Numerical analysis for CO_2 absorption and regeneration behaviors in porous solid sorbent by modified unreacted-core model

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IMPRES

Conclusions/Summary

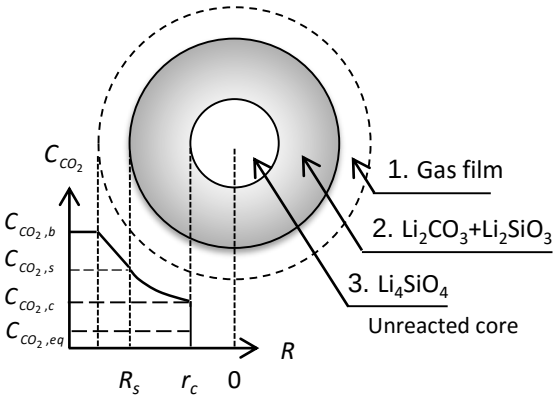
Lithium ortho-silicate (Li_4SiO_4) is a suitable solid sorbent for capturing CO_2 from solid oxide fuel cells. CO_2 absorption reactors packed with porous-solid spherical pellets of Li_4SiO_4 show unsteady temperature distribution and capture ratio behavior owing to the unsteady CO_2 absorption rate and highly exothermic process. The CO_2 absorption rate of this sorbent reportedly depends on temperature, CO_2 concentration, and CO_2 accumulation, expressed as the weight change of the sorbent.

In this study, the modified unreacted core model is proposed to simulate the mechanism of CO_2 absorption of a porous-solid spherical pellet. Important properties such as the reaction rate constant of the unreacted core surface (k_c), the coefficient of mass transfer through the gas film (k_f), and the coefficient for effective diffusion through the product layers (D_{eff}) that characterize the behavior of the sorbent were empirically derived using thermogravimetry and a diluted packed-bed reactor. The reaction rate $S'k_c$ and the mass transfer coefficient k_f can be expressed by the Arrhenius law and forced convection mass transfer correlation for flow in packed beds, respectively. The diffusivity D_{eff} obtained by unreacted core model has a peak value at a certain temperature to fit experimental data and is underestimated at other temperatures of slow reaction rates. The Bruggeman model is commonly used to D_{eff} and a modified model using linearly decreasing porosity ε with CO_2 absorption is proposed in this work.

Numerical analysis by applying these parameters to the modified unreacted core model adequately explained the complicated CO_2 absorption and regeneration behaviors.

Unreacted core model of porous pellet

$$Li_4SiO_4 + CO_2 \leftrightarrow Li_2SiO_3 + Li_2CO_3$$



1. **Rate of CO_2 mass transfer through the gas film**

$$N_{CO_2,1} = 4\pi R_s^2 k_f \left(C_{CO_2,b} - C_{CO_2,s}\right)$$

2. **Rate of CO_2 mass transfer through the product layer**

$$N_{CO_2,2} = 4\pi D_{eff} \frac{C_{CO_2,s} - C_{CO_2,c}}{1/r_c - 1/R_s}$$

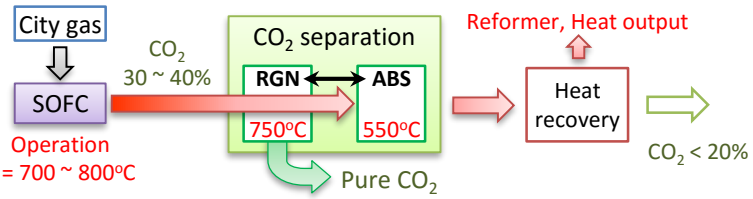
3. **Rate of CO_2 absorption at the surface of the unreacted core**

$$N_{CO_2,3} = S'k_c \left(C_{CO_2,c} - C_{CO_2,eq}\right)$$

Over all CO_2 absorption rate

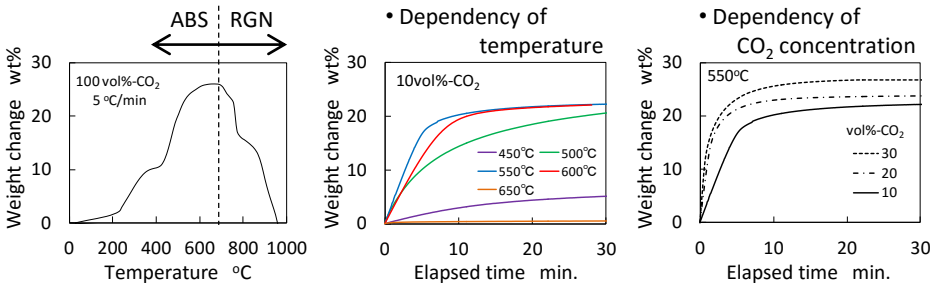
$$\frac{dW}{dt} = \frac{4\pi R_s^2 M_{CO_2}\left(C_{CO_2,b} - C_{CO_2,eq}\right)}{\frac{1}{k_f} + \frac{R_s}{D_{eff}}\left[\left(1 - \frac{w}{w_{max}}\right)^{-1/3} - 1\right] + \frac{4\pi R_s^2}{S'k_c}\left(1 - \frac{w}{w_{max}}\right)^{-2/3}}$$

Capturing CO_2 from Solid oxide fuel cells



CO_2 absorption/regeneration behavior of lithium silicate

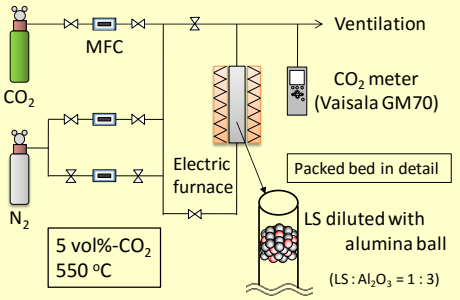
Thermogravimetric analysis of lithium silicate under various conditions



Experimental formulation

• Gas film mass transfer coefficient: k_f

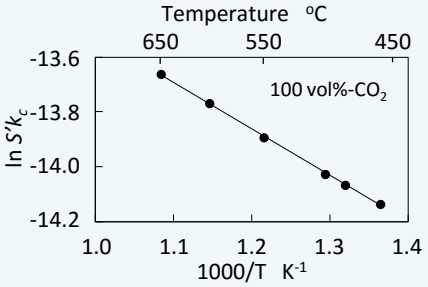
Experimental apparatus for diluted packed bed



$$Sh = 2.76 + 0.155 Re_p^{0.6} Sc^{1/3}$$

• Reaction rate: $S'k_c$

Arrhenius plot of $S'k_c$ by thermogravimetry



$$\frac{S'k_c}{4\pi R_s} = 2.47\times10^{-2} \exp\left(-\frac{1.45\times10^4}{RT}\right)$$

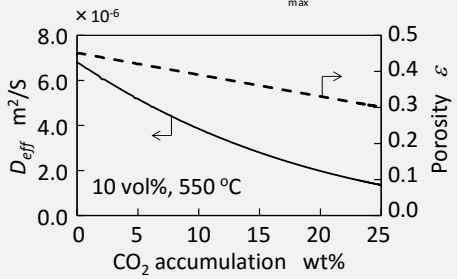
Photo: ϕ=5mm spherical LS pellet from Toshiba Corporation

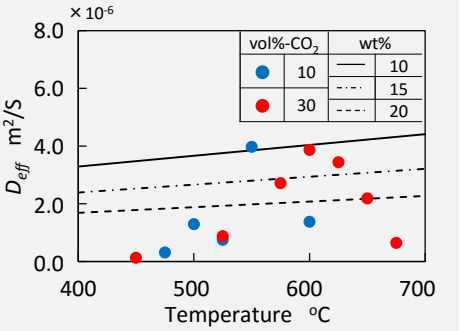
• Effective diffusion coefficient: D_{eff}

Modified Bruggeman model

$$D_{eff} = \varepsilon^{\alpha} D_{pore} \quad , \quad \frac{1}{D_{pore}} = \frac{1}{D_{CO_2,N_2}} + \frac{1}{D_{kn}}$$

$$\varepsilon = \varepsilon_0 - 0.15\,X \quad , \quad X = \frac{w}{w_{max}}$$

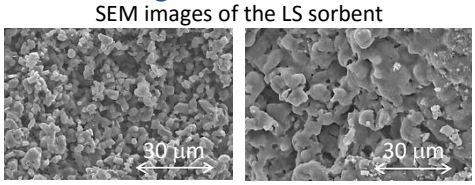




*Plots: Obtained from dW/dt at 10% weight change lines: Calculated by Modified Bruggeman model

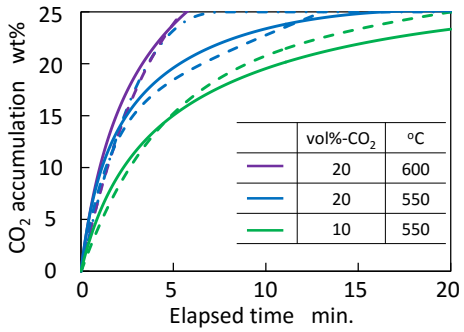
Changes in LS structure

SEM images of the LS sorbent



(a) Before absorption (b) After absorption at 550°C

Prediction of CO_2 absorption behavior



*Solid lines: experimental (diluted packed bed reactor)
Dashed lines: analytical ($\varepsilon = \varepsilon_0$ - 0.15X)
Chain line: analytical (ε: constant)