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D-65396 Walluf, Germany
Tel. (061 23) 700-0
Fax (061 23) 700-122

Postal address:
D-65173 Wiesbaden, Germany

Project Manager:
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Editor-in-Chief:
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Editorial Advisory Board:
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Structural transformations in Ca-based sorbents used for SO₂ emission control

By W. Jozewicz and B. K. Gullett, Research Triangle Park, USA *)

Summary — Economizer temperature injection of Ca-based sorbents is an option for dry control of SO₂ emissions from coal-fired boilers. Their reactivity with SO₂ was found to be a function of their specific surface areas. In the course of this work, Ca(OH)₂ sorbents with specific surface areas from 2 to 79 m²/g and porosities from 0.02 to 0.48 were produced from a number of commercial sources in a laboratory-scale hydrator by "single" or "double" hydration. Single hydration produced Ca(OH)₂ from CaCO₃-derived CaO with specific surface areas up to 17.3 m²/g and porosities up to 0.29. Double hydration produced Ca(OH)₂ from Ca(OH)₂-derived CaO with specific surface areas up to 23 m²/g and porosities up to 0.33. In both types of hydration, a significant correlation was observed between the measured specific surface area and porosity of the CaO and its hydration product, Ca(OH)₂. Ca(OH)₂ sorbents were calcined in a flow reactor operated at 550°C and 1 s residence time to simulate conditions encountered by the solids during economizer injection and to investigate their response to economizer temperature. A correlation could be found between structural properties of Ca(OH)₂ and the product of its calcination in the flow reactor. Calcination of higher specific surface area/porosity Ca(OH)₂ resulted in higher specific surface area/porosity CaO. Similar pore size distributions were measured for CaO produced from calcination of Ca(OH)₂ with similar specific surface area, regardless of the source of Ca(OH)₂. Based on the structural response of Ca(OH)₂ following 550°C and 1 s exposure in the flow reactor, Ca(OH)₂ with a high specific surface area (55–60 m²/g) and high porosity (approximately 0.40) is recommended for economizer injection application.

Zusammenfassung — Die Injektion von Ca-Sorbentien in den Vorwärmer stellt eine Möglichkeit dar, die SO₂-Emission eines kohlegefeuerten Dampfkessels zu vermindern. Es hat sich gezeigt, daß deren Reaktivität gegenüber SO₂ von ihrer spezifischen Oberfläche abhängt. Für diese Untersuchungen wurden Ca(OH)₂-Sorbentien mit spezifischen Oberflächen von 2 bis 79 m²/g und Porositäten von 0,02 bis 0,48 aus verschiedenen im Handel erhältlichen Ausgangsstoffen in einer Labor-Hydratationseinrichtung durch „einfache“ und „doppelte“ Hydratation hergestellt. CaO aus CaCO₃ ergibt bei einfacher Hydratation ein Ca(OH)₂ mit einer spezifischen Oberfläche bis zu 17,3 m²/g und Porositäten bis 0,29, bei doppelter Hydratation ein Ca(OH)₂ mit einer spezifischen Oberfläche bis 23 m²/g und Porositäten bis 0,33. Bei beiden Arten der Hydratation wurde ein signifikanter Zusammenhang zwischen spezifischer Oberfläche und Porosität des CaO und seines Hydratationsprodukts Ca(OH)₂ beobachtet. Ca(OH)₂-Sorbentien wurden in einem Fließbett-Reaktor bei 550°C und 1 s Verweilzeit calciniert, um die Bedingungen nachzuahmen, denen der Feststoff beim Eindüsen in den Wärmetauscher ausgesetzt ist und um seine Reaktion bei der Wärmetauscher-Temperatur zu untersuchen. Es ergab sich ein Zusammenhang zwischen den Gefügeeigenschaften des Ca(OH)₂ und dem Produkt der Calcination im Fließbett-Reaktor. Die Calcination von Ca(OH)₂ mit höherer spezifischer Oberfläche und Porosität lieferte auch ein CaO mit einer höheren spezifischen Oberfläche und Porosität. Bei gleicher spezifischer Oberfläche hatte das CaO eine ähnliche Porengrößenverteilung wie das Ca(OH)₂, aus dem es hergestellt worden war, unabhängig von dessen Herkunft. Aufgrund des Verhaltens des Ca(OH)₂ im Fließbett-Reaktor bei 550°C und 1 s Verweilzeit wird empfohlen, zum Eindüsen in den Wärmetauscher ein Ca(OH)₂ mit hoher spezifischer Oberfläche (55–60 m²/g) und hoher Porosität (etwa 0,40) zu verwenden.

Résumé — L'injection de sorbants Ca dans le préchauffeur est un moyen de diminuer l'émission SO₂ d'une chaudière chauffée au charbon. Il s'est révélé, que leur réactivité à l'encontre de SO₂ dépend de leur surface spécifique. Pour les études présentées ont été fabriqués, à partir de différentes substances disponibles dans le commerce, des sorbants Ca(OH)₂ de surfaces spécifiques de 2 à 72 m²/g et de porosités de 0,02 à 0,48, ceci dans un équipement de laboratoire et par „simple“ ou „double“ hydratation. Avec une hydratation simple, CaO à partir de CaCO₃ donne un Ca(OH)₂ d'une surface spécifique jusqu'à 17,3 m²/g et des porosités jusqu'à 0,29 et, avec double hydratation, un Ca(OH)₂ d'une surface spécifique jusqu'à 23 m²/g et des porosités jusqu'à 0,33. Pour les deux modes d'hydratation a été observée une corrélation significative entre surface spécifique et porosité du CaO et de son produit d'hydratation Ca(OH)₂. Des sorbants Ca(OH)₂ ont été calcinés dans un réacteur à lit fluidisé, à 550°C et 1 s de durée de séjour, afin de simuler les conditions auxquelles est exposé le solide lors de l'injection dans l'échangeur de chaleur et pour étudier sa réaction à la température de l'échangeur de chaleur. On a constaté une relation entre les caractéristiques de structure du Ca(OH)₂ et du produit de calcination dans le réacteur à lit fluidisé. La calcination de Ca(OH)₂ de surface spécifique et porosité plus élevées a donné aussi un CaO de plus grande surface spécifique et porosité. Pour une surface spécifique égale, le CaO avait une distribution des dimensions des

Strukturelle Umwandlungen in Sorbentien auf Ca-Basis zur Verminderung der SO₂-Emission

Changements structuraux de sorbants à base de Ca pour la réduction des émissions SO₂

*) The authors wish to thank Wojciech Kozłowski (Acurex Environmental) for reactor operation/analyses and George R. Gillis (U.S. EPA/AEERL) for equipment construction/maintenance support.

pores semblable à celle du Ca(OH)_2 dont il avait été fabriqué, quelle que soit sa provenance. Compte tenu du comportement du Ca(OH)_2 dans le réacteur à lit fluidisé, à 550°C et 1 s de séjour, il est conseillé d'utiliser, pour l'injection dans l'échangeur de chaleur, un Ca(OH)_2 d'une grande surface spécifique (55–60 m²/g) et d'une forte porosité (env. 0,40).

Resumen — La inyección de adsorbentes de Ca en el precalentador representa una posibilidad de reducir la emisión de SO_2 de las calderas de vapor con calefacción de carbón. Ha quedado demostrado que su reactividad frente al SO_2 depende de la superficie específica. Para estos ensayos, se han fabricado adsorbentes Ca(OH)_2 con superficies específicas de 2 a 79 m²/g y porosidades de 0,02 a 0,48, a partir de diferentes materias de partida, usuales en el comercio, en una instalación de hidratación, de laboratorio, mediante procesos de hidratación „simple“ y „doble“. CaO a partir de CaCO_3 da, en el caso de la hidratación simple, un Ca(OH)_2 con una superficie específica de hasta 17,3 m²/g y porosidades de hasta 0,29, y en caso de doble hidratación, un Ca(OH)_2 con una superficie específica de hasta 23 m²/g y porosidades de hasta 0,33. Para ambas clases de hidratación, se ha observado una relación significativa entre la superficie específica y porosidad del CaO y su producto de hidratación Ca(OH)_2 . Los adsorbentes de Ca(OH)_2 se calcinaron en un reactor de lecho fluidizado, a 550°C y 1 s de permanencia, para simular las condiciones, a las que el sólido está expuesto durante su inyección en el intercambiador de calor y para estudiar su reacción ante la temperatura del intercambiador de calor. Se ha podido establecer una relación entre las características de la estructura del Ca(OH)_2 y el producto de la calcinación en el reactor de lecho fluidizado. La calcinación de Ca(OH)_2 de mayor superficie específica y porosidad dio también un CaO de mayor superficie específica y porosidad. A igual superficie específica, el CaO registraba una distribución del tamaño de poros similar al Ca(OH)_2 , a partir del cual había sido fabricado, independientemente de la procedencia de éste. Debido al comportamiento del Ca(OH)_2 en el reactor de lecho fluidizado, a 550°C y 1 s de permanencia, se recomienda utilizar, para la inyección en el intercambiador de calor, un Ca(OH)_2 de gran superficie específica (55–60 m²/g) y de elevada porosidad (0,40 aprox.).

Cambios estructurales en adsorbentes a base de Ca, para reducir la emisión de SO_2

1. Introduction

The cost of calcium hydroxide [Ca(OH)_2] sorbent injected into the convective pass of a coal-fired boiler (economizer) for dry sulfur dioxide (SO_2) control constitutes a significant part of the overall operating expenses of the process. In the process [1, 2], Ca(OH)_2 is injected into the economizer at temperatures ranging from 425 to 650°C. Upon injection, Ca(OH)_2 undergoes partial decomposition (calcination) to calcium oxide (CaO), thus forming a mixture of $\text{Ca(OH)}_2/\text{CaO}$. The mixture reacts with SO_2 and carbon dioxide (CO_2) to form two major stable products [3]: calcium sulfite (CaSO_3) and calcium carbonate (CaCO_3).

Reaction of the sorbent with SO_2 during economizer injection was found [4] to be a strong function of Ca(OH)_2 specific surface area in the range 12 to 38 m²/g. However, Ca(OH)_2 with specific surface area of over 70 m²/g can be produced by hydration of carefully prepared CaO [5]. These sorbents could, potentially, offer the benefit of increased removal of SO_2 . However, only incremental increases of SO_2 capture resulted from the use of 40 m²/g Ca(OH)_2 (compared to typical commercial Ca(OH)_2 [$\text{C}^\circ\text{-Ca(OH)}_2$] with approximately 20 m²/g specific surface area) when tested for a possible furnace injection (1000°C) application [6]. Similarly, measurements (at the conditions simulating furnace injection) on calcined sorbents with a specific surface area exceeding 50 m²/g indicated rapid deterioration of the pore structure due to thermal sintering [7], a phenomenon likely accompanied by decreased reactivity. Additionally, it is not clear whether the specific surface area or the porosity is responsible for the increased reactivity with SO_2 of high specific surface area/porosity sorbents [8]. A theoretical study undertaken to elucidate the relative importance of these two structural parameters for increased reactivity indicated that maximum increases in SO_2 reactivity are most easily achieved through increases in sorbent porosity [9].

The review of literature data [10, 11] indicates that conversion with SO_2 at furnace injection conditions may be more sensitive to porosity than to specific surface area development in the sorbent. Simons demonstrated [11] that, for any given porosity and reaction duration, sorbent conversion approaches an asymptotic level with increasing specific surface area and suggested increasing sorbent porosity as the most promising way to enhance sulfation. Numerous authors have shown that the specific surface area of Ca(OH)_2

injected into the furnace reaches a maximum value early (within milliseconds) during the injection process [12–14]. Borgwardt [15] determined the initial (maximum) specific surface area of CaO obtained from the calcination of $\text{C}^\circ\text{-Ca(OH)}_2$ to be 77 m²/g. As explained by Irabien et al. [16], the maximum in specific surface area of Ca(OH)_2 [calcined in a thermogravimetric analyzer (TGA) at temperatures from 350 to 750°C for a fixed amount of time] results from two opposing phenomena: specific surface area generation during the calcination of Ca(OH)_2 to CaO and specific surface area reduction due to sintering of the calcination product. The rate of Ca(OH)_2 sintering was independent of particle size between 2 and 20 μm , but was strongly dependent on temperature and impurities [17]. Therefore, substantially less Ca(OH)_2 sintering (or no sintering at all) would be expected at economizer rather than at furnace injection conditions.

Experimental results detailing the calcination/sintering response of sorbents during economizer temperature injection are limited. The time required for complete calcination of 25 m²/g pressure-hydrated dolomitic hydroxide during batch calcination in an electric furnace with nitrogen (N_2) sweep was given [18] as 8 min at 540°C. In another work [19], only 20 percent of $\text{Ca(OH)}_2\text{-CaO}$ transition was measured after 10 min exposure of 8 m²/g Ca(OH)_2 to dry N_2 in a TGA operated at 400°C. The limited amount of data is especially true for Ca(OH)_2 with high initial specific surface areas. Consequently, it is not clear how well very high specific surface area sorbents will react with SO_2 during economizer temperature injection conditions. Based on the results referenced above for 25 and 8 m²/g Ca(OH)_2 , incomplete Ca(OH)_2 to CaO calcination is expected for $\text{C}^\circ\text{-Ca(OH)}_2$ at conditions representative of economizer injection (550°C, 1 s residence time). It is not clear, however, what the calcination and sintering behavior would be for Ca(OH)_2 with high specific surface area. Consequently, it is not known what the reactivity benefit would be from using high specific surface area Ca(OH)_2 for economizer injection.

The objective of this work was to research methods of producing Ca(OH)_2 sorbents of high specific surface areas and porosities from a number of commercial sources and then to determine their structural response to calcination/sintering at economizer temperature injection conditions. Sorbent particle size was not considered in this work, since it is a function of CaCO_3 type and grind used for the production of

the sorbent. A certain degree of particle size change is likely to occur as a result of CaCO_3 calcination and subsequent hydration. However, varying hydration techniques is not likely to significantly change the particle size of the sorbent. Therefore, investigation of the particle size response to the economizer temperature is not included in this study. SO_2 was omitted in this work because the objective of the research was to observe calcination and sintering behavior without the additional complication of sulfation, which would effectively mask the specific surface area and pore structure changes of interest through product layer buildup and pore plugging. The objectives of the research were achieved by producing Ca(OH)_2 sorbents with specific surface areas ranging from below 10 to above 70 m^2/g by means of a "double hydration" [from $\text{C}^\circ\text{-Ca(OH)}_2$] or "single hydration" (from commercial CaCO_3). Well dispersed Ca(OH)_2 solids were calcined in N_2 in an entrained-flow reactor (flow reactor) operated at 550°C and 1 s to determine their structural response to economizer temperatures.

TABLE 1: Commercial sources of Ca(OH)_2 [$\text{C}^\circ\text{-Ca(OH)}_2$]

$\text{C}^\circ\text{-Ca(OH)}_2$ type	Specific surface area [m^2/g]	Porosity
Linwood	14	0.13
Longview	9	0.12
Marblehead	19	0.16
Mississippi	19	0.18

2. Experimental

2.1 Materials and hydration

Four $\text{C}^\circ\text{-Ca(OH)}_2$ sources were used throughout the study to produce double-hydration-derived Ca(OH)_2 [2°-Ca(OH)_2]. They were obtained from Linwood, Longview, Marblehead, and Mississippi Lime Companies, from which they derived their names. Measured structural properties of $\text{C}^\circ\text{-Ca(OH)}_2$ are presented in Table 1. The specific surface areas and porosities of the $\text{C}^\circ\text{-Ca(OH)}_2$ varied from 9 to 19 m^2/g and from 0.12 to 0.18, respectively. The progression of steps during the double hydration process as well as nomenclature used throughout this paper are shown in Fig. 1a.

A double hydration method was used to produce 2°-Ca(OH)_2 with a wide range of specific surface areas and porosities. This method is known [20] to yield Ca(OH)_2 with high spe-

cific surface area. In the first step, $\text{C}^\circ\text{-Ca(OH)}_2$ was calcined in a flat bed to CaO [1°-CaO] at 600°C for 16 h in a Lindberg furnace under a N_2 flow of 6 l/min. 1°-CaO produced in this way was 10–20 percent Ca(OH)_2 as measured by a TGA, and upon hydration with a water/alcohol mixture yielded 2°-Ca(OH)_2 with a specific surface area from 29 to 79 m^2/g . Methyl alcohol (CH_3OH) was used to enhance the specific surface area/porosity in 2°-Ca(OH)_2 . The volumetric ratios of CH_3OH :water ranged from 0.1:1 to 5:1. It is believed that CH_3OH evaporates completely by the time hydration is complete, resulting in a sorbent without hydration-induced impurities that could affect its pore structure during sintering and/or reaction with SO_2 . An X-ray diffraction analysis of selected 2°-Ca(OH)_2 revealed Ca(OH)_2 as the only crystalline phase present. Other known methods of producing high specific surface area Ca(OH)_2 include use of sugar or sodium salts [21]. However, the residues of these additives in the sorbent could potentially affect the sintering behavior of Ca(OH)_2 .

The lowest specific surface area of 2°-Ca(OH)_2 produced by double hydration (29 m^2/g) was outside the range of specific surface areas measured for $\text{C}^\circ\text{-Ca(OH)}_2$ used throughout this study (9–19 m^2/g in Table 1). Therefore, since an investigation over the widest possible range of specific areas was desired, one commercial CaCO_3 was obtained with the intent to produce sorbents with specific surface areas in the range of $\text{C}^\circ\text{-Ca(OH)}_2$ by a single hydration [1°-Ca(OH)_2]. Longview CaCO_3 was crushed to a median particle size (D_{50}) of 7.0 μm (1.3 m^2/g and 0.014 porosity) and calcined in a flat bed to CaO [1°-CaO] at 1000°C for 16 h in a Lindberg furnace under a N_2 flow of 6 l/min. This procedure yielded 1°-CaO with a 2.1 m^2/g specific surface area and 0.014 porosity. Single hydration was carried out with water only or with CH_3OH /water mixtures. The volumetric ratios of CH_3OH :water used for single hydration ranged from 1:1 to 10:1. The nomenclature used to describe single hydration is shown in Fig. 1b.

Hydration (both double and single) was conducted in a laboratory-scale hydrator consisting of a 0.4 l Pyrex beaker suspended in a constant 74°C bath. A mechanically propelled stirrer was used to mix the CH_3OH and water with CaO . Each hydration was conducted by loading 10 g of dry CaO into the hydrator and allowing it to achieve thermal equilibrium in the bath. The stirrer was started, and a single rapid addition of the CH_3OH and water mixture at 67°C was syringed into the hydrator in the desired molar ratio of $\text{H}_2\text{O}:\text{CaO}$. After 15 min, the hydration vessel was purged of remaining water vapor with N_2 , leaving a thoroughly dry product.

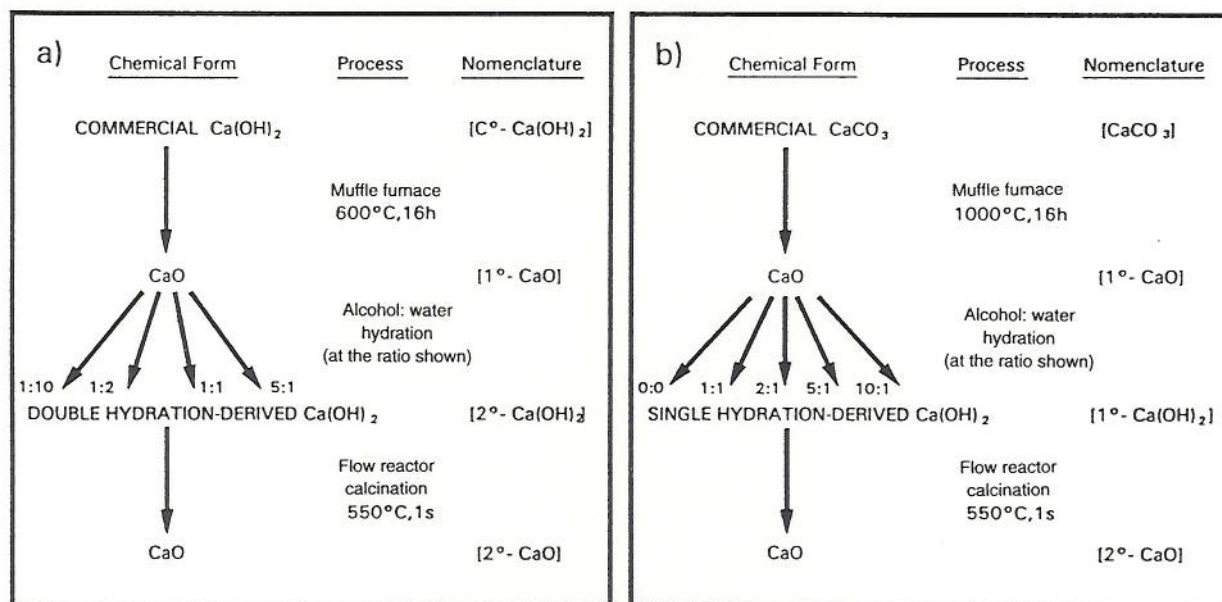


FIGURE 1: Nomenclature used throughout the paper to describe double hydration (a) and single hydration (b)

2.2 Reactor

The electrically heated, isothermal flow reactor into which 1°-Ca(OH)_2 or 2°-Ca(OH)_2 was injected to produce calcined solids [2°-CaO] for structural studies is shown in Fig. 2. The reaction chamber consists of two concentric, 3.35 m long quartz tubes heated by three tube furnaces in series. The inner quartz tube has a 15 mm ID, and the outer tube has a 50.8 mm OD. Premixed gases enter the reactor at the bottom of the annulus between the inner and outer tubes and are heated as they move upward. At the top of the reactor they enter the inner tube with the injected sorbent and move down through the calcination zone. 1°-Ca(OH)_2 or 2°-Ca(OH)_2 was fed from a fluidized bed feed tube through 1.9 mm ID syringe tubing. Gases and calcined 1°-Ca(OH)_2 or 2°-Ca(OH)_2 [2°-CaO] exited the reactor through an air-cooled heat exchanger that quenched the reactant stream to approximately 280°C . 2°-CaO solids were captured in a cyclone. For this work the reactor was operated isothermally at a nominal temperature of 550°C and residence time of 1 s to simulate conditions encountered by sorbent during economizer injection. The gas composition was 95 volume percent N_2 , and 5 volume percent oxygen (O_2).

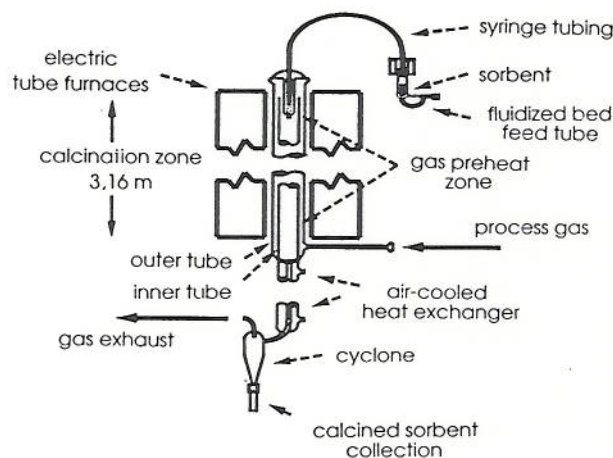


FIGURE 2: Schematic of the flow reactor

2.3 Analyses

Specific surface area, porosity, and pore size distribution were measured by N_2 adsorption/desorption in a Micromeritics ASAP autoanalyzer. Porosity was determined from the volume of adsorbed gas up to a partial pressure of 0.9855, representing void volume in cylindrical pores up to 3000 Å in diameter. Pore size distributions were measured to determine the development of pore volume in fine pores which fill very fast with products of the reaction with SO_2 and, therefore, yield limited contribution to reactivity. Sorbents intended for structural analysis were fed from the fluidized bed feeder and, after passing through the flow reactor, were separated from the gas. Solids were immediately transferred to a sample vial, sealed and placed in a vacuum desiccator. Same-day calcination/structural analysis was implemented to minimize possible rehydration or recarbonation of solids. The degree of hydration and extent of calcination were measured using a Perkin Elmer TGA7 thermogravimetric analyzer. The particle size distribution was measured by the X-ray sedimentation technique in a Micromeritics Sedi-graph. The purity of 2°-Ca(OH)_2 phase was measured by X-ray diffraction using a Siemens Diffractometer.

3. Results

3.1 Calcination of $\text{C}^\circ\text{-Ca(OH)}_2$ to a constant structure 1°-CaO

Initially, four $\text{C}^\circ\text{-Ca(OH)}_2$ sources were used to produce numerous 2°-Ca(OH)_2 sorbents by double hydration in order to investigate the effect of calcium source on the development of structure by 2°-Ca(OH)_2 . For each of the four $\text{C}^\circ\text{-Ca(OH)}_2$ sources, 1°-CaO of constant structure (constant spe-

cific surface area and porosity) was used and only hydration parameters were varied to produce 2°-Ca(OH)_2 with dissimilar specific surface areas and porosities. As evident from Table 2, the four 1°-CaO sorbents had approximately the same specific surface areas ($20 \text{ m}^2/\text{g}$) and porosities (0.30), following calcination of $\text{C}^\circ\text{-Ca(OH)}_2$ in the Lindberg furnace. Similar pore size distributions were measured for the four 1°-CaO sorbents resulting from 16 h calcination of $\text{C}^\circ\text{-Ca(OH)}_2$ in the muffle furnace (600°C) with N_2 sweep gas. The four 1°-CaO materials tested had most of their pore volume contained in the 100–300 Å pore size range.

TABLE 2: Structure development accompanying calcination of $\text{C}^\circ\text{-Ca(OH)}_2$ in Lindberg furnace at 600°C for 16 hours

$\text{C}^\circ\text{-Ca(OH)}_2$ type	1°-CaO Product Specific surface area [m^2/g]	Porosity
Linwood	23	0.33
Longview	19	0.25
Marblehead	19	0.30
Mississippi	17	0.29

3.2 Hydration of a constant structure 1°-CaO

The four 1°-CaO sources were used to create 2°-Ca(OH)_2 sorbents possessing varying combinations of specific surface area and porosity. These 2°-Ca(OH)_2 sorbents were then calcined in the flow reactor to study the relation between their structural properties and those of the resulting 2°-CaO . The population of 2°-Ca(OH)_2 produced from the four sources of $\text{C}^\circ\text{-Ca(OH)}_2$ by double hydration is presented in Fig. 3, giving porosity as a function of specific surface area. Specific surface areas and porosities of $\text{C}^\circ\text{-Ca(OH)}_2$ are also shown in Fig. 3 for comparison. Complete structural data for 2°-Ca(OH)_2 are given in Table 3. The specific surface areas of 2°-Ca(OH)_2 ranged from 29 to $79 \text{ m}^2/\text{g}$ and porosities from 0.26 to 0.50. For each commercial source, the measured D_{50} of 2°-Ca(OH)_2 decreased as its specific surface area increased. No specific commercial source of $\text{C}^\circ\text{-Ca(OH)}_2$ could be selected as producing sorbents [2°-Ca(OH)_2] with higher specific surface area upon completion of the second step of double hydration. Rather, the specific surface area appeared to be proportional to the volumetric ratio of CH_3OH :water used.

The lowest specific surface area for sorbents produced by double hydration and discussed above was $29 \text{ m}^2/\text{g}$. Single hydration was used, therefore, to produce sorbents with specific surface areas below $30 \text{ m}^2/\text{g}$. Longview 1°-CaO of con-

TABLE 3: Structural data for 2°-Ca(OH)_2

Sorbent type	Specific surface area [m^2/g]	Porosity
Linwood	35	0.27
Linwood	51	0.36
Linwood	59	0.39
Linwood	70	0.43
Longview	35	0.26
Longview	54	0.36
Longview	74	0.48
Marblehead	36	0.27
Marblehead	46	0.33
Marblehead	56	0.36
Marblehead	69	0.46
Mississippi	29	0.29
Mississippi	50	0.34
Mississippi	79	0.48

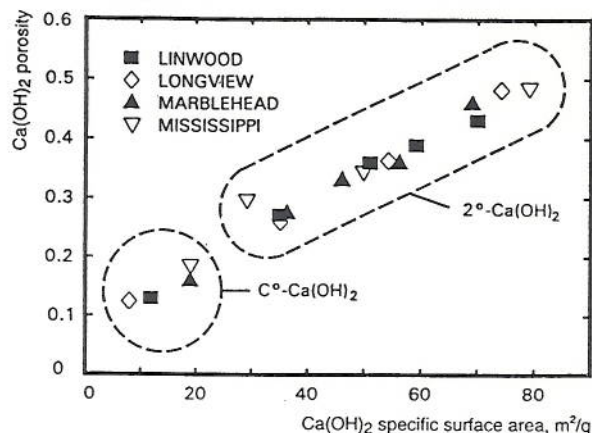


FIGURE 3: Population of 2°-Ca(OH)₂ sorbents produced from the four commercial C°-Ca(OH)₂ precursors for this study

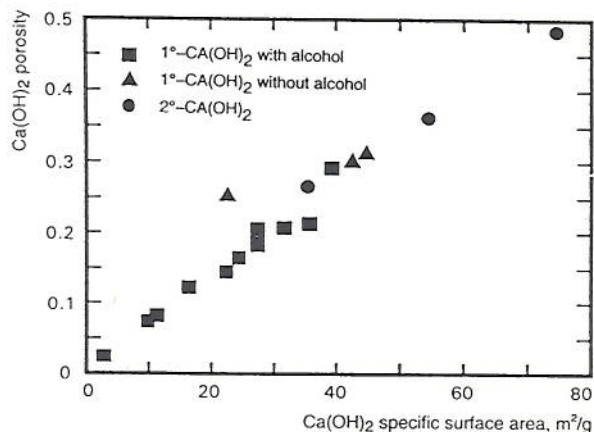


FIGURE 4: The population of Longview Ca(OH)₂ produced for this study

stant structure (2.1 m²/g and 0.014) was used to produce all of the 1°-Ca(OH)₂. This population is presented in Fig. 4 giving porosity as a function of specific area of Ca(OH)₂. The specific surface areas of Longview 1°-Ca(OH)₂ ranged from 2 to 44 m²/g and the porosities from 0.02 to 0.31. Four hydration parameters were varied to produce 1°-Ca(OH)₂ with specific surface areas more closely representative of C°-Ca(OH)₂ than measured for 2°-Ca(OH)₂. These parameters (temperature of water, temperature of solids, CH₃OH:water ratio, and amount of water) were only used as a means to expand the range of specific surface area of Ca(OH)₂ and no systematic study of their effect on structural parameters was intended in this work. Longview 2°-Ca(OH)₂ is also shown in Fig. 4 to demonstrate the continuation of the specific surface area/porosity development trend, regardless of the hydration method used to produce Ca(OH)₂. Combined data for single [1°-Ca(OH)₂] and double hydration [2°-Ca(OH)₂] Longview Ca(OH)₂ demonstrate that specific surface area and porosity of Ca(OH)₂ are closely related, regardless of the hydration procedure.

In order to study the development of 2°-Ca(OH)₂ structure with increasing specific surface area, pore size distributions were measured. Fig. 5 presents results of pore size distribution analyses for Longview 2°-Ca(OH)₂ with specific surface areas varying from 74 to 35 m²/g. These pore size distributions are typical of those for 2°-Ca(OH)₂ sorbents from all four sources. For each of these, the pore size distribution of the 1°-CaO used for its production is shown for comparison. It can be seen that the increase in specific surface area for low specific surface area 2°-Ca(OH)₂ (35 m²/g) sorbents took place primarily in pores smaller than 200 Å when compared to the pore size distribution of 1°-CaO used to produce them. Intermediate surface area 2°-Ca(OH)₂ (54 m²/g) also consisted mostly of pores smaller than 200 Å. The gradually increasing volume of pores smaller than 200 Å is accompanied by

increasing surface area. For the sorbent with the highest specific surface area produced (74 m²/g), a dramatic volume increase of pores both larger and smaller than 200 Å can be seen compared to the pore size distribution of 1°-CaO used to produce them. Only sorbents produced with Longview 1°-CaO are shown in Fig. 5. However, similar trends were observed for the other 1°-CaO sources investigated here.

For the four C°-Ca(OH)₂ sorbents used in this study, the 2°-Ca(OH)₂ of comparable specific surface area revealed similar pore size distributions. Comparison of the pore size distribution of 1°-CaO and its low specific surface area 2°-Ca(OH)₂ for any of the four C°-Ca(OH)₂ sorbents used here indicates that all of them developed their specific surface areas by creation of significant volume in pores smaller than 200 Å.

3.3 Calcination of CaCO₃ to a variable structure 1°-CaO

Based on the results for 2°-Ca(OH)₂ structure formation presented above for four sources of C°-Ca(OH)₂, it appears that, for constant calcination conditions, 1°-CaO with similar specific surface area, porosity, and pore size distribution will be created. Subsequently, for constant parameters of hydration of 1°-CaO, 2°-Ca(OH)₂ with similar surface area, porosity, and pore size distribution will be produced. An additional series of experiments was performed with Mississippi CaCO₃ with the goal of producing a variable structure 1°-CaO in order to observe how structural properties of CaO would be transferred into those of Ca(OH)₂ resulting from hydration.

Mississippi CaCO₃ was ground in a bench scale attritor and then six size fractions were made, with D₅₀ ranging from 0.61 to 106 µm. These size-fractionated samples of CaCO₃ were calcined for 16 h in the muffle furnace at temperatures ranging from 700 to 1080°C. Based on TGA results, each sample

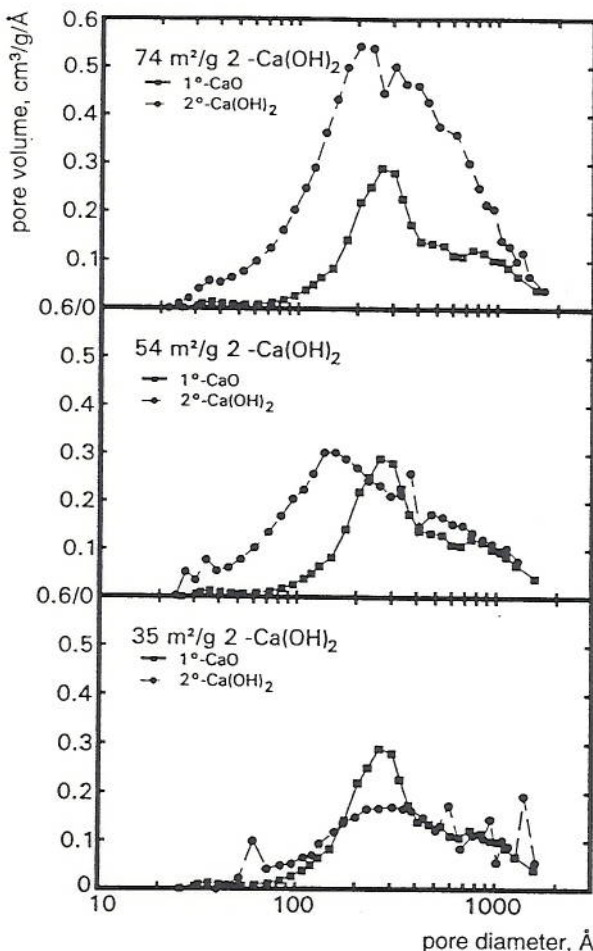


FIGURE 5: Development of structure by 2°-Ca(OH)₂ sorbents produced from Longview 1°-CaO

was 95 percent calcined (less than 5 percent CaCO_3 remaining). As a result of calcination, 1°-CaO was produced with specific surface areas and porosities ranging from 0.7 to $17.3 \text{ m}^2/\text{g}$ and from 0.004 to 0.29, respectively. For any CaCO_3 particle size, the specific surface area and porosity of 1°-CaO increased with decreasing calcination temperature. The whole population of 1°-CaO produced is plotted in Fig. 6 giving 1°-CaO porosity as a function of 1°-CaO surface area. A co-linearity of measured specific surface area and porosity of 1°-CaO was observed.

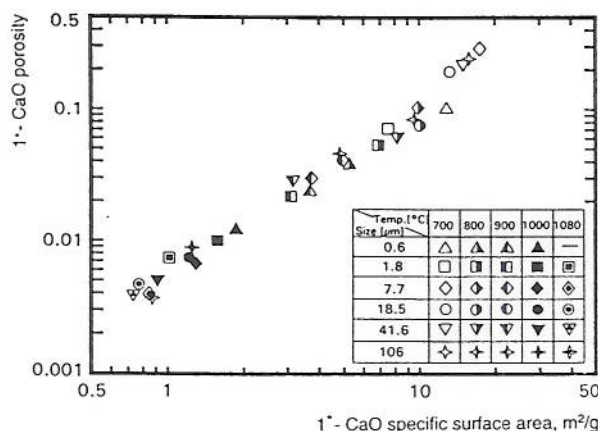


FIGURE 6: Population of Mississippi 1°-CaO produced for this study

3.4 Hydration of a variable structure 1°-CaO

In the next step, samples of Mississippi 1°-CaO with widely ranging specific surface areas and porosities described above (Fig. 6) were used to produce 1°-Ca(OH)_2 using varying hydration parameters. The goal of this step was to investigate whether the specific surface area and porosity of Ca(OH)_2 could be decoupled when hydrating CaO precursors with widely variant porosities and specific surface areas. Five Mississippi 1°-CaO sources with specific surface areas and porosities ranging from 1.2 to $17 \text{ m}^2/\text{g}$ and 0.008 to 0.29, respectively, were used to produce 1°-Ca(OH)_2 . The results are shown in Fig. 7. They were statistically analyzed for co-linearity of specific surface area and porosity both collectively [for all of the 1°-Ca(OH)_2 sorbents produced with five dissimilar 1°-CaO sources] and precursor-specific [separate analysis for each family of 1°-Ca(OH)_2 from a single 1°-CaO]. It was concluded, both for collective and precursor-specific analysis, that even though there was evidence of departure from specific surface area/porosity co-linearity, the specific surface area and porosity measurements were along a fairly narrow band. 1°-CaO with $17 \text{ m}^2/\text{g}$ and 0.29 resulted in 1°-Ca(OH)_2 having the least co-linear surface area and porosity values.

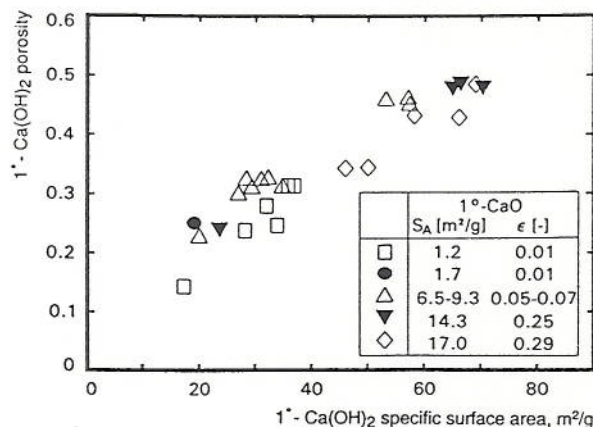


FIGURE 7: Population of Mississippi 1°-Ca(OH)_2 produced for this study

3.5 Flow reactor calcination of 2°-Ca(OH)_2 and 1°-Ca(OH)_2

Following injection into the economizer region, Ca(OH)_2 undergoes (partial) calcination to CaO . The resulting $\text{Ca(OH)}_2/\text{CaO}$ mixture reacts with SO_2 . Knowledge of any existing correlation between structural properties of Ca(OH)_2 and the $\text{Ca(OH)}_2/\text{CaO}$ mixture resulting from its calcination would aid in sorbent selection for economizer capture of SO_2 by more accurately evaluating the effect of using a high specific surface area Ca(OH)_2 for injection. 2°-Ca(OH)_2 sorbents produced from four $\text{C}^\circ\text{-Ca(OH)}_2$ sources were calcined in the flow reactor operated under fixed conditions of temperature and residence. The flow reactor calcination conditions were selected to be 550°C and 1 s to adequately simulate temperature and residence time of the sorbent during economizer injection.

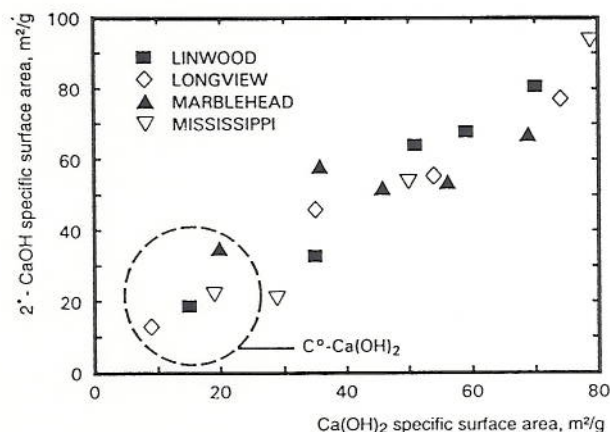


FIGURE 8: Correlation between the specific surface area of 2°-Ca(OH)_2 and 2°-CaO (constant calcination conditions of 550°C and 1 s) produced from the four commercial $\text{C}^\circ\text{-Ca(OH)}_2$ precursors

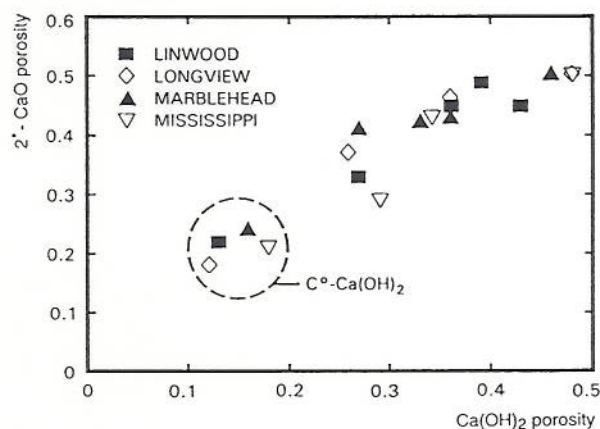


FIGURE 9: Correlation between porosity of 2°-Ca(OH)_2 and 2°-CaO (constant calcination conditions of 550°C and 1 s) produced from the four commercial $\text{C}^\circ\text{-Ca(OH)}_2$ precursors

Results of the calcination study of 2°-Ca(OH)_2 are presented in Figs. 8 and 9. Fig. 8 shows the correlation between the resulting specific surface area of 2°-CaO and the specific surface area of the 2°-Ca(OH)_2 precursor for the four commercial materials investigated throughout this work. The corresponding correlation for porosity is given in Fig. 9. In both figures, results of the four $\text{C}^\circ\text{-Ca(OH)}_2$ sorbents are highlighted. No specific commercial source-derived 2°-Ca(OH)_2 yielded 2°-CaO with distinguishably higher specific surface area and/or porosity upon calcination at constant conditions. Rather, 2°-Ca(OH)_2 sources with higher specific surface areas and porosities up to approximately 0.4 yielded 2°-CaO sorbents with higher specific surface areas following the calcination in the flow reactor (550°C , 1 s). It appears that increasing 2°-Ca(OH)_2 porosity above 0.40 did not result in a

significant increase of 2°-CaO porosity. 2°-Ca(OH)₂ porosity of 0.40 would occur with specific surface areas of 55–60 m²/g (Figs. 3 and 4). Similar pore size distributions were measured for 2°-CaO produced by calcination of 2°-Ca(OH)₂ of similar specific surface area, regardless of the source of 2°-Ca(OH)₂.

For the four 2°-Ca(OH)₂ sources tested here, only limited pore volume change took place upon 550°C, 1 s flow reactor calcination of 2°-Ca(OH)₂ to 2°-CaO. Typical TGA-based composition of C°-Ca(OH)₂ calcined in the flow reactor at 550°C for 1 s revealed approximately 40–50 percent C°-Ca(OH)₂ and 60–50 percent 2°-CaO. Truly then, the product of 2°-Ca(OH)₂ calcination in the flow reactor at the above conditions is a 2°-Ca(OH)₂/2°-CaO mixture. For clarity, however, this product is termed 2°-CaO throughout this paper.

One precursor (Marblehead) was selected to examine whether the limited change of pore volume occurred over the entire range of 2°-Ca(OH)₂ specific surface areas. Marblehead 2°-Ca(OH)₂ sorbents with specific surface areas ranging from 36 to 69 m²/g were calcined in the flow reactor at 550°C, 1 s. Pore size distributions of the resulting Marblehead 2°-CaO are shown in Fig. 10 and compared to their 2°-Ca(OH)₂ precursors. Pore volume change resulting from the calcination was a function of an initial 2°-Ca(OH)₂ pore volume. Compared to the initial 2°-Ca(OH)₂, 9 and 6 percent decreases of pore volume in 2°-CaO were observed following calcination of 0.38 and 0.25 cm³/g (69 and 56 m²/g) 2°-Ca(OH)₂. Calcination of 0.17 cm³/g (36 m²/g) 2°-Ca(OH)₂ resulted in a 27 percent increase of pore volume in 2°-CaO.

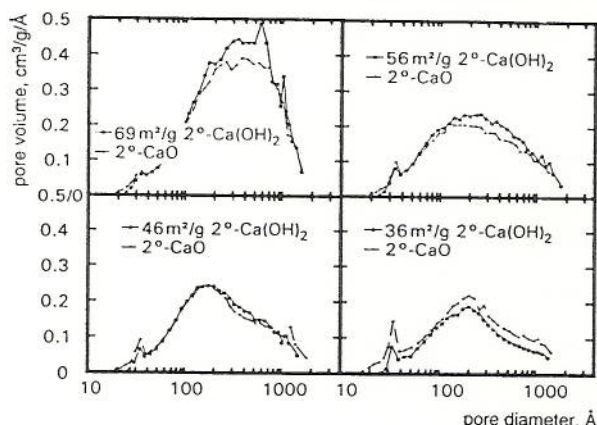


FIGURE 10: Changes of pore size distribution accompanying calcination of Marblehead 2°-Ca(OH)₂ to 2°-CaO

Only 1 percent increase was noted for 0.22 cm³/g (46 m²/g) 2°-Ca(OH)₂ calcination. The response of the specific surface area was similar. Increase of pore volume by a mechanism of opening micropore structure following the evacuation of water film would be expected for Ca(OH)₂ that undergoes calcination to CaO. Decrease of pore volume by a mechanism of neck growth between adjacent particles or grains with consequent rounding of pores located at the intersection of grain boundaries would be expected for calcined Ca(OH)₂ that undergoes thermal sintering. Therefore, based on results presented above, it appears that, upon calcination of 2°-Ca(OH)₂ with 46 m²/g specific surface area (0.22 cm³/g pore volume), 2°-CaO is approaching the optimum calcination/sintering specific surface area [16]. Consistent with this interpretation, calcined 69 and 56 m²/g 2°-Ca(OH)₂ sorbents appear to have somewhat passed the optimum (already at the sintering stage), while calcined 36 m²/g 2°-Ca(OH)₂ sorbent appears to have not reached the optimum (still at the dehydration stage). However, 2°-Ca(OH)₂ sorbent with the highest pore volume (0.38 cm³/g) retained the highest pore volume among 2°-CaO sorbents resulting from calcination.

Additional results of flow reactor calcination (550°C, 1 s) of selected Longview 1°-Ca(OH)₂ sorbents are given in Fig. 11, showing the correlation between the specific surface areas of Longview 1°-Ca(OH)₂ and its calcination product, 2°-CaO.

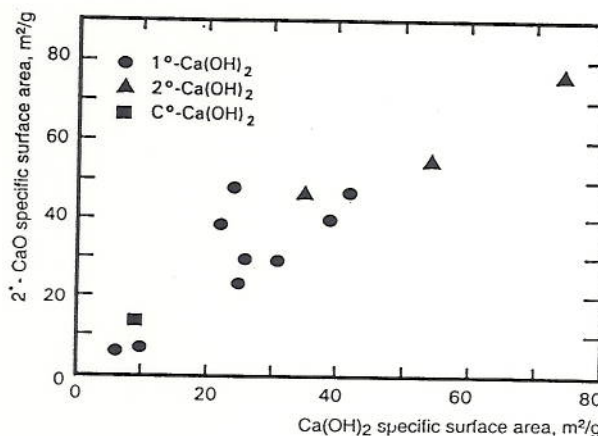


FIGURE 11: Correlation between specific surface area of Longview 1°-Ca(OH)₂ and 2°-CaO (constant calcination conditions of 550°C and 1 s)

In the figure, results for the calcination of Longview 2°-Ca(OH)₂ and Longview C°-Ca(OH)₂ are shown for comparison. Similar to the results presented earlier for 2°-Ca(OH)₂ from the four sources of C°-Ca(OH)₂, 2°-CaO with higher specific surface area/porosity was produced following 550°C, 1 s calcination of 1°-Ca(OH)₂ with higher specific surface area/porosity.

4. Discussion

Structural properties of the sorbent (specific surface area and porosity) are responsible for its reactivity with SO₂. For example, let us consider an imaginary Ca(OH)₂ sorbent with measured initial porosity (ϵ_0) and initial specific surface area (S_{A0}). Following exposure to SO₂ at economizer temperatures, a level of conversion (X_0) would be measured for this sorbent. If it were possible to produce two Ca(OH)₂ sorbents, one with increased specific surface area such that $S_{A1} = 1.5 \cdot S_{A0}$ and unchanged porosity $\epsilon_1 = \epsilon_0$ and another with increased porosity such that $\epsilon_2 = 1.5 \cdot \epsilon_0$ and unchanged specific surface area $S_{A2} = S_{A0}$, they would likely [11] yield different levels of conversions (X_1 and X_2 , respectively) upon exposure to SO₂. Literature data reviews [10, 11] and our earlier study of sorbent reactivity at economizer conditions [9] indicate that the descending order of measured conversions would be X_2 , X_1 , and X_0 . However, it was not possible throughout this study to selectively increase porosity at constant specific surface area of the sorbent, as evident from Figs. 3, 4 and 7. Families of Ca(OH)₂ plotted in these figures revealed co-linearity of specific surface area and porosity. Co-linearity occurred for two 2°-Ca(OH)₂ production schemes used throughout this work: constant structure 1°-CaO/variable hydration parameters (Fig. 3) and variable structure 1°-CaO/variable hydration parameters (Figs. 4 and 7).

In this work, extensive hydration experiments created a family of Ca(OH)₂ sorbents with only small variations of porosity for a constant specific surface area. For the four commercial precursors, structural properties of Ca(OH)₂ sorbents were related to those of the parent CaO. For constant hydration conditions, higher specific surface area/porosity CaO resulted in higher specific surface area/porosity Ca(OH)₂. Specific surface areas and porosities of a family of CaO were also co-linear for a variety of initial CaCO₃ particle sizes and changing calcination conditions (Fig. 6).

Based on the analysis of calcination data presented in Figs. 8–11, it appears that Ca(OH)₂ with a high specific surface area (55 to 60 m²/g) and porosity (0.40) may be developing the most desirable structure for the economizer injection application. Increasing the specific surface area of Ca(OH)₂ up to 55–60 m²/g resulted in increasing specific surface area of

CaO. This trend was reflected by porosity which, for the CaO originating from 55–60 m²/g Ca(OH)₂, was approximately 0.40. Increasing the specific surface area of Ca(OH)₂ beyond 55–60 m²/g also resulted in the increase of CaO specific surface area. However, only limited increases in CaO porosity were observed. In light of the porosity importance [10, 11] for sulfation, Ca(OH)₂ with specific surface area of 55–60 m²/g would be selected as the optimum sorbent. This structurally based prediction has not been verified by measuring the sorbents' reactivity with SO₂ at conditions representative of economizer injection.

5. Conclusions

CaO with widely varying specific surface areas (0.7 to 17.3 m²/g) and porosities (0.004 to 0.29) can be produced by calcination of CaCO₃ in a Lindberg furnace with N₂ sweep. However, for all CaO produced, there was good correlation between resulting specific surface areas and porosities, regardless of calcination conditions. It was not possible to selectively increase the specific surface area or porosity of CaO.

Ca(OH)₂ sorbents having high specific surface areas (up to 79 m²/g) and porosities (up to 0.48) can be produced by the double hydration method. For the four sources of Ca(OH)₂ investigated, there was good correlation between Ca(OH)₂ specific surface area and porosity, regardless of the source. Ca(OH)₂ sorbents of low and intermediate surface areas consists mostly of pores below 200 Å. Dramatic increase in the volume of pores larger than 200 Å could be seen for sorbents produced with the highest specific surface area. It was not possible to selectively increase specific surface area or porosity of Ca(OH)₂. Additionally, the structure of Ca(OH)₂ was dictated by the structure of a parent CaO. High specific surface area/porosity CaO was needed to produce high specific surface area/porosity Ca(OH)₂.

A correlation could be found between structural properties of Ca(OH)₂ and the product of its calcination in the flow reactor operated at conditions simulating economizer injection (550°C and 1 s residence time). For fixed conditions of calcination in the flow reactor, calcination of higher specific surface area/porosity Ca(OH)₂ resulted in higher specific surface area/porosity CaO. Relative changes in specific surface area/pore volume between Ca(OH)₂ and CaO were a function of the initial Ca(OH)₂ specific surface area/pore volume. Following fixed calcination conditions, high specific surface area Ca(OH)₂ lost pore volume, whereas low specific surface area Ca(OH)₂ gained pore volume. Similar pore size distributions were measured for CaO produced from calcination of Ca(OH)₂ with similar specific surface area, regardless of the source of Ca(OH)₂.

Based on the observed specific surface area and pore volume response to conditions representative of economizer region, Ca(OH)₂ sorbents with high specific surface areas (56 to 69 m²/g) appear to be desirable for economizer injection application. The above structurally based prediction has not been verified by measurement of the sorbents' reactivity with SO₂.

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