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KINETICS OF SILICOTHERMIC REDUCTION OF CALCINED DOLOMITE IN FLOWING ARGON ATMOSPHERE

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The Pidgeon process is currently the dominant silicothermic process route to produce magnesium. Calcined dolomite is briquetted with ferrosilicon and reduction is carried out at $1100 - 1200\ ^oC$. The reduction can be written as:

$$2\ CaO.MgO_{(s)} + xFeSi_{(s)} \rightarrow 2Mg_{(g)} + Ca_2SiO_{4(s)} + xFe_{(s)} \qquad (1)$$
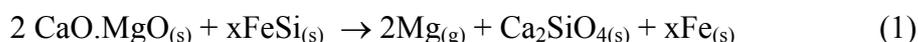
The magnesium vapour extracted is removed using vacuum condition to condense as a dense metal. Thermodynamic analysis of this process has been carried out in the past to predict the distribution of the metal impurities in condensed magnesium. The results suggested that a number of impurities in different phases formed in the region between reaction zone and condenser. The thermodynamic results only are not sufficient to describe the process, and the knowledge of the kinetics of the Pidgeon process is required. Kinetics plays important role to give more insight to the process such as for process design and control.

The kinetics phenomena in the Pidgeon process are relatively complex. It is a heterogeneous reaction which includes three different solid react and produce vapour and another solids. There have been a number of kinetic studies of the Pidgeon process in vacuum condition, but very limited literature available for the reduction in flowing inert gas atmosphere. The kinetics phenomena will include the intrinsic chemical kinetics of reaction, transfer of magnesium vapour to the surface through pores, and transfer of vapour from the surface to the bulk.
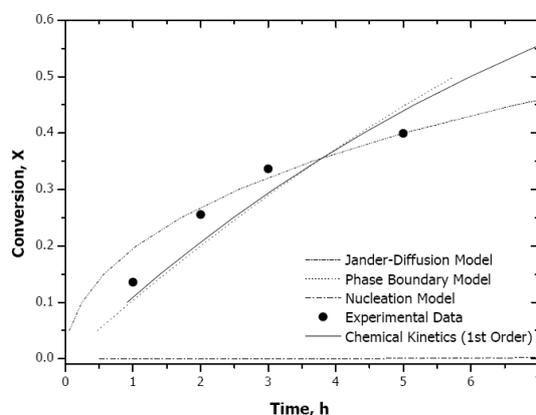

Figure 1. Comparison of Different Kinetic Models and Experimental Data of Magnesium Recovery at 1150 ^oC.

In this study, the experimental data from Morsi *et al* [1] which studied silicothermic in flowing argon at 0.08 L/min to 1 L/min was analysed using a number of kinetic models

based on the controlling step, such as diffusion models, phase boundary model, nucleation model, and intrinsic chemical reaction model. Diffusion model can represent the experimental data as described in Figure 1. The available diffusion models were also examined. The three dimension diffusion models, such as Jander, Serin-Ellickson, Ginstling-Brounshtein, and Valensi-Carter models can represent the experimental data, as seen in Figure 2, with the Ginstling-Brounshtein model ($1 - 2/3X(1-X)^{2/3} = Kt$) and Jander model ($[1-(1-X)^{1/3}]^2 = Kt$) fit mostly the experimental data at different operating temperature. This suggests that the overall reaction is controlled by diffusion of solid reactant through the product layer.
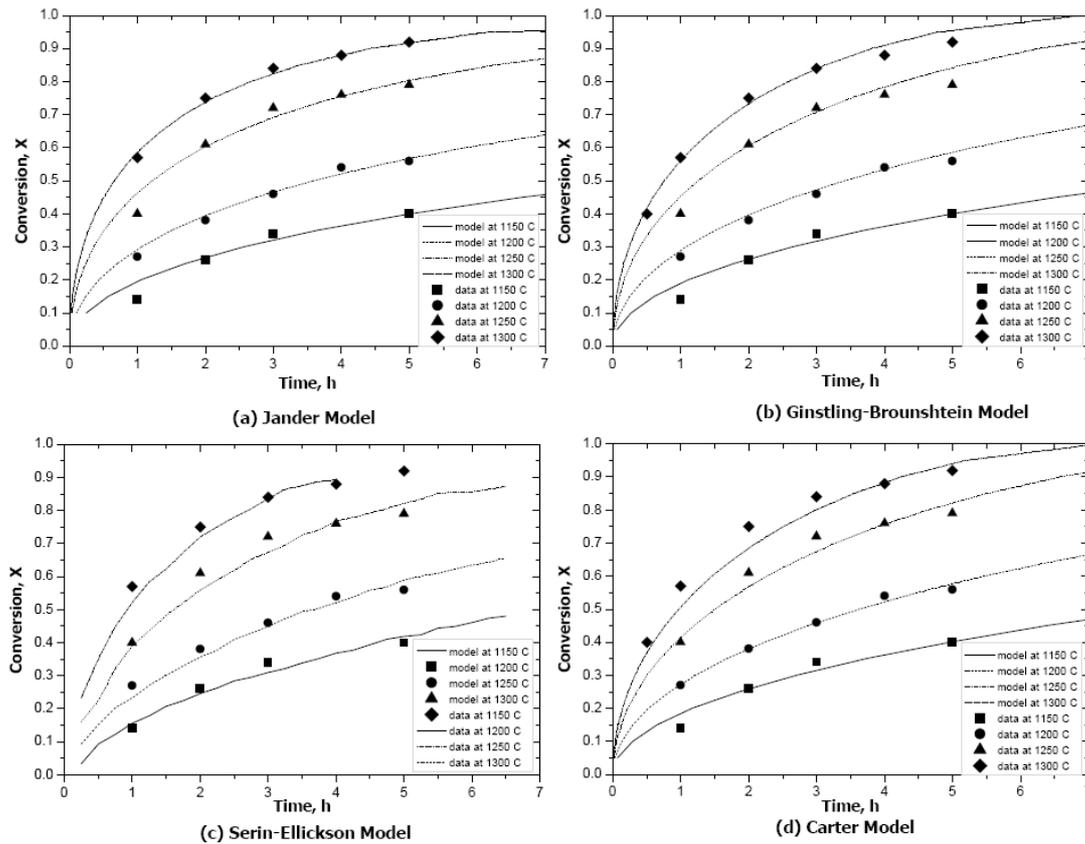

Figure 2. Three Dimensional Diffusion Models

Mass transfer effect of magnesium vapour from the surface to the bulk was also observed. The calculations were also based on Morsi et al's data. On the mass transfer of magnesium vapour, the transfer of magnesium vapour through the pores is found via Knudsen diffusion.

The mass transfer is expressed as:

$$j = \frac{M}{RT} K_c (P_B - P_S) \qquad (2)$$

where j is magnesium diffusion flux ($gcm^{-2}s^{-1}$), K_c is mass transfer coefficient, P_B is the pressure of magnesium in the bulk, and P_S is pressure of magnesium at the surface of briquette. The mass transfer coefficient is calculated by Warner relation [2], which is a modified Ranz-Marshall relation [3] for the gas stream passed in the tube:

$$K_c = \frac{1.15D}{2r_s}\left(2.0 + 0.6N_{Re}^{1/2}N_{Sh}^{1/3}\right) \qquad (3)$$

r_s is radius of the pellet, N_{Re} is Reynold number, and N_{Sc} is Schmidt number. The magnesium diffusivity and viscosity is calculated from Chapman-Enskog theory. The results are presented in Figure 3. The external mass transfer of magnesium vapour to the bulk phase is quite small. With Kc is 9 to 10 cm.s^{-1}, which resulted to pressure drop of 1 to 2 mmHg. These results suggest that at low flow rate, argon gas is saturated with magnesium vapour.
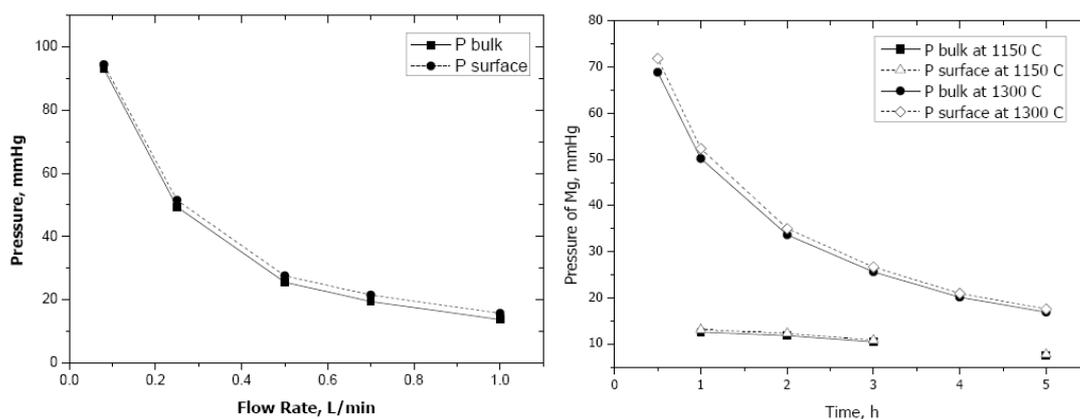

Figure 3. Calculated Pressure of Magnesium Vapour in the Surface of Briquette and Bulk Phase with (a) Different Flow Rate, and (b) Different Reaction Time

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1.   Morsi, I.M., et al., Silicothermic Reduction of Dolomite Ore Under Inert Atmosphere. Canadian Metallurgical Quarterly, 2002. **41**(1): p. 15-28.
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