Oxidation Reaction of Calcium Sulfide in an Advanced PFBC Condition(II) — Sulfation Reaction and Grain Model Application —

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The effects of particle size, O_2 concentration, temperature, and sorbent type on sulfation of calcium sulfide were investigated at temperatures of 650 to 850°C. Calcium sulfide particle is oxidized to $CaSO_4$ through reaction: $CaS + 2O_2 \rightarrow CaSO_4$ when reaction temperature is below 850°C. CaS particle with a diameter below 0.005 mm was found to achieve complete conversion to $CaSO_4$. However, CaS particle with a diameter above 0.02 mm wasn't be completely converted to $CaSO_4$ due to the pore blockage of sulfate product layer. A kinetic study of the sulfation reaction ($CaS + 2O_2 \rightarrow CaSO_4$) has shown its activation energy to be 57.2 kJ/mol. A grain model has been developed to analyze the oxidation reaction within a CaS particle. The effects of temperature, O_2 concentration, particle size and type of limestone on the reaction process were discussed.

Key Words

PFBC system, Calcium sulfide, Sulfation reaction, Grain model

1. Introduction

Advanced PFBC systems have worked on a topping cycle linking a pressurized fluidized bed gasifier with a PFBC boiler. This system has several advantages such as system simplification and high desulfurization efficiency by in-furnace $DeSO_x$, higher plant efficiency (42-48%) through use of a gas turbine of a 1300°C class or more, and lower auxiliary power consumption. As for desulfurization cycle, limestone is used to capture H_2S in gasifier, and then spent sorbent out of gasifier, mostly being in the form of calcium sulfide (CaS), is desirable to be oxidized to $CaSO_4$ in PFBC boiler, so that solid waste can be disposed and reused with safety.

For oxidation reaction of CaS to $CaSO_4$, it was reported¹⁾ that there were still unreacted CaS left in the inner of CaS particle due to larger molar volume of product $CaSO_4$. In our previous paper²⁾, it was found that at temperatures above 900°C CaS was first oxidized to CaO

with release of SO_2 through reaction :

and then formed CaO and SO_2 reacted with in-diffusing O_2 to form $CaSO_4$ in the outer of particle by reaction :

However, there must be loss of sulfur (SO_2 emission) during the conversion of CaS to $CaSO_4$ through reaction (1) and (2). Therefore, direct conversion of CaS to $CaSO_4$ by reaction :

is necessary to be considered.

The present work is an attempt to determine the possibility that sulfur in calcium sulfide during combustion can be retained in the form $CaSO_4$ through reaction (3). The effects of particle size, temperature, oxygen concentration, and sorbent type on complete conversion of CaS to $CaSO_4$ were investigated. A grain model was applied to get optimal conditions for full conversion of CaS to $CaSO_4$.

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2. Experimental Section

Oxidation experiments were conducted by the use of a TG-DTA apparatus (Rigaku, TG8110D). Approximately 20 mg CaS sample was heated up to the required temperatures between 650 and 850°C in N₂ atmosphere, and then the gas environment was changed to O₂ with concentrations of 1% to 21%. The exit SO₂ gas from TG with the intervals of 4-minute sampling time was analyzed quantitatively by a FPD gas chromatograph, which was calibrated by a mixture containing 496.5 ppm SO₂ in N₂ before each test.

CaS samples were prepared through sulfurization reaction in a fluidized bed (a quartz glass tube of I.D, 38mm and 500mm height). Limestone was firstly calcined in N₂ atmosphere at 900°C until no CO₂ was detected by a TCD gas chromatograph, then reactant gas was changed to 4500 ppm H₂S-8.4% H₂-N₂ gas mixture. The sulfidation reaction followed with various reacting times so as to obtain the samples with different CaS contents. The CaS contents of the samples before/after oxidation were confirmed by the methylene blue method. Three types of limestones produced in Gifu prefecture and a coral leaf were used in this study. The sorbent particles were crushed and sieved; the fraction in this study comprised four ranges: below 0.005 mm, 0.148 to 0.212 mm (mean diameter = 0.20 mm), 0.420 to 0.590 mm (mean diameter = 0.50 mm), and 0.710 to 1.000 mm (mean diameter = 0.90 mm). A pure CaS reagent with 0.02 mm in diameter (Kanto Chemical Co., INC.) was also used. The mean pore diameter and porosity of each sample were obtained by the analyzer Pore Size 9320

(Shimadzu). BET analysis (Quantasorb) using liquid N₂ sorption gave the specific area of each CaS sample. The properties of sorbents and CaS samples are listed in Table 1.

3. Experimental Results

3.1 Effect of particle size and O₂ concentration

The effect of conversion on particle size was determined at 800°C in 10% O₂ atmosphere with Kinsensan limestone particles (0.005, 0.20, 0.50 and 0.90 mm) and a pure CaS powder reagent (0.02 mm). Experimental results are shown as the data points in Fig. 1. During all oxidation experiments, concentration of SO₂ gas in the product gas was below a few ppm, so that reaction (1) is reasonable to be neglect for this study. The smaller CaS particle size is, the higher conversion of sulfation is. The 0.005 mm particle achieved 100% conversion of CaS to CaSO₄.

Fig. 2 shows the effect of O₂ concentration ranging from 1 % to 21% O₂ at 800°C for 0.50 mm diameter particle of Kinsensan. Experimental data show that the reaction slows down with the increase of conversion. High oxygen concentration benefits the conversion of CaS to CaSO₄.

The initial reaction rate constants in 1-21% O₂ with the 0.90 mm particles of four different limestones and 0.005 mm CaS particle of Kinsensan limestone were obtained. The activation energy of sulfation reaction, 57.2 kJ/mol, was obtained as shown in Fig. 3, which is almost the same as that of Davies³⁾.

Table 1 Limestones and CaS samples used in this study

Sorbent type	Content of CaO (wt.%)	Content of MgO (wt.%)	Symbol of CaS	Diameter (mm)	CaS content (mol%)	Specific area (m ² /g)	Average pore diameter a ₀ (Å)	Porosity ε ₀
Kinsensan Limestone	55.53	0.31	K0	0.005	100	10.25	1165	0.50
			K1	0.20	80			
			K2	0.50	82			
			K3	0.90	85			
Osaka Limestone	55.47	0.45	O2	0.50	50	13.39	1048	0.51
White Limestone	54.87	0.74	W2	0.50	50	14.50	1262	0.52
Coral Leaf	55.12	0.41	C2	0.50	50	8.30	2159	0.54
CaS Reagent				0.02	100	10.68	1175	0.51

Fig. 1 Comparison of experimental (data points) and theoretical (solid line) average conversion of sulfation at 800°C, 10% O₂ with the four sized particles of Kinsensan and 0.02 mm CaS reagent

Fig. 2 Comparison of experimental (data points) and theoretical (solid line) average conversion of sulfation reaction at 800°C with the 0.50 mm diameter particle of Kinsensan for 1-21% O₂

Fig. 3 Arrhenius plot of apparent reaction rate constants

Fig. 4 The SEM picture of cross sections and line analysis of 0.90 mm reacted particle of Kinsensan limestone at 800°C in 21% O_2 atmosphere

3.2 Analysis of Product layer

For better understanding of product layer, the analytical results of cross section of the reacted CaS particle (0.90 mm, Kinsensan) at 800°C in 21% O_2 by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analyzer (EDX) are shown in Fig. 4. Along with the radial position from the surface of sample the intensities of oxygen and sulfur increased and reached relatively constant levels. And then the intensity of oxygen decreased to reach the level of base line, the intensity of sulfur quickly increased to be at a high level. These results indicate that there is CaSO_4 formed in the surface of particle, O_2 can not diffuse into the inner of particle. Atomic ratios of O to Ca from particle surface in 1, 10 and 21% O_2 atmospheres for the reacted CaS particle (0.90 mm, Kinsensan) are shown in Fig. 5. The atomic

ratio of O/Ca decreases with the normalized radial position from the particle surface, and basically becomes zero in the radial position between 0.90 and 0.94. Within the region with higher level of oxygen intensity, the product layer consists of about 80% CaSO_4 and 20% CaS for the case of 21% O_2 . Fig. 6 shows the atomic ratios of O to Ca for three-sized reacted particles at 800°C in 21% O_2 atmosphere. Assuming that the product layer corresponds to the ratio of $\text{O}/\text{Ca} > 2.8$, there are $4\ \mu\text{m}$, $5\ \mu\text{m}$ and $5.2\ \mu\text{m}$ product layers for three sized particles under 21% O_2 condition, which probably indicates that the thickness of product layer has no relationship to the particle size. The results in Figs. 5 and 6 show that CaS exists near the surface of particle. The surface of the sample used in Fig. 4 was also checked by X-Ray Diffraction (XRD). The results in

Fig. 5 Comparison of experimental and calculated molar ratio of sulfur to oxygen for the 0.90 mm Kinsensan particle at 800°C in 1-21% O₂ atmosphere

Fig. 6 Comparison of experimental and calculated molar ratio of oxygen to calcium for the three sized Kinsensan particles at 800°C in 21% O₂ atmosphere

Fig. 7 XRD result of 0.90 mm reacted CaS particle of Kinsensan at 800°C in 21% O₂ atmosphere

Fig. 7 suggest that CaS exists near the surface of particle and the product layer is a mixture of CaSO_4 and CaS. The reason may be that the pore on the surface has been blocked due to CaSO_4 formed, so that there must still be unreacted CaS left in the center of grain in the particle surface when the reaction stops.

4. Grain Model

The concept of grain theory, dealt with many previous authors⁴⁻¹⁰, is useful for the analysis of reaction process. According to this theory, it is assumed that a porous particle is comprised of spherical grains of uniform size separated by pores through which the reacting gases diffuse. As the reaction proceeds, the reaction product is formed on the surface of grains.

The CaS particle consists of grains; the interstices between grains form the system of pores. The grains are assumed to be nonporous. The following phenomena are included in the reaction process.

1. External mass transfer of O_2 from bulk gas flow to the external particle surface.
2. Molecular diffusion and Knudsen diffusion through pores at constant oxygen concentration.
3. Reaction between O_2 and CaS grain according to an unreacted core model with product layer diffusion control, taking into account the expansion of grains and eventual blocking of pores.
4. An irreversible first-order reaction for reaction between O_2 and CaS grain.

The mathematical model is based on an assumption of pseduostationarity. This means that the O_2 concentration profile in the particle is derived from a stationary mass balance, taking diffusion and chemical reaction into account. From the stationary concentration profile, the local rate of oxidation is calculated, which is integrated with respect to time to yield the local degree of oxidation.

Based on unreacted shrinking core mechanism, the rate of an irreversible first-order reaction for a spherical grain can be expressed in dimensionless form⁵:

$$d\xi/dt^* = -1 \quad (4)$$

where

$$\xi = (1 - X_{\text{CaS}})^{1/3} \quad (5)$$

$$t^* = 1/2k_s [A_p/(3V_p)] C_{\text{O}_2} t \quad (6)$$

where

$$A_p = 4\pi r_g^2 \quad (7)$$

$$V_p = 4/3\pi r_g^3 \quad (8)$$

Substituting Eqs (5), (6), (7) and (8) in Eq. (4), we can obtain

$$d(1 - X_{\text{CaS}})^{1/3} / dt = -1/2 k_s [A_p/(3V_p)] = -1/2 k_s / r_g \quad (9)$$

Rewriting Eq. (9) we obtain

$$dX_{\text{CaS}}/dt = 3/2 k_s / r_g C_{\text{O}_2} (1 - X_{\text{CaS}})^{2/3} \quad (10)$$

The pseduostationary mass balance in a spherical particle is expressed as

$$D_e \left(\frac{d^2 C_{\text{O}_2}}{dR^2} + \frac{2dC_{\text{O}_2}}{RdR} \right) = r_A = C_{\text{so}} dX_{\text{CaS}}/dt \quad (11)$$

with the boundary and initial conditions:

$$\left. \begin{aligned} D_e (dC_{\text{O}_2}/dR) &= k_f (C_{\text{O}_2}^d - C_{\text{O}_2}) R = R_0 \\ dC_{\text{O}_2}/dR &= 0 \quad R=0 \end{aligned} \right\} t > 0 \quad (12)$$

$$C_{\text{O}_2} = 0, r_A = 0 \quad t = 0 \quad (13)$$

The mass transfer coefficient on the external is given by

$$k_f = N_{\text{sh}} / (D_m d_p) \quad (14)$$

where Sherwood number is calculated by Ranz-Marshall's formula¹¹

$$N_{\text{sh}} = 2.0 + 0.6 N_{\text{Re}}^{1/2} N_{\text{Sc}}^{1/3} \quad (15)$$

The molecular diffusion coefficient is calculated as follows¹²:

$$D_m = 0.1883 [T^3 (M_{\text{O}_2} + M_{\text{N}_2}) / (M_{\text{O}_2} M_{\text{N}_2})]^{1/2} / (P \sigma_{\text{O}_2-\text{N}_2}^2 \Omega_d) \times 10^{-4} \quad (16)$$

$$\sigma_{\text{O}_2-\text{N}_2} = (\sigma_{\text{O}_2} + \sigma_{\text{N}_2})/2 \quad (16-1)$$

$$\Omega_d = 1.06036/T_n^{0.1561} + 0.19300 / \exp(0.47635T_n)$$

$$+ 1.03587 / \exp(1.52996T_n)$$

$$+ 1.76474 / \exp(3.89411T_n) \quad (16-2)$$

$$T_n = T/G \quad (16-3)$$

The Knudsen diffusion coefficient is calculated by⁹

$$D_k = 9700 a (T/M_{\text{O}_2})^{1/2} \times 10^{-4} \quad (17)$$

where a is the radius of pore within particles, which is calculated as:

$$a = a_0 (\epsilon / \epsilon_0) [(1 - \epsilon_0)/(1 - \epsilon)]^{2/3} \quad (18)$$

where a_0 is the initial radius of pore within particles.

The voidage among particle changes with the conversion of CaS as

$$\epsilon = \epsilon_0 (1 - \epsilon_0) (Z-1) f_s X_{\text{CaS}} \quad (19)$$

where f_s is the initial volume fraction of solid reactant in particle; Z is the ratio of molar volume of solid product to solid reactant, which is expressed as

$$Z = (M_{\text{CaSO}_4} / \rho_{\text{CaSO}_4}) / (M_{\text{CaS}} / \rho_{\text{CaS}}) \quad (20)$$

Bosanquet formula¹³ is used for the calculation of effective diffusion coefficient:

$$D_e = \epsilon / \tau (D_m + D_k) / (D_m D_k) \quad (21)$$

where τ is expressed as⁷⁾

$$\tau = (1/\epsilon)^m \quad (22)$$

The average conversion of CaS, X_{CaS} can be calculated by

$$X_{CaS} = (3 \int_0^{R_0} R^2 X_R dR) / R_0^3 \quad (23)$$

The parameter values used in theoretical calculations are also listed in Table 1. The coupled equations (10) and (11) are approximated by finite difference formulation and solved numerically as a boundary value problem by Gauss method. Preliminary calculations show that a net with fifty grid points on the particle radius and a time step as large as 1 second can provide a numerical solution with sufficient accuracy.

5. Comparison of experimental and calculated results

Numerical value of the tortuosity factor τ needs to be calculated. By fitting calculated data to the ones determined experimentally for 0.50 mm particle of Kinsensan, the value of parameter m in Eq. 22 is chosen as ϵ_0/ϵ as shown in Fig. 8.

Grain model is described that accounts for a variable effective diffusivity that results from the change of pore size inside the reacting solid particle. The effective diffusivity is separated into a molecular diffusion coefficient and a Knudsen diffusion coefficient. Fig. 9 shows

the effect of sulfation conversion on effective diffusivity with sample W2 (0.50 mm, white limestone) in 10% O_2 at temperatures of 800°C. The value of the effective diffusivity on the surface of particle (radial distance = 1) drops about 2 orders of magnitude at conversion level of about 0.07, and gradually tends to be zero due to pore closure. It is suggested that at initial stage of sulfation both molecular diffusion and Knudsen diffusion contribute to effective diffusion coefficient, and with the decrease of pore size ($CaSO_4$ formation) effective diffusion coefficient is mainly determined by Knudsen diffusion coefficient.

The model predictions have been compared with the experimental data. In Figs. 1 and 2, the solid lines represent the calculated results under the same experimental operating conditions. In Fig. 1, the smallest particle can achieve 95% conversion of CaS to $CaSO_4$, and the largest particle only reaches 5% conversion. The calculated conversions of 0.20 and 0.50 mm particles are about 5-10% higher than the experimentally measured values. The results in Fig. 2 indicate that changeable effective diffusivity with conversion of sulfation in the model reasonably can describe sulfation process. When the effective diffusivity decreases to be very small, the O_2 concentration in the reaction front tends to become zero, resulting in the cease of sulfation reaction. The solid lines in Figs. 5 and 6 represent the calculated

Fig. 8 Comparison of experimental conversion for 0.50 mm particle of Kinsensan at 800°C in 10% O_2 atmosphere with the calculated one with various values of m

Fig. 9 Local effective diffusivity vs conversion for 0.50 mm CaS particle sulfation in 10% O_2 atmosphere at temperatures of 800°C

Fig. 10 Effect of the type of limestone on average conversion of oxidation reaction at 800°C in 10% O_2 with the 0.50 mm diameter particles by theoretical calculation

O/Ca atomic ratios, which have the same trend as those of experimental ones although the calculated values were smaller than those from EDX probably due to the effect of oxygen in air on the experimental measurements.

Fig. 10 shows the effect of sorbent type on sulfation conversion with 0.50 mm diameter CaS samples at temperature of 800°C, in 10% O_2 atmosphere. Large pore size results in high sulfation conversion of CaS grain. Thus, there is high conversion for CaS particle of coral leaf Due to its large pore diameter. The CaS particle of Osaka limestone has smaller pore diameter, so that the lower conversion is yielded.

The product sulfate has twice the molar volume of the reactant sulfide, so that the sulfation reaction is limited by diffusion through product layer, or pore blocking. Complete conversion of CaS to CaSO_4 is imperative, so it is needed that all CaS content should be consumed before the pore blocking. The levels of sulfidation corresponding to thickness of layers of CaS are required for different particle sizes and oxygen concentrations. The required maximum CaS contents in the sorbent of coral leaf for the complete conversion to sulfate through reaction (1) are calculated as shown in Fig. 11. It is indicated that higher O_2 concentration can make the sorbent with a higher level of sulfidation be completely

Fig. 11 The required initial CaS molar fractions in particles to attain complete conversion to sulfate in 1-21% atmospheres at 800°C

converted. 21% O_2 concentration can make complete conversion of the pure CaS below 0.01 mm. For the above 0.50 mm CaS particle the maximum sulfidation level is limited to 15%, whose CaS content can be completely consumed if the O_2 concentration is kept up to 21%. For complete conversion of CaS to $CaSO_4$, there should be below 7%, 3% and 1.5% sulfidation levels for 1, 3, 5 mm sorbent particles, respectively.

6. Conclusion

The oxidation reaction of calcium sulfide was performed in a TG apparatus with different limestones at temperature ranging from 650 to 850°C in 1-21% O_2 concentration. It is found that only O_2 atmosphere determines the final conversion of sulfation if temperature is fixed. The complete conversion was achieved for the CaS particle below 0.005 mm in above 1% O_2 atmosphere.

A theoretical grain model is described that accounts for a variable effective diffusivity that results from the change of pore size insider the reacting solid particle. The effective diffusivity is separated into a molecular diffusion coefficient and a Knudsen diffusion coefficient. By fitting the model calculations to experimental results, $\varepsilon_0/\varepsilon$ is chosen to determine a tortuosity factor in the model. The variable effective diffusivity in the model reasonably describes the sulfation process. The model provides a satisfactory fit to average conversions of oxidation reaction determined by independent experiments for various operating conditions and the particles of dif-

ferent limestones. It is also given that the model prediction of the required maximum initial CaS content of coral leaf for complete conversion through sulfation reaction in 1-21% O_2 atmosphere at 800°C.

[Nomenclature]

a	radius of pore within particles	[m]
a_0	initial radius of pore within particles	[m]
A_p	surface area of grain	[m ²]
C_{O_2}	concentration of O_2	[mol/m ³]
$C_{O_2}^b$	concentration of O_2 in the bulk flow	[mol/m ³]
C_{so}	initial CaS concentration	[mol/m ³]
D_k	Knudsen diffusivity	[m ² /s]
D_m	molecular diffusivity	[m ² /s]
D_e	effective diffusivity	[m ² /s]
d_p	particle diameter	[m]
f_c	initial volume fraction of solid reactant in the particle	[-]
G	parameter in Eq.16-3	[K]
k_s	reaction rate constant	[m ⁴ /mol.s]
k_t	mass transfer coefficient	[m/s]
M	molecular weight	[kg/mol]
N_{Sh}, N_{Re}, N_{Sc}	number of Sherwood, Reynold and Schmidt	[-]
P	pressure	[Pa]
R	radial distance from the center of particle	[m]

R_0	initial radius	[m]	<i>Fluidized Bed Combustion</i> , Canada, 1, 387 (1997)
r_A	reaction rate	[m ⁴ /mol.s]	2) Z. B. Dong, A. Sato, M. Okada and Y. Ninomiya, <i>Kagaku Kogaku Ronbunshu</i> , 25 (4), in press (1999)
r_g	radius of crystal grain	[m]	3) Davies, N. H., A. N. Hayhurst and K.M. Laughlin, <i>Proc. of the 25th Symposium on Combustion, The Combustion Institute</i> , 211-218 (1994)
T	absolute temperature	[K]	4) Szekeley, J. and J.W. Evans, <i>Chemical Engineering Science</i> , 25, 1091-1107 (1970)
T_n	temperature given by Eq.16-3	[K]	5) Szekeley, J. and J.W. Evans, H.Y. Sohn, <i>Gas-Solid Reaction</i> , Academic Press, New York (1976)
t	reaction time	[s]	6) Papanastassiou, D. and G. Bistsianes, <i>Met. Trans</i> , 4, 477 (1973)
t^*	dimensionless reaction time	[-]	7) Sohn, H.Y. and J. Szekeley, <i>Chem. Eng. Sci.</i> , 29, 630 (1974)
U	space velocity of reactant gas	[m/s]	8) Miloslav Hartman and Robert W. Coughlin, <i>AIChE</i> , 20 (3), 490-498 (1976)
V_P	volume of gain	[m ³]	9) M. Hasatani, M. Yuzawa and N. Arai, <i>J.Chem. Eng. Japan</i> , 8 (1), 45-50 (1982)
X_{CaS}	conversion of CaS to CaSO ₄	[-]	10) K.Dam-Johansen, P.F.B.Hansen and K.Ostergaard, <i>Chem. Eng. Sci.</i> , 46 (3), 847-853 (1991)
$X_{CaS\infty}$	maximum conversion of CaS to CaSO ₄	[-]	11) W. E. Ranz and W. R. Marshall, Jr., <i>Chem. Eng. Prog.</i> , 48, 141 (1952)
Z	ratio of molar volume of solid product to reactant	[-]	12) <i>Kagakubinran</i> , The Society of Chemical Engineers, Japan, Maruzen Company, 99-101 (1988)
ϵ	porosity with particle at t time	[-]	13) Bosanquet, C.H., <i>British TA Report</i> , BR-507 (1944)
ϵ_0	initial porosity with particle	[-]	
$\sigma_{O_2-N_2}$	mole separation at collision	[nm]	
Ω_d	collision function given by Eq.16	[-]	
ρ	density of solid	[kg/m ³]	
τ	tortuosity factor	[-]	
δ	thickness of product layer	[m]	
ξ	dimensionless parameter in Eq.5	[-]	
- References**
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