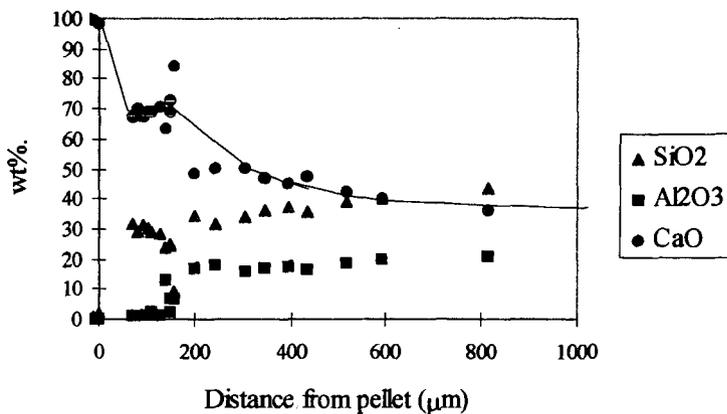


Figure 5: Forced Dissolution Concentration Profile around lime Pellet,  $\text{SiO}_2/\text{Al}_2\text{O}_3=2.25$ , at  $1450^\circ\text{C}$

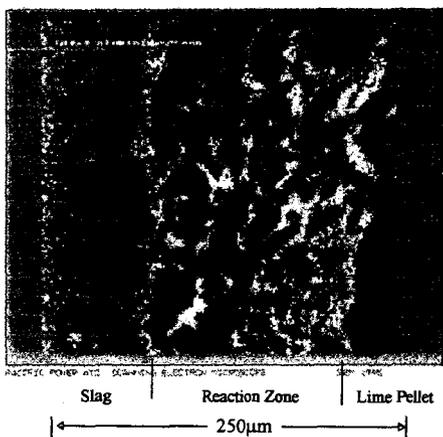


Figure 6: Aluminium Intensity Map

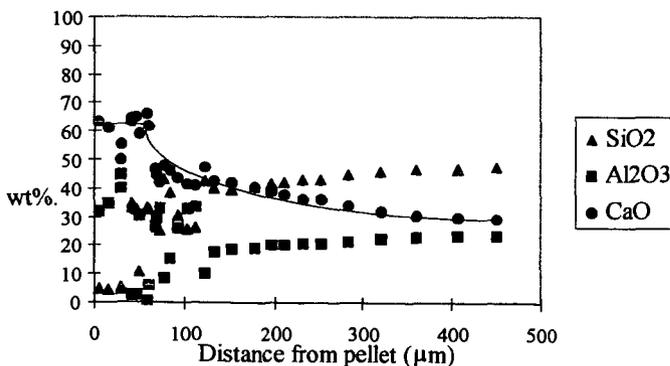


Figure 7: Forced Dissolution Concentration Profile around lime Pellet,  $\text{SiO}_2/\text{Al}_2\text{O}_3=2.25$ , at  $1650^\circ\text{C}$