

Activation and Reactivity of Novel Calcium-Based Sorbents for Dry SO₂ Control in Boilers

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SUMMARY

Chemically modified calcium hydroxide ($\text{Ca}(\text{OH})_2$) sorbents developed in the U.S. Environmental Protection Agency's Air and Energy Engineering Research Laboratory (AEERL) for sulfur dioxide (SO_2) control in utility boilers were tested in an electrically heated, bench-scale isothermal flow reactor. Novel surfactant-modified $\text{Ca}(\text{OH})_2$ (SM- $\text{Ca}(\text{OH})_2$) sorbents were compared with conventional $\text{Ca}(\text{OH})_2$ produced by dry hydration (DH- $\text{Ca}(\text{OH})_2$) to determine why modified sorbents have a higher reactivity with SO_2 .

Sorbents were activated in the flow reactor. Activated sorbents (SM- CaO and DH- CaO) were size classified with an inertial cascade impactor downstream of the flow reactor. The structure of each separated fraction (six trays plus preimpactor, D_{50} from 0.74 to $>11.9 \mu\text{m}$) was characterized by nitrogen adsorption. For each size fraction measured, the surface area was higher for SM- CaO than for DH- CaO . It was concluded, therefore, that retardation of the sintering process was the primary advantage of the modified sorbent. The effect of thermal sintering was to increase median pore size by eliminating fine pores (below 100 Å).

Changes in the pore structure of $\text{Ca}(\text{OH})_2$ sorbents reacting with SO_2 were also investigated. Small amounts of SO_2 (below 100 ppm) in the combustion gas present during calcination at 900 °C modified the structure of sorbents. These sorbents typically had higher surface areas and porosities than sorbents calcined in the absence of SO_2 , suggesting that small amounts of calcium sulfate product are capable of slowing the solid state diffusion process of sintering.

INTRODUCTION

Dry sorbent injection technology is a low capital cost process compared with conventional wet flue gas desulfurization. Ongoing research in the U.S. Environmental Protection Agency (EPA) is currently focused on limestone injection multistage burner (LIMB) technology capable of simultaneous control of nitrogen oxide (NO_x) and SO_2 emissions. Major operating expenses of this process are associated with the cost of sorbent; it is, therefore, of paramount importance to ensure that as large a portion of injected sorbent as possible will react with SO_2 . In this process, hydrated lime ($\text{Ca}(\text{OH})_2$) decomposes to produce active quicklime (CaO), which, in turn, simultaneously reacts with SO_2 and is sintered. Fundamental research on the sulfation process by Borgwardt [1] and Hartmann *et al.* [2] indicated that intraparticle resistances control the removal of SO_2 for particles below 50 μm and that high porosity of CaO was important to achieve high levels of conversion of sorbents, respectively.

Numerous studies that followed described the effect of smaller particle size on reactivity [3 - 5]. However, no clear dependence could be found between the achieved degree of conversion and structural parameters such as median particle size, porosity, and surface area of various hydrates tested. Surface area of nascent CaO (created as a result of thermal decomposition of hydrated lime in the boiler) was also investigated and was believed to be the major factor affecting the conversion of sorbent. Borgwardt and Bruce [6] showed that reactivity increases with the square of BET surface area of nascent CaO over the range 2 to 63 m^2/g . A recent study by

Borgwardt [7] was directed toward explaining the mechanism of sintering of nascent CaO and demonstrated that the process was governed by lattice diffusion. The importance of having sorbent with a fine particle size that is capable of yielding high surface area CaO upon the decomposition of Ca(OH)_2 in the boiler has been accepted. However, no clear correlation has been found between reactivity, surface area, and porosity of raw Ca(OH)_2 . Therefore, it becomes clear that the major thrust of research and development work should be oriented toward designing a sorbent that would have fine particle size and be resistant to the sintering process after calcination. The latter feature would allow a significant part of the CaO surface area developed as a result of thermal decomposition of Ca(OH)_2 to be retained.

Chemically modified calcitic sorbents were developed by Kirchgessner and Lorrain [8] under the EPA's research program and were shown to have significantly lower median particle sizes than conventional atmospheric lime hydrates. Kirchgessner and Jozewicz [9] documented that differences in the rates of sintering were also responsible for the increased reactivity of chemically modified sorbents. They also observed that the presence of SO_2 during calcination allowed sorbents to retain higher pore volumes than in the absence of SO_2 [10]. Under current market conditions for calcium hydroxide (\$50 - 70/ton F.O.B.) and calcium lignosulfonate (\$40/ton F.O.B.), it has been estimated that increases in SO_2 capture greater than 3 - 5 relative per cent will produce an economic benefit.

The objective of this study was to investigate the activation of surfactant-modified sorbents (calcination without SO_2 present) and to characterize the structure of sorbents as a function of particle size. Another objective was to quantify the changes in the pore structure of CaO reacting to varying degrees with SO_2 while simultaneously decoupling the effects of thermal sintering.

EXPERIMENTAL

The Ca(OH)_2 tested in this study and discussed in the sections on Properties of CaO and Effect of SO_2 during calcination was produced from a commercial CaO obtained

from the Longview Lime Division of the Dravo Lime Company in Saginaw, Alabama. The Ca(OH)_2 discussed in the section on Properties of Ca(OH)_2 was produced from Presque Isle limestone calcined in the laboratory furnace. Calcium lignosulfonate was the additive used most often in the modified Ca(OH)_2 . This material is a partially desugared variety of lignosulfonate available in the form of a water-soluble dry powder from the Georgia Pacific Corporation under the trade-name Lignosite.

Hydrate discussed in the sections on Properties of CaO and Effect of SO_2 during calcination were produced in a steam-jacketed Ross Ribbon Blender. To produce conventional Ca(OH)_2 , the blender was loaded with 6.8 kg of pulverized CaO and allowed to reach a temperature of 30 to 50 °C. A total of 3.7 kg of water was then added at a constant rate for 40 min. The blender was run for an additional 20 min while the heat of reaction drove off excess water, leaving a dry Ca(OH)_2 product (DH-Ca(OH)_2). The procedure for producing surfactant-modified Ca(OH)_2 (SM-Ca(OH)_2) was identical except that 3.7 kg of water contained 0.102 kg of Lignosite. This yields an SM-Ca(OH)_2 product containing approximately 1 wt.% of calcium lignosulfonate, a concentration that was shown by Kirchgessner and Lorrain [8] to be optimal for enhancement of SO_2 capture.

Hydrates discussed in the section on Properties of Ca(OH)_2 were produced in a laboratory-scale hydrator. Limestone was calcined to CaO at 1000 °C for 16 h in a Lindberg furnace under a nitrogen flow of 6 l/min. Hydration was conducted in a laboratory-scale hydrator consisting of a 0.4-l Pyrex beaker suspended in a constant 100 °C bath. A mechanically propelled stirrer was used to mix the water and lime. Each hydration was conducted by loading 10 g of dry lime into the hydrator and allowing the lime to achieve thermal equilibrium in the bath. The stirrer was started, and a single, rapid addition of 100 °C water was syringed into the hydrator in the molar ratio of $\text{H}_2\text{O}/\text{CaO} = 2.6$. After 15 min, the hydration vessel was purged of remaining water vapor with nitrogen, leaving a thoroughly dry product. Modified hydrates were produced by dissolving a sufficient amount of additive in the hydration water to produce the desired mass

concentration of additive in the product $\text{Ca}(\text{OH})_2$.

The differential isothermal flow reactor into which the hydrates were injected is shown in Fig. 1. The reaction chamber consists of two concentric 3.35 m-long quartz tubes heated by three Lindberg tube furnaces. The inner tube has a 15 mm inner diameter (ID), and the outer tube has a 50.8 mm outer diameter (OD). Premixed gases enter the reactor between the inner and outer tubes and are preheated as they move upward. At the top of the reactor, the gases enter the inner tube with the sorbent and move downward through the reaction zone. Sorbent particles are separated from the gas in the cyclone. Sorbent is fed from a feed tube by a vibration-activated fluidized feeder through 1.19-mm ID syringe tubing. The reactor was operated at normal temperatures of 700 - 1000 °C and nominal residence times of 0.6 - 2.0 s. Residence time was adjusted by varying the gas flow from 17.77 to 4.07 l/min at standard temperature and pressure (25 °C, 760 mmHg). The gas was composed of from 0 to 3000 ppm SO_2 , 5 vol.% oxygen, and the

balance of nitrogen (compressed air used as a source of oxygen).

The flow reactor has been designed for laminar flow with a Reynolds number of 315 - 635 to allow for accurate control of particle residence time, recognizing that a poor mixing environment has been created. With a cold sorbent carrier gas flow of less than 9% of the total gas flow, particles reach furnace temperatures in less than 5 ms. In order to prevent SO_2 starvation around the particles, sorbent feed rates and SO_2 concentrations are generally controlled to produce S/Ca of 10 or greater. It has been verified experimentally that SO_2 depletion does not occur at these levels. At very low SO_2 concentrations, however, depletion must be considered as a possibility.

Aerodynamic particle size analyses of hydroxides were performed with a Meteorological Research Incorporated (MRI) inertial cascade impactor under ambient temperature. Sorbents were fed directly from the feeder tube into the impactor at the same rates as if they were fed into the flow reactor. In the impactor, the gas stream with particles suspended in it passed through a set of seven stages of decreasing orifice diameters. Each stage separated particles with enough inertia to impact the plate and remain on it. The range of the median particle diameter D_{50} measured by the MRI impactor was from 0.52 to 33.5 μm . Particle size analyses of CaO were performed using a heated Gelman inertial impactor. The median particle diameter D_{50} of particles that could be classified was 0.44 to 7.5 μm in increments of the seven stages. A preimpactor collected all particles larger than 11.9 μm . This particular impactor is used because of its ability to withstand temperatures up to 800 °C. It also offered the possibility of limiting the exposure time of freshly calcined CaO to the ambient air, which would be necessary if the MRI inertial impactor were used.

Specific surface area, porosity, and pore size distribution were measured by the nitrogen adsorption/desorption BET method in a Micromeritics Digisorb 2600 Autoanalyzer. The calcium utilization of reacted sorbents was calculated based on the results of analysis for calcium by atomic absorption spectrophotometry and for sulfate by ion chromatog-

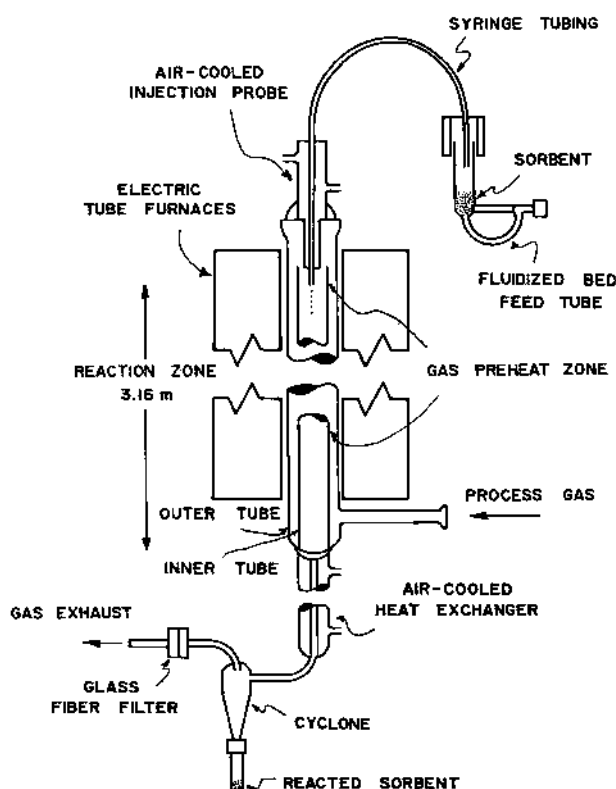


Fig. 1. Differential flow reactor.

raphy. The morphology of calcined/sulfated sorbents was investigated by an SEM.

RESULTS AND DISCUSSION

Properties of $\text{Ca}(\text{OH})_2$

Studies of hydrates that were chemically modified with surfactant were initiated in the AEERL at Research Triangle Park, North Carolina. Kirchgessner and Lorrain [8] showed that the primary effect of chemical modification on properties of $\text{Ca}(\text{OH})_2$ was significantly reduced median particle size compared with conventional $\text{Ca}(\text{OH})_2$. They used Lignosite as an additive. Other surfactants were also investigated during this study, and they are presented in the Table. Also given in the Table are the concentrations of surfactants that were used as well as the resulting median particle diameters of SM- $\text{Ca}(\text{OH})_2$. For the additives tested, median particle size varied from 2.9 to 10.2 μm when 5 wt.% of sodium hexametaphosphate (Calgon) and 50 ppm of K-XP 82, respectively, were used. The typical median particle size of hydrated lime without the additive (DH- $\text{Ca}(\text{OH})_2$) was between 10 and 12 μm . The surface areas of SM- $\text{Ca}(\text{OH})_2$ were not measured routinely following earlier findings indicating a lack of correlation between the surface area of $\text{Ca}(\text{OH})_2$ and its reactivity. It will only be mentioned here that typical DH- $\text{Ca}(\text{OH})_2$ had a surface area of approximately 20 m^2/g , whereas, for SM- $\text{Ca}(\text{OH})_2$ produced by the addition of 1 wt.% of Lignosite, this value was approximately 15 m^2/g .

In an attempt to correlate the median particle size of chemically modified sorbent with the reactivity of the sorbent towards SO_2 , each chemically modified sorbent was reacted with SO_2 in the flow reactor. The flow reactor was operated at 1000 $^\circ\text{C}$, 1 s residence time, and 3000 ppm SO_2 (with 5% oxygen and the balance of nitrogen) for this series of experiments. The results are presented in Fig. 2, which presents calcium utilization increase in relative percentage as a function of median particle size in micrometres. Surfactant modification can reduce sorbent particle size. Although beneficial, sorbent size reduction is not a prerequisite for increased SO_2 capture. Reducing the median particle size from 10 to 5 μm resulted in

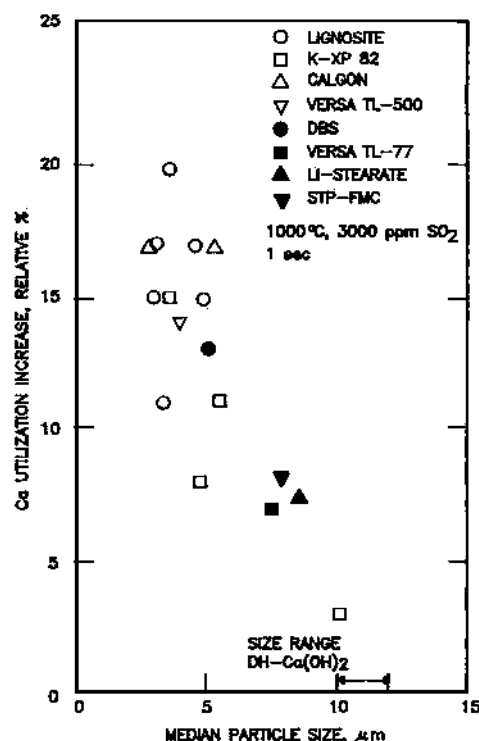


Fig. 2. The effect of median particle size of the chemically modified sorbents on their reactivity towards SO_2 .

a relative increase in calcium utilization of 3 to 17%. Further reduction to 3.5 μm particle size resulted in a relative increase of as much as 20% compared with 10 μm particle size. The recent study by Simons [11], that used his validated model and an assumed porosity of CaO of 60%, predicted increases of reactivity for corresponding particle diameters of 10 and 15 μm , respectively. The comparison of those data with the data obtained during this study indicates that some effect other than particle size decrease must be responsible for the enhanced reactivity of surfactant-modified sorbent. Lignosite was the additive selected for structural studies; therefore, when SM- $\text{Ca}(\text{OH})_2$ is mentioned further in this paper, it represents $\text{Ca}(\text{OH})_2$ modified with 1 wt.% of Lignosite.

Properties of CaO

The properties of nascent CaO that are thought to determine its reactivity towards SO_2 are surface area, porosity, pore size distribution, and resistance to sintering. Two sorbents were examined in the course of this work: DH- CaO , which was CaO formed as a result of decomposition of hydrated lime

TABLE

Additives used to produce chemically modified sorbents

Name	Chemical	Formula	Vendor	Weight concentration of additive (%)	Ca(OH) ₂ D ₅₀ (μm)
Lignosite	Calcium lignosulfonate	^a	Georgia-Pacific Corporation	0.5	4.85
Lignosite	Calcium lignosulfonate	^a	Georgia-Pacific Corporation	1.0	4.60
Lignosite	Calcium lignosulfonate	^a	Georgia-Pacific Corporation	1.5	3.60
Lignosite	Calcium lignosulfonate	^a	Georgia-Pacific Corporation	2.0	3.20
Lignosite	Calcium lignosulfonate	^a	Georgia-Pacific Corporation	3.0	2.96
Lignosite	Calcium lignosulfonate	^a	Georgia-Pacific Corporation	4.0	3.30
K-XP 82	Polyacrylic acid (partially neutralized)	CH ₃ CHCOOHX	B.F. Goodrich	10 ⁻³	4.80
K-XP 82	Polyacrylic acid (partially neutralized)	CH ₃ CHCOOHX	B.F. Goodrich	2 × 10 ⁻⁴	6.50
K-XP 82	Polyacrylic acid (partially neutralized)	CH ₃ CHCOOHX	B.F. Goodrich	10 ⁻⁴	3.70
K-XP 82	Polyacrylic acid (partially neutralized)	CH ₃ CHCOOHX	B.F. Goodrich	5 × 10 ⁻⁵	10.20
Calgon	Sodium hexametaphosphate	(NaO) ₂ PO(NaOPOO) _n (NaO) ₂ POO ^b	Beecham Products	1.0	5.30
Calgon	Sodium hexametaphosphate	(NaO) ₂ PO(NaOPOO) _n (NaO) ₂ POO ^b	Beecham Products	5.0	2.90
Versa TL-500	Sodium polystyrene sulfonate	[CH ₃ CHC ₆ H ₄ SO ₃ Na] _n ^c	National Starch and Chemical Corporation	1.0	4.00
Versa TL-77	Sodium polystyrene sulfonate	[CH ₃ CHC ₆ H ₄ SO ₃ Na] _n ^d	National Starch and Chemical Corporation	1.0	7.50
DBS	Sodium dodecylbenzene sulfonate	C ₁₂ H ₂₅ C ₆ H ₄ SO ₃ Na	Aldrich Corporation	1.0	5.10
Li-Stearate #306	Lithium stearate	CH ₃ (CH ₂) ₁₆ COOLi	Witco Chemical Corporation	1.0	8.50
STP	Sodium tripolyphosphate	Na ₅ P ₃ O ₁₀	FMC Corporation	1.0	7.80

^a Estimated formula: C₆C_{2.93}H_{7.86}O_{2.07}(OCH₃)_{0.88}(SO₃M)_{0.48}(COOH)_{0.03}.^b n = 25 - 20.^c Molecular weight = 500 000.^d Molecular weight = 70 000.

without additives (DH-Ca(OH)_2), and SM-CaO , which resulted from decomposition of surfactant-modified hydrated lime (SM-Ca(OH)_2). The surface areas that both sorbents have developed after calcination are compared in Fig. 3 and plotted as a function of temperature in the flow reactor. Residence time in the flow reactor was chosen to be 1.25 s and the calcining gas was nitrogen with 5 vol.% of oxygen. Within the temperature range investigated, the surface area developed by the SM-CaO was higher than that of DH-CaO .

Figure 4 presents porosities and median pore sizes for DH-CaO and SM-CaO as a function of the temperature in the flow reactor. As temperature conditions become more severe, both sorbents lose their porosity. At the stringent sintering conditions of 1000 °C for 1.25 s, a theoretical porosity of 50% has been reduced to 29 and 25% for the SM-CaO and DH-CaO , respectively. The lower part of Fig. 4 shows the median pore sizes for each temperature. As has been explained by Kirchgessner and Jozewicz [9], a significant portion of the sintering process involves filling the smaller pores. The expected transformation is that the median pore size will become larger at more advanced stages of sintering. This trend would reflect the filling of the smallest pores as a result of the transfer of materials from grain boundaries and surfaces to the pores. It can be seen in Fig. 4 that, at a given residence time, higher temperatures yield larger median pore sizes. For each set of conditions of residence time and

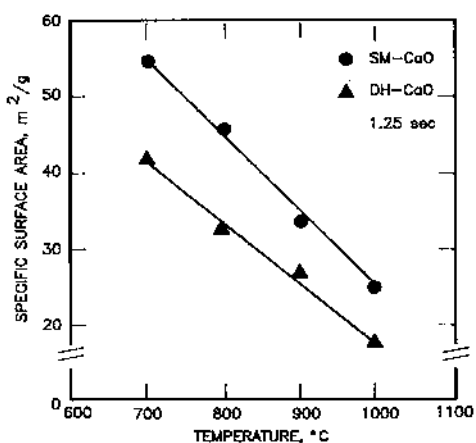
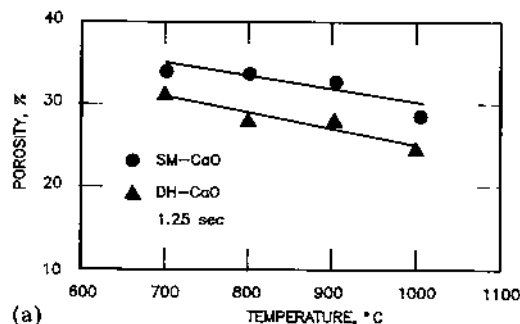
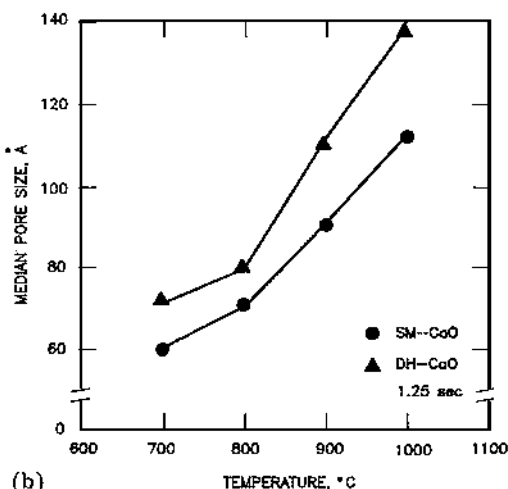


Fig. 3. Specific surface area decay of DH-CaO and SM-CaO as a function of temperature in the flow reactor.



(a)



(b)

Fig. 4. Structural changes of sintered sorbents.

temperature, DH-CaO developed a higher median pore size than SM-CaO , a result of more advanced sintering. The difference becomes more pronounced at higher temperatures. For example, at 700 °C the median pore size was 71 and 60 Å and at 1000 °C it was 135 and 110 Å for DH-CaO and SM-CaO , respectively.

Additional evidence for the difference in sintering behavior between DH-CaO and SM-CaO is given in Fig. 5, which shows the

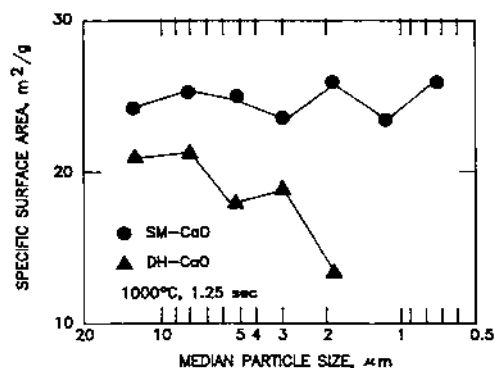


Fig. 5. Ability of Lignosite to retard sintering of SM-CaO .

surface area of calcines (DH-CaO and SM-CaO) plotted as a function of particle size. This set of data was produced with a heated Gelman inertial cascade impactor attached directly downstream of the flow reactor. This setup minimized the contact of freshly calcined material with the ambient air. The flow reactor was operated at 1000 °C, 1.25 s residence time, with the process gas composed of 5 vol.% of oxygen and the balance nitrogen. As can be seen in Fig. 5, for each particle size measured, SM-CaO developed a higher surface area than DH-CaO. The difference is particularly pronounced for particles smaller than 3 μm . For example, for the 1.83 μm particle size, measured surface area was 13.5 and 26 m^2/g for DH-CaO and SM-CaO, respectively. From the decreasing surface area with decreasing particle size of DH-CaO, it can be interpreted that sintering is more advanced in fine particles of DH-CaO. For the whole range of SM-CaO particle size measured (11.9 to 0.74 μm), the surface area revealed little change, varying between 23.5 and 26 m^2/g . The comparison of results for DH-CaO and SM-CaO presented in Fig. 5 indicates that surfactant-modified sorbent (SM-Ca(OH)₂) underwent significantly decreased sintering compared with conventional dry hydrated lime (DH-Ca(OH)₂). With a reduction of particle size (below 5 μm) having been shown to be of secondary importance and an enhanced dehydration rate ineffective in increasing the reactivity of the modified sorbent with SO₂ [9], a reduced rate of sintering appears to be the most acceptable explanation of superior reactivity of surfactant-modified sorbent.

Scanning electron microscope examination was conducted to characterize the morphology of sorbent undergoing thermal sintering. Two extreme cases are shown in Figs. 6 and 7 to better illustrate the dramatic changes of the morphology. Figure 6 shows the SEM photograph of the surfactant-modified sorbent which has been calcined in the flow reactor operated at 700 °C and 0.6 s residence time. Single grains of submicron size can be seen. Their rounded contours indicate that sintering has already begun under these conditions of time and temperature in the flow reactor. Figure 7 presents the SEM photograph of the same sorbent, which has been sintered at 1000 °C and 2.0 s residence

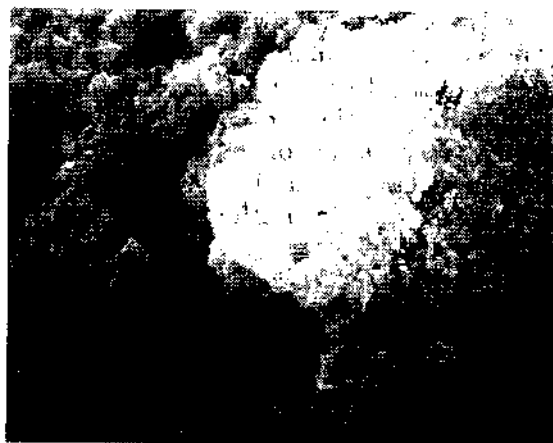


Fig. 6. SEM photograph of SM-CaO calcined at 700 °C, 0.6 s, no SO₂; $\times 20\,000$.

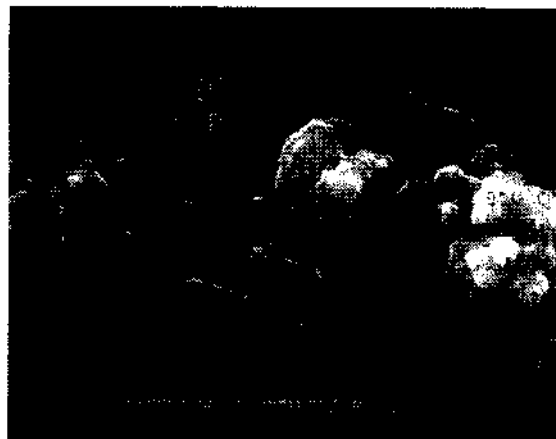


Fig. 7. SEM photograph of SM-CaO calcined at 1000 °C, 2.0 s, no SO₂; $\times 5000$.

time. Individual grains have, to a large degree, disappeared and have become part of a sintered mass of CaO. The grains that are visible have significantly increased in size, and some are several microns in diameter.

Effect of SO₂ during calcination

Upon dehydration in the boiler, nascent CaO undergoes complex reactions of simultaneous sintering and reaction with SO₂. Both processes affect the surface area and, ultimately, pore size distribution of the sorbent. As a result of sintering, fine pores are lost first, and the resulting pore size distribution has an increased median pore size [9]. Gullett and Bruce [12] refined our understanding of changing pore structure and postulated that, as a result of reaction with SO₂, pore volume declines throughout the

entire range of pore sizes with the preferential decline of pore volume in smaller pores. However, during their study, they varied the sorbent residence time in the reactor to obtain different levels of conversions. As a result of this approach, the decline in pore volume was a combined effect of sintering and build-up of the product of reaction with SO_2 . To avoid the effect of thermal sintering during this study, the residence time of the sorbent in the reactor was kept constant and different levels of conversion were effected by varying the SO_2 concentration from 0 to 3000 ppm SO_2 . The change of volume in the meso-pore region (20 - 500 Å) was measured in an attempt to examine the effect of having SO_2 present during the calcination process. In Fig. 8, the points on the vertical axis represent the pore volumes that the sorbents will sinter to (at 0.8 s residence time and 900 °C) without the SO_2 present during calcination. The next points to the right in Fig. 8 represent the pore volume after exposure to 50 ppm SO_2 and the resulting conversion of about 3%. As can be seen, higher pore volume resulted for both sorbents with the SO_2 present than without SO_2 . Similar results have been reported earlier for 1000 °C [10] and explained by the fact that SO_2 diffusing into pores and reacting with CaO would reinforce the structure against sintering, perhaps by interfering with the solid-state, diffusion-related exchange of lattice vacancies and migrating reactant species at the pore face. The results from the Kirchgessner and Jozewicz [10] study are

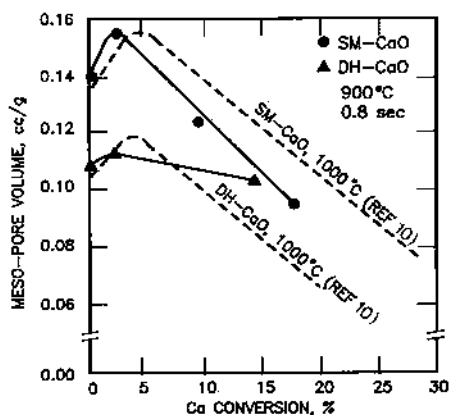


Fig. 8. The effect of SO_2 present during calcination at 900 °C (—, from Kirchgessner and Jozewicz [10]).

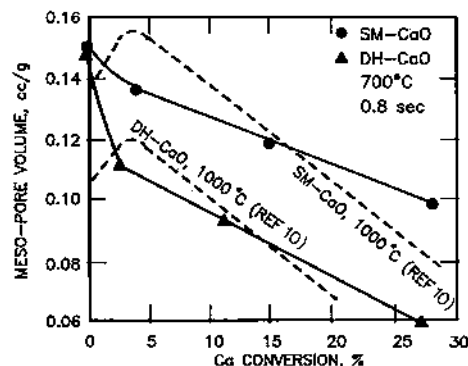


Fig. 9. Calcination at 700 °C with SO_2 present (---, from Kirchgessner and Jozewicz [10]).

shown with broken lines in Fig. 8. Figure 9 presents the volume available in the meso-pore region at increasing levels of conversion for sorbents exposed to SO_2 at 700 °C for 0.8 s. Contrary to the results presented for 900 and 1000 °C, no pore volume increase could be seen for sorbents reacting with SO_2 at 700 °C. This fact could be explained by the significantly lower diffusivity of SO_2 at 700 °C than at 1000 °C. When estimated from the Chapman-Enskog theory (Lennard-Jones parameters not corrected for polar component), the diffusivity of SO_2 in the gas would be 3.577 and 5.483 cm^2/s at 700 and 1000 °C, respectively. With lower diffusivity, there may not be enough SO_2 available for the early reaction with the sorbent to increase its resistance to the thermal sintering.

Figure 10 presents results from the same experiments shown in Figs. 8 and 9, plotting

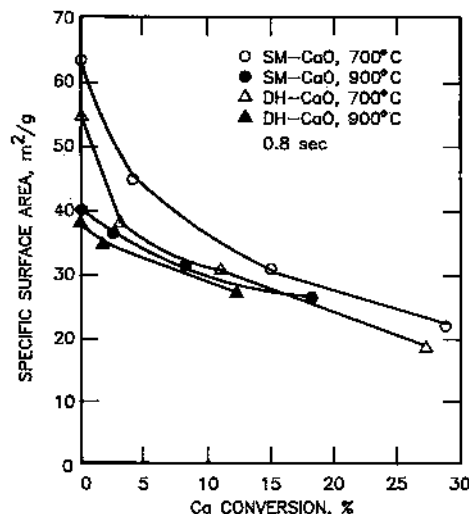


Fig. 10. Fine pore volume loss during calcination of DH-CaO and SM-CaO.

the specific surface area *versus* conversion of SM-CaO and DH-CaO. As can be seen, the increase in pore volume shown in Fig. 8 is not accompanied by corresponding increases of specific surface areas at 900 °C. This is probably due to the fact that fine pores (which contribute a significant part of the specific surface area) would be the first removed by sintering [10] and occluded by the reaction product [12]. The effect of fine pore plugging and/or filling seems to be dominant despite the ability of Lignosite and SO₂ to reduce sintering of pores of this size.

CONCLUSIONS

The following conclusions can be drawn from the results of this study:

(1) The enhancement of the reactivity of calcitic sorbents with SO₂ was possible as an effect of chemical modification during the hydration process.

(2) Surfactant modification can reduce sorbent particle size. Although beneficial, particulate size reduction was not a prerequisite for increased SO₂ capture.

(3) Some effect (probably inherent in the structure of nascent CaO) other than particle size must be responsible for the enhanced reactivity of surfactant-modified sorbents.

(4) Thermal sintering is retarded in surfactant-modified sorbent compared with a conventional dry hydrated sorbent. This is evident by the higher surface area and porosity of nascent SM-CaO compared with that of nascent DH-CaO.

(5) The effect of thermal sintering of calcitic sorbents is the increase in the median pore size as a result of filling fine pores by the transfer of matter from grain boundaries and surfaces to the pores.

(6) Surfactant-modified sorbent has the capability to retard sintering, even in sub-micron particles.

(7) The presence of SO₂ during calcination at higher temperatures favorably affects the structure of sorbents. The deposition of sulfate may interfere with the solid-state diffusion process of sintering. Fine pore filling and/or plugging seem to be the predominant factors in the decay of surface area.

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