Study and Kinetic Modeling of Direct Sulfation of Iranian Limestones by Sulfur Dioxide at High CO_2 Partial Pressure

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ABSTRACT: *The direct sulfation of three high purity Iranian limestones and one precipitated calcium carbonate from different sources, containing more than 97 % $CaCO_3$, were studied in a specially designed fixed bed reactor under atmospheric pressure, in the presence of excess CO_2 to prevent decomposition of $CaCO_3$. Experiments were carried out over a range of particle sizes from 1.6-2.5 µm at four temperatures (750, 800, 850, 900 °C), and SO_2 concentration of 2400 ppm. The particle size and temperature showed a dominant influence on the variation of conversion with time. The results of experiments show that the Shrinking Unreacted Core Model can be used to predict the behavior of sulfation of limestone. This simple model reveals that the reaction rate is the controlling step. The parameter of model, chemical rate constant (K_s), was obtained as: $K_s = 0.1 \exp (-6.2/RT)$ cm/s. Model predictions are in good agreement with expeimental data.*

KEY WORDS: *Direct sulfation, Desulfurization, Limestone, Shrinking core model, Gas solid reaction.*

INTRODUCTION

Sulfur dioxide is a harmful gas, which is formed in many industrial plants such as those using coal as fuel. Emission of SO_2 from fossil fuel fired boilers is widely regarded as an important environmental problem, and many different processes are being used for the reduction of such emissions. The use of limestone to reduce SO_2 emissions from coal fired power plants has been investigated during the last thirty years [1-14]. Sulfation behavior of limestone under high CO_2 concentration in O_2/CO_2 coal combustion has been studied by *Liu et al*.

They suggest the mechanism of direct sulfation of limestone under high CO_2 concentration, different from that of CaO-SO_2 sulfation is one of the factors to account for its high sulfation efficiency [15]. Also a literature review of the direct sulfation reaction is presented by *Giulin Hu et al*. Various subjects, such as the influence of the reaction conditions, gas concentration, temperature and pressure, limestone properties and additives to the reaction kinetics, the reaction mechanism and modeling are discussed by them [16].
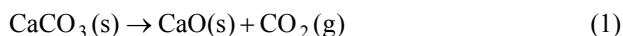
At low CO_2 partial pressures and/or high temperatures, calcinations of $CaCO_3$ occurs rapidly as follows:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad (1)$$

This reaction is followed by a sulfation of CaO:

$$CaO(s) + SO_2(g) + \frac{1}{2}O_2(g) \rightarrow CaSO_4(s) \qquad (2)$$
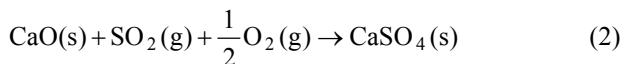
At temperatures below the decomposition temperature of $CaCo_3$, the following reaction is believed to occur (direct sulfation):

$$CaCO_3(s) + SO_2(g) + \frac{1}{2}O_2(g) \rightarrow CaSO_4(s) + CO_2(g) \quad (3)$$
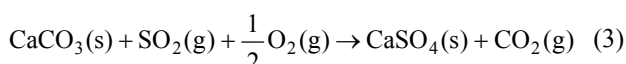
Reaction (3) differs from reaction (1) and (2) in that CO_2 is generated at the reaction interface and CaO crystals are not formed. Therefore it is expected that sulfation rate and conversion would be different, in these two cases.

However, in the presence of suitable catalyst, $SO_2(g)$ can be converted to $SO_3(g)$ and the reaction then proceeds as follows:

$$CaCO_3(s) + SO_3(g) \rightarrow CaSO_4(s) + CO_2(g) \qquad (4)$$

Snow et al. [4] have shown that the rate of $CaCO_3$ decomposition to CaO is much faster than the rate of direct sulfation so that even brief exposure to calcination conditions will cause decomposition and deactivation instead of sulfation. Also, they have shown that , the direct sulfation of calcite crystals with particles sizes in the range of 2-50 μm can be described as a shrinking core process with relatively small diffusional resistance and an activation energy of 15.3 kcal/mol. The photomicrographs of the calcium sulfate layer formed from CaO showed that this layer is not porous.

Spartinos and *Vayenas* [17] found that for the case of both limestone and CaO, the sulfation rate decays with $t^{-1/2}$ throughout most of the sulfation process, indicating that SO_2 diffusion through the product $CaSO_4$ layer is the rate limiting step.

Sulfation of $CaCO_3$ was modeled by *Snow et al.*[4] by considering each of particles to react as a spherical shrinking core with reaction control at the core interface and diffusion control. They showed that, for reaction control, the initial rate is inversely proportional to particle diameter whereas, for product layer control, the rate is inversely proportion to the square of particle diameter.

The shrinking unreacted core model that was developed by *Szekely* [18] was used in the study of *Hajaligol et al.* [3]. Their results indicated that sulfation reaction was diffusionally controlled in some cases and under mixed control in other cases. They found that, as the temperature increases and the particle diameter decreases, the reaction became less diffusional controlled, but never became completely controlled by the chemical reaction.

Direct sulfation of limestone at elevated pressures has been studied by *Qiu et al.* using a pressurized thermogravimetric analyzer. They found the degree of sulfation decreased with rising total pressure when the partial pressure of SO_2 was kept constant [19].

A variable diffusivity shrinking core model that allows temporal and spatial variation of the effective diffusivity in the solid product layer was developed by *Krishnan et al.* [6]. They showed that the effective diffusivity decreases very fast with the distance from the external surface of the particles. Very good agreement between experimental results and model predictions was generally observed when the estimated functional form of effective diffusivity was introduced in the variable diffusivity shrinking core model.

Brogren and *Karlsson* [12] developed a model based on penetration theory to calculate the dynamic absorption rate of SO_2 into a droplet of limestone slurry. Their calculations showed that the absorption of SO_2 into a limestone spray scrubber is to a large extending liquid side controlled.

The objective of the present work is to extend the information available on the effects of reaction time, temperature and particle size for the direct conversion of three different type of Iranian limestone and one precipitated $CaCO_3$ to $CaSO_4$. The shrinking core model is also used to analyze the experimental data obtained by a specially designed fixed bed reactor.

EXPERIMENTAL

The sulfation experiments were conducted in a specially designed fixed bed reactor, shown in Fig. 1, that can handle weights up to 300 mg. Three types of Iranian limestone (IP, PS, IB) and one precipitated $CaCO_3$ were used in all of the work reported here. Summary of the chemical analysis and physical properties of the limestones are presented in tables 1 and 2.

The sulfation procedure consisted of heating the sample (150-300 mg) at a rate of 50 °C/min to a temperature 50 °C less than the desired peak temperature, establishing isothermal conditions with the gas stream contains 93 % CO_2 and 7 % O_2 at a total pressure of 1 atm. After reaching this temperature, heating rate was reduced to 10 °C/min for about 5 minutes. At peak temperature, SO_2 was added to gas stream in desired concentration (2400 ppm). Isothermal reaction temperature was varied from 750 °C to 900 °C. The XRD spectrum of the samples as reported by several researchers shows that the product in this reaction and procedure is anhydrous calcium sulfate with a molar volume of 46 cm^3/mol [20].

RESULTS

Figs. 2 and 3 show the effect of temperature on the conversion of IP and precipitated $CaCO_3$ as a function of reaction time during direct sulfation. The experiments carried out at different temperature show that the increase in temperature results in an increase in the conversion of limestones. At a fixed reaction time, conversion increases as temperature increases for all particle sizes considered. As expected, at a given reaction time, amount of conversion is higher for smaller particle size, which is due to higher BET surface area. Effect of particle size on conversion for IP-limestone is shown in Fig. 4. These effects are more pronounced at higher temperature.

In Fig. 5 comparison between conversions of different types of limestone are shown. These results show that precipitated $CaCO_3$ shows higher conversion compared to the other types of limestone used in the present study.

MODELING AND DISCUSSION

Various models such as the unreacted core model and the pore model have been previously presented for gas-solid reactions [1, 4, 11, 18, 21, 22]. Images taken from reacted particles by *Dam-Johansen* and *Ostergaard* [20] show that the shrinking unreacted core mode (SUCM) can be used to describe the direct sulfation reaction with reasonable accuracy. According to this model the solid particle is assumed to be non-porous with the reaction taking place on a thin rim at its surface (the Sharp Interface Model-SIM). As the reaction proceeds the boundary of the reaction moves towards the interior of the particle.
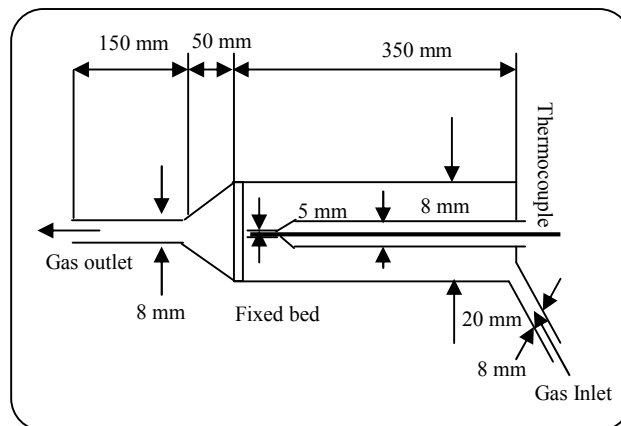

Fig. 1: *Schematic diagram of specially designed fixed bed reactor for direct sulfation of limestone.*

Table 1: Chemical Analysis of Limestones (wt %).

Compound	IP	PS	IB	Precipitated $CaCO_3$
$CaCO_3$	97.5	97.1	97.3	98.93
$MgCO_3$	2.36	2.77	2.27	0.87
Na_2O	-	-	0.027	-
Al_2O_3	0.009	-	0.109	0.024
P_2P_5	0.0086	0.0062	0.0071	0.032
S	0.015	0.017	0.116	0.0256
Cl	0.019	0.018	0.018	0.042
Sc_2O_3	0.016	0.017	0.011	-
K_2O	-	-	0.0088	-
TiO_2	0.01	0.006	0.012	-
V_2O_5	0.005	0.003	-	0.004
MnO	0.004	0.013	0.014	0.011
Fe_2O_3	0.032	0.029	0.105	0.035
CuO	0.0018	0.0016	0.0022	-
ZnO	0.0036	0.0014	0.004	0.023
SrO	0.02	0.02	0.035	0.028

Table 2: BET Surface Areas and Average Particle Sizes of Limestones.

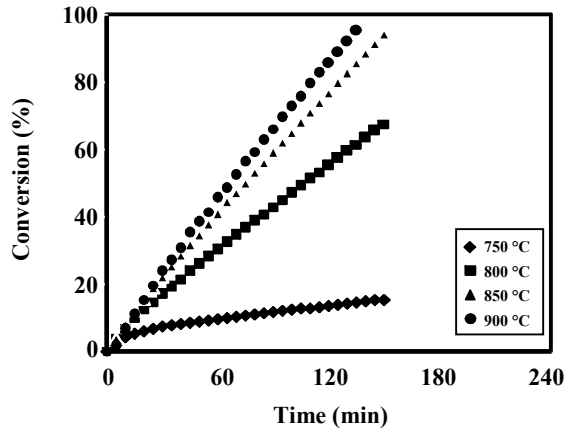| Limestone	Ave. Particle Size (μm)	BET Surface Area (m^2/g)
IP	1.6	4.23
IP	2.5	3.86
PS	2	3.32
IB	2.3	2.85
Precipitated $CaCO_3$	1.7	6.89

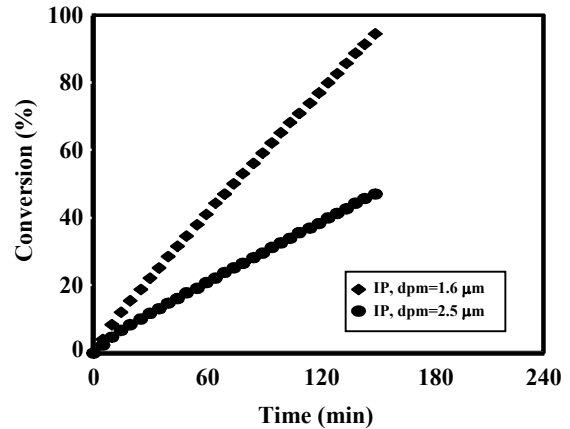**Fig. 2: Effect of temperature on the sulfation of IP - CaCO₃ with an average particle diameter of 1.6 μm.**

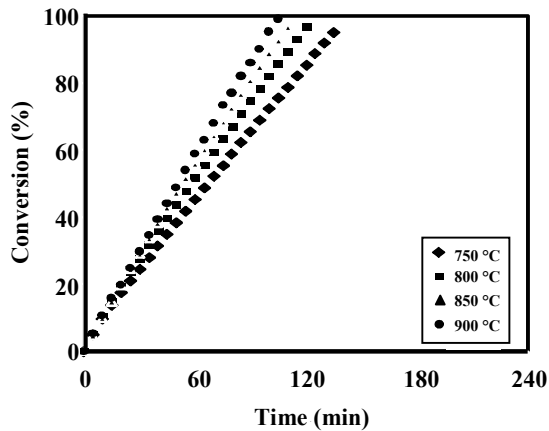**Fig. 4: Effect of average particle diameter on the sulfation of IP - CaCO₃ at 850 °C.**

Fig. 3: Effect of temperature on the sulfation of Precipitated - CaCO₃ with an average particle diameter of 1.7 μm.

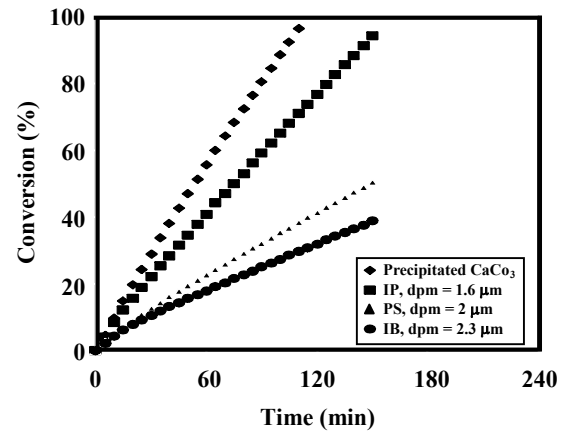**Fig. 5: Effect of type of CaCO₃ on the sulfation of CaCO₃ at 850 °C.**

The resistance against the gas diffusion includes the diffusion resistance at the gas film, diffusion in the product shell, and chemical reaction at the surface.

In the specially designed reactor used in the present study the gas phase resistance and ash layer diffusivity are negligible and only chemical reaction rate is considerable. For spherical particles, the relationships between conversion and reaction time have been modeled as [18]:

$$t = \tau_{rxn} g(x) \tag{5}$$

$$\tau_{rxn} = \rho_s d_{p_0} / 2bk_s C_{Ag} \tag{6}$$

$$g(x) = 1 - (1 - x_B)^{1/3} \tag{7}$$

It should be noted that for very small particle sizes it can be assumed that the process is chemically controlled.

In this circumstance chemical rate constant K_S is easily deduced. For the first order chemical reaction, K_S is assumed to follow Arrhenius type behavior:

$$K_S = K_{S0} \exp(-E/RT) \tag{8}$$

K_S Was derived from results of experiments as follows:

$$K_S = 0.1 \exp(-6.2/RT) \quad cm/s \tag{9}$$

In Fig. 6 the results obtained from experiments at different temperatures are compared with model predictions. It can be seen that there is excellent agreement between the experimental results and model prediction the good agreement is due to the use of small particle size (1.6-2.5 μm) and the special design of fixed bed reactor which eliminates the gas phase resistance.
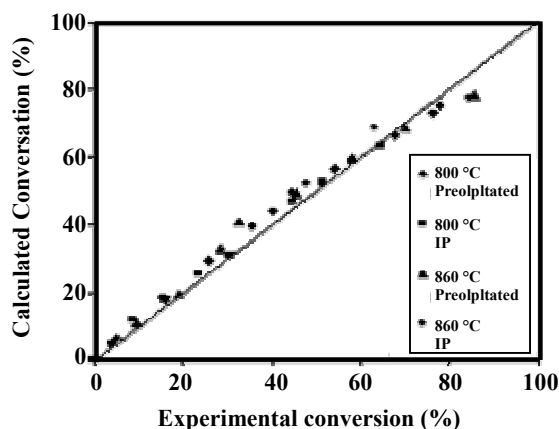
Fig. 6.:Comparison of experimental results and model predictions for different limstones sulfation at different temperatures.

As expected, the sulfation results using Iranian limestones and precipitated calcium carbonate show large effects of particle size and temperature. The measured direct sulfation conversion-time relation for different conditions reflect the combination of a temperature activated rate constant and the reduction in the available surface area of core.

In the case of reaction control, the rate is obviously inversely proportional to particle diameter. For the 1.6 and 2.5 μm particle sizes used in the present study the rate of sulfation was found to be inversely proportioned to the particle diameter.

The larger particles showed even higher rates than predicted by this diameter effect. This is believed to be caused by development of cracks in the larger particles which result in an effectively smaller size. This effect is enhanced at higher temperatures since the cracks increase with increasing temperature.

The results of sulfation experiment further, indicate that, at 900 °C under isothermal condition above 90 % sulfation can be achived for precipitated calcium carbonate after 100 min, while for IP limestone with an average particle size of 1.6 μm slightly lower sulfation was obtained. When temperature drops to 850 °C or less the sulfation rate for precipitated calcium carbonate becomes slightly less than 90 % at 100 min while this effect for IP limestones are considerable.

These times, while too long for use of this process in a standard pulverized coal fired furnace, is suitable for sorbent residence time for fluidized bed combustors. In these combustors direct sulfation allows higher conversions to be attained compared to the practice of direct limestone injection where local conditions can cause calcinations to precede sulfation.

Comparing the sulfation rate of Iranian limestones and precipitated calcium carbonate shows that, under similar conditions, conversion of precipitated calcium carbonate is higher than IP limestone whereas the sulfation rate of IP limestone is higher than PS and IB limestones.

CONCLUSIONS

1- In a specially designed fixed bed reactor, the process of direct sulfation was found to be totally controlled by the chemical reaction at the solid surface, with activation energy of 6.2 kcal/mol.

2- For the very small size of particles employed in the present study 1.6-2.5 μm, the effect of ash layer diffusivity on conversion was found to be negligible.

3- The experiment carried out at different temperature show that the increase in temperature results in an increase in conversion of limestone.

4- The amount of limestone conversion is higher for smaller particle size, which is due to higher BET surface area.

5- The higher conversion obtained with precipitated $CaCO_3$ compared with IP limestone and compared with IB limestone can be attributed is due to their higher BET surface areas.

Nomenclatures

B	Molar ratio (gas reactant to solid reactant)
C_{Ag}	SO_2 concentration in gas phase (mol/cm^3)
d_{p_0}	Initial diameter of solid particles (cm)
E	Activation energy (Eq. (8)) (kcal/gmol)
g(x)	The function of conversion, (Eq. (7)), under total control of the chemical reaction
K_S	Chemical reaction rate constant (cm/s)
K_{S0}	Pre - exponential constant (Eq. (8)), (cm/s)
R	Universal gas constant (1.987 cal/mol.K)
t	Time (s)
T	Temperature (K)
X_B	Conversion of solid

Greek Letters

ρ_s Solid density (mol/cm^3)

τ_{rxn} Characteristic time for complete stone conversion under total control of the chemical reaction

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