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DIFFUSIONAL STUDY OF THE EFFECT OF SODIUM CHLORIDE ON LIMESTONE SULFATION IN FLUIDIZED-BED COMBUSTION. PART 2

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ABSTRACT

The effective diffusivity of argon through calcined Greer limestone is given during sulfation, salt addition, and additional sulfation. The corresponding extents of sulfation are also presented. The effective diffusivity of SO_2 decreases as sulfation takes place. Introduction of sodium chloride vapor to the system rearranges the sulfated product layer structure, thus increasing the effective diffusivity of SO_2. This increases the SO_2 capture capacity of Greer limestone by more than 200% at sulfation temperatures above 840 °C.

INTRODUCTION

It is important to utilize the maximum amount of calcined limestone to capture SO_2 in a fluidized-bed combustor. Increasing the SO_2 absorption capacity of calcined limestone means that a lesser amount of limestone is required and a lesser amount of solid waste would be produced. Results of recent work on the effect of NaCl on calcination and sulfation of limestone are summarized by Shearer et al. [1]. Bardakci [2,3] constructed a single-pellet high-temperature diffusion cell to measure the effective diffusivity of gases through the Greer limestone pellet during calcination and sulfation of limestone. It was shown that the effective diffusivity of gases increases with calcination, increasing sintering time and increasing temperature. It decreases rapidly during the sulfation.

In this paper the effective diffusivity of argon through Greer limestone is given during sulfation, salt addition, and additional sulfation. Additionally, the corresponding extent of sulfation is given as a function of sulfation time. The extents of sulfation before and after salt addition are compared.

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EXPERIMENTAL

A cylindrical pellet (typically 0.31 cm thick by 2.1 cm diameter) was manufactured using a diamond coring drill bit and a carborundum saw. The limestone used (Greer Limestone Co., Morgantown, WV) had an average calcium carbonate content of 75%. This pellet was mounted in a specially designed high-temperature diffusion cell (see Fig. 1) [2,4], using the same principle as that of Wicke and Kallenbach [5]. The diffusion cell reactor was mounted in a tube furnace which was kept at a selected fixed temperature. Argon gas was passed radially across one face of the pellet while nitrogen gas was passed radially across the other face. The temperature was measured at each pellet face. The differential pressure between the two sides of the pellet was maintained at 0.00 ± 0.08 cm of water by the aid of a computer system. The computer also measured and controlled flow rates and absolute pressures of each stream. In addition, it automatically injected samples from each stream into a gas chromatograph, integrated the output, and performed calculations including the effective diffusivity of argon and nitrogen through the reactive porous pellet. After the complete calcination and some sintering of Greer limestone, the sulfation was started. During sulfation pure nitrogen gas was pased over one side of the pellet. A special gas mixture which consisted of about 1% O_2 and 500 ppm SO_2 in argon was passed over the other side of the pellet. The exit gas SO_2 concentration was measured continuously with a TECO pulsed fluorescent SO_2 analyzer (model 40).

The inlet SO_2 concentration was fixed and there was no SO_2 on the nitrogen side of the pellet. Using the fixed gas-flow rate and inlet and exit SO_2 concentrations a mass balance for SO_2 was performed to calculate the extent of sulfation.

Before any sulfation experiment started, about 1 g of salt was loaded in a stainless steel closed boat which was attached to the end of an alumel wire as shown in Fig. 2. After the sulfation was almost stopped, pure oxygen gas was passed across the sulfated side of the pellet. This is done to stop dissociation of $CaSO_4$. That fact was confirmed by the total lack of SO_2 in the exit streams of both sides of the pellet during the salt additions. When salt addition was desired, under oxygen gas atmosphere in the inlet stream

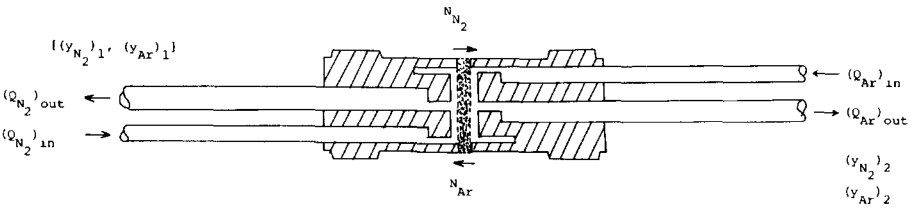

Fig. 1. Single pellet high temperature diffusion cell reactor.

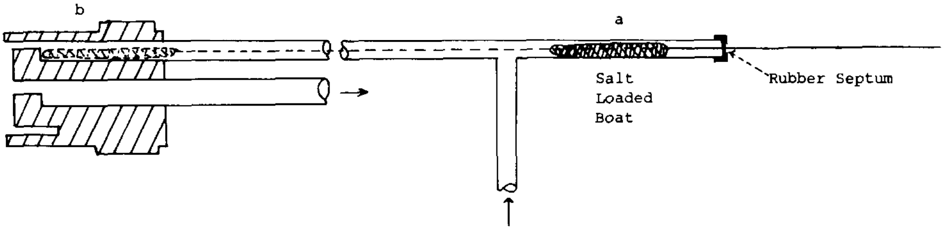

Fig. 2. Schematic diagram of salt addition during the experiment. (a) Before adding NaCl. (b) During NaCl addition.

of the sulfated shell side of the pellet, the stainless steel boat was pushed into the furnace such that the boat was close to the pellet. After the effective diffusivity of gases increased, the special gas mixture with SO_2 and O_2 was passed across the sulfated pellet for additional sulfation. During additional sulfation the NaCl boat was kept close to the pellet so that the effect of salt vapors was continued. After sulfation the pellets were taken out of the diffusion cell reacter, the samples were taken from the sulfated edge of the pellet and were analyzed to find the saturation conversion, using a LECO sulfur analyzer. Surface areas of the samples taken from the other side, that is the unsulfated side of the pellets, were analyzed using a Quantachrome monosorb surface area analyzer.

RESULTS AND DISCUSSION

During test C6, salt vapor was introducted to the system. In Fig. 3 the effective diffusivity of argon gas through the calcined Greer limestone is given as a function of calcination time, and the salt addition increased the effective diffusivity of argon. Table 1 summarizes the sulfation data. The effective diffusivity of argon is plotted as a function of sulfation time in Fig. 4. In all tests the effective diffusivity of argon decreases as sulfation time increases. Since salt was introduced to the system during test C6, argon diffusivity is much higher at the beginning of the test compared to that of test C2 which is carried out 3°C below the test C6 temperature. The corresponding extent of conversion is plotted in Figs. 5–8, shown with open circle data points.

Since the molar volume of $CaSO_4$ is greater than that of CaO, the porosity of the reacting part of the pellet decreases, thus decreasing the permeability or diffusitivy of SO_2 and terminating the sulfation reaction, although CaO is available for sulfation behind the almost non-porous sulfated product layer.

After near complete sulfation of the surface layer, salt vapors were introduced and the effective diffusivity of oxygen increased in all three tests.

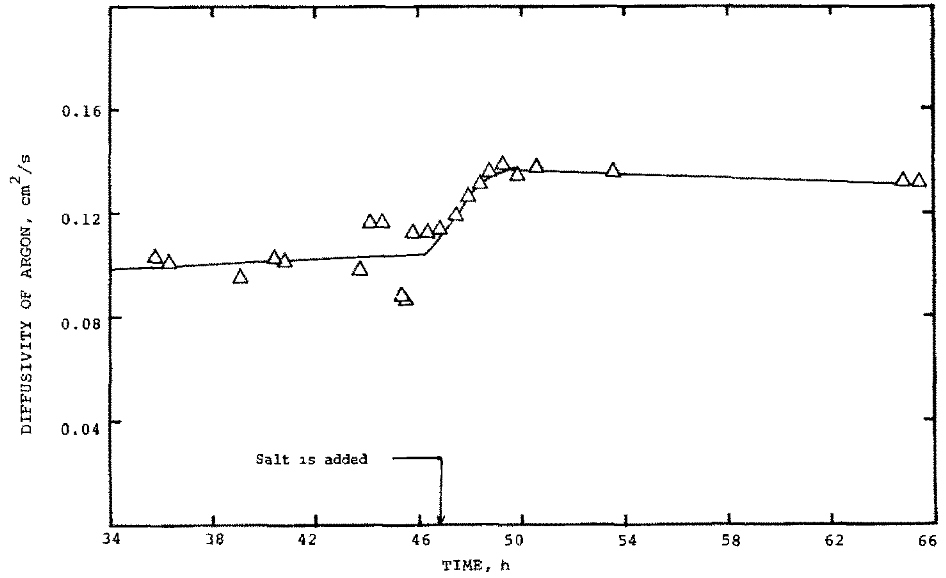

Fig. 3. Diffusivity of argon through calcined Greer limestone before and after salt (NaCl) vapor effect. Temperature 843°C, run No. R1.

In Fig. 9 gas diffusivities are shown during the salt vapor addition and additional sulfation. The melting point of NaCl is 800.4°C. Hence, we do not see much effect of NaCl during test C9 which is carried out at 757°C.

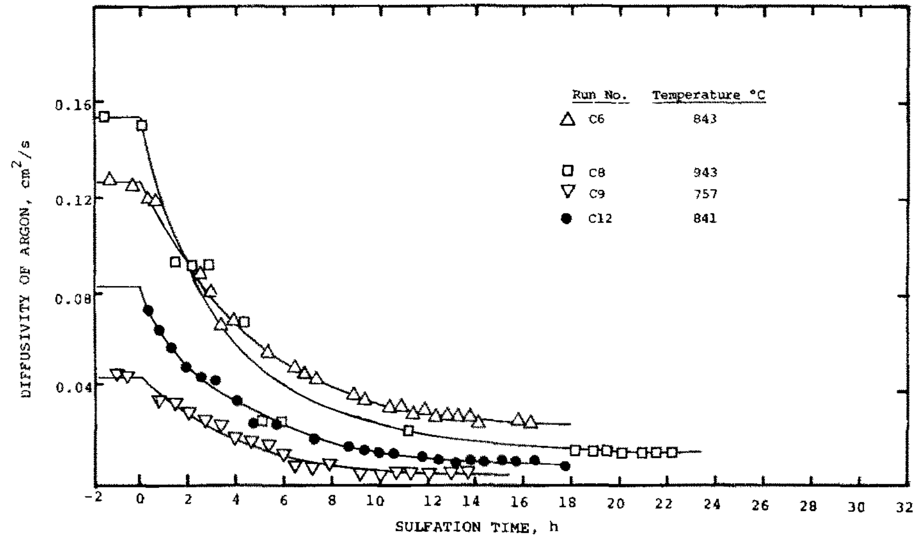

Fig. 4. Diffusivity of argon through the partially sulfated, calcined Greer limestone as a function of sulfation time.

TABLE 1

Sulfation data

Run No.	Temperature (°C)	Initial SO_2 concentration (ppm)	Pellet thickness (cm)	Sulfate area ($m\ g^{-1}$)	Saturation conversion at the sulfated side
C6	843	540	0.3460	2.41	0.43
C8	942	550	0.3295	2.24	0.48
C9	757	550	0.3260	5.45	0.29
C12	840	508	0.3168	3.14	0.47

During the additional sulfation, effective diffusivities of argon were also decreased as sulfation took place, except during test C12. This is due to the additional salt introducted after 4 h sulfation. The corresponding extent of conversion to calcium sulfate after the salt effects are also given in Figs. 6–8.

In Table 2 maximum extent of conversions before and after salt additions are summarized. The SO_2 capture capacity of Greer limestone was increased by 226, 17, and 217% in tests C8, C9, and C12, respectively.

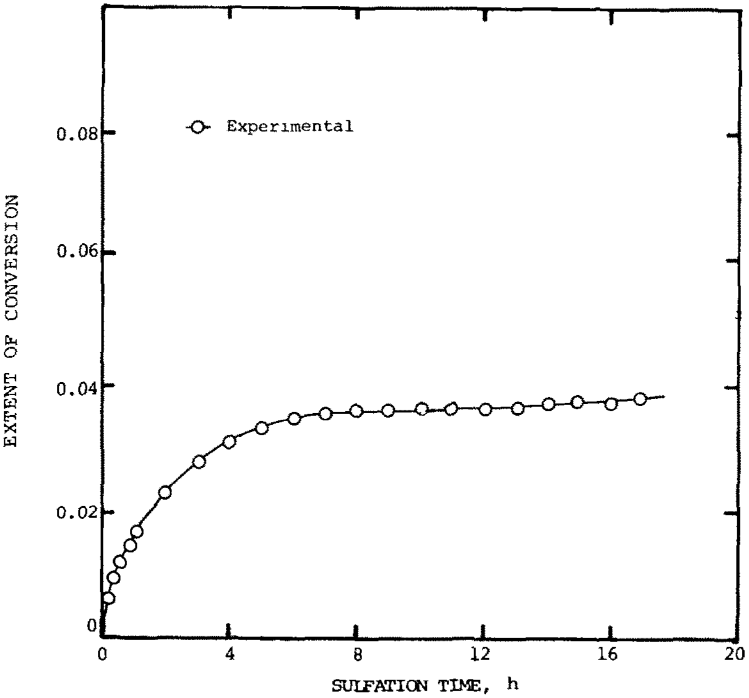

Fig. 5. Extent of conversion as a function of sulfation time. Temperature 843°C, run No. C6.

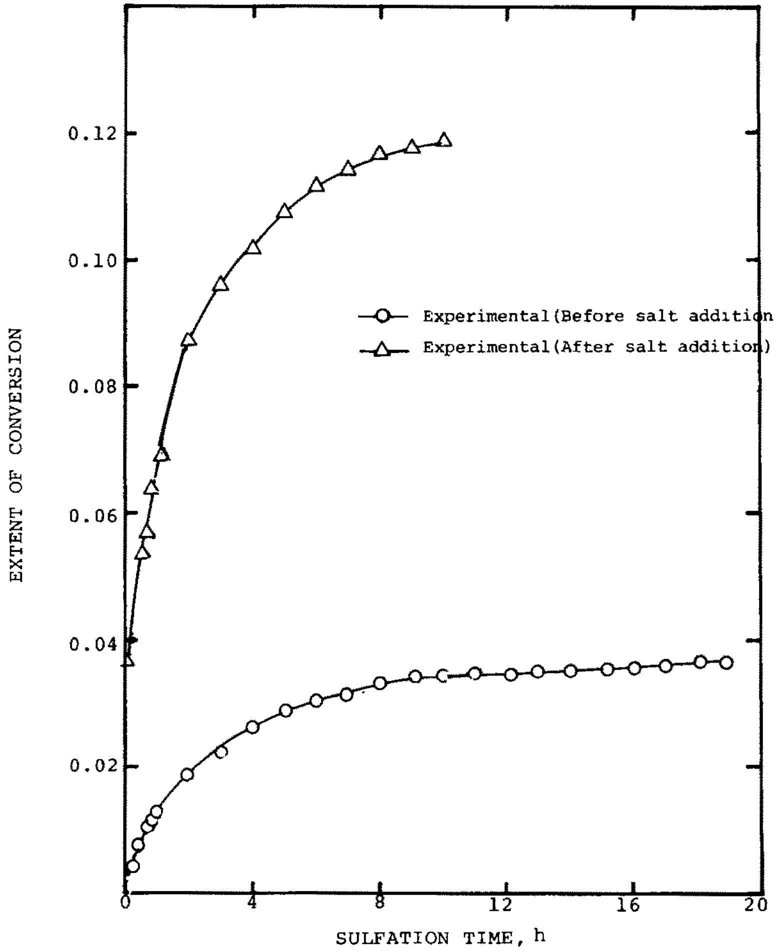

Fig. 6. Extent of conversion as a function of sulfation time. Temperature 943° C, run No. C8.

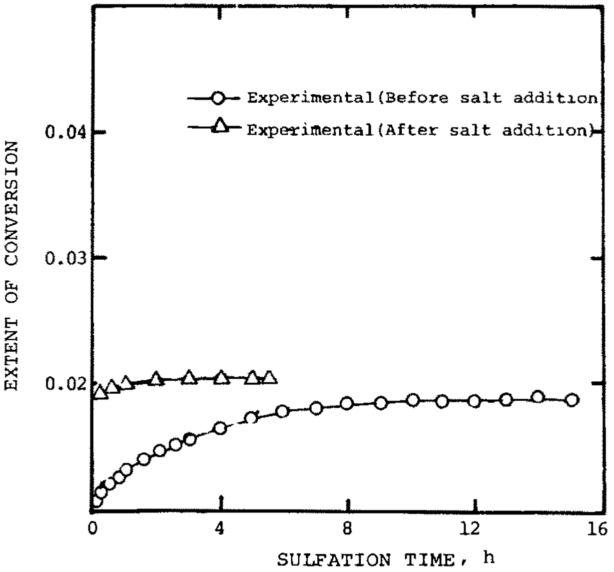

Fig. 7. Extent of conversion as a function of sulfation time. Temperature 757° C, run No. C9.

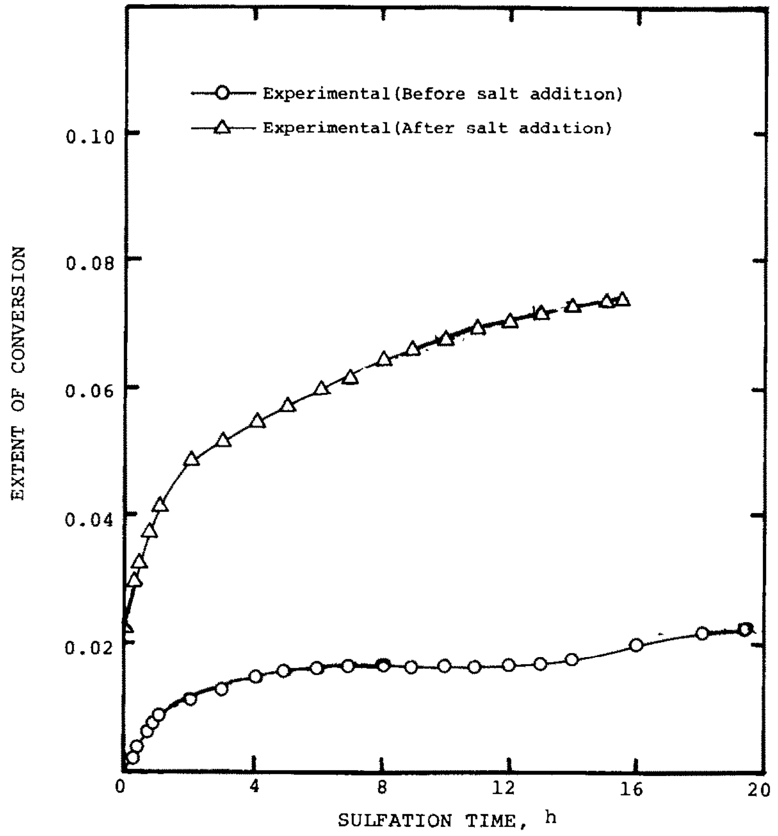

Fig. 8. Extent of conversion as a function of sulfation time. Temperature 841°C, run No. C12.

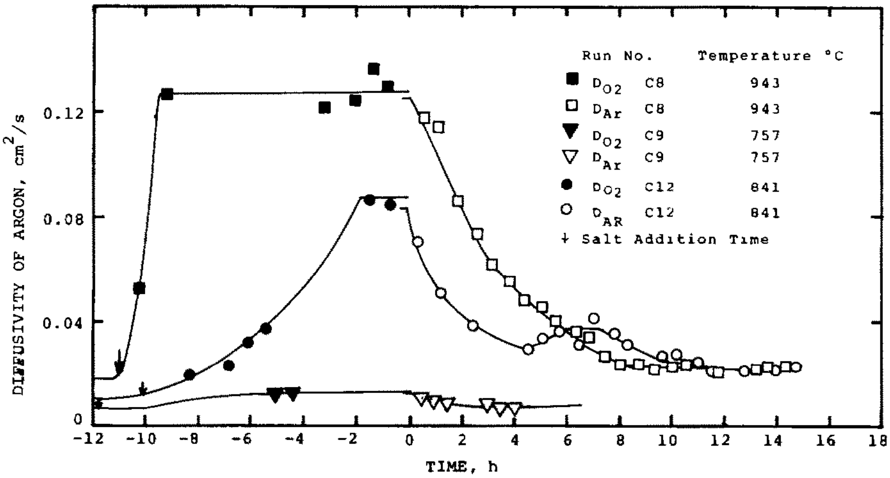

Fig. 9. Diffusivity of argon after salt addition and during additional sulfation.

TABLE 2

Maximum sulfated shell thickness

Run No.	Temperature (°C)	Maximum extent of conversion		Average sulfated shell thickness (mm) [a]	
		Before salt addition	After salt addition	Before salt addition	After salt addition
C6	843	–	0.0373	–	0.3009
C7	847	–	0.0609	–	0.4365
C8	942	0.0366	0.1194	0.2512	0.8182
C9	756	0.0173	0.0204	0.2059	0.2386
C12	840	0.0233	0.0739	0.1583	0.5001 (0.4980) [b]

[a] Shell thickness = (pellet thickness) × (overall conversion)/(saturation conversion).

[b] This result is obtained from X-ray analysis.

CONCLUDING REMARKS

Sulfation of calcined Greer limestone is a strongly diffusion-limited reaction. The porosity of the sulfated product layer and effective diffusivity of SO_2 decrease as the sulfation reaction takes place. Introduction of NaCl vapor to the system rearranges the sulfated product layer so that additional sulfation takes place, thus increasing the SO_2 capture ability of Greer limestone by more than 200% at sulfation temperatures above 840°C.

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