Characterization of Lignosulfonate-Modified Hydrated Lime Powders

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Lignosulfonate-modified hydrated lime powders are known to have increased reactivity when utilized for SO_2 removal in flue gas. This enhancement is attributed to a lower degree of agglomeration and smaller primary crystal sizes of the modified hydrates (Jozewicz and Kirchgessner, 1989; Kirchgessner and Lorrain, 1987). SEM micrographs show that the lignosulfonate alters the nucleation and growth process of hydrates in water and reduces the tendency to form agglomerates. BET nitrogen adsorption measurements and room-temperature carbonation reaction experiments correlate the effect of lignosulfonate on the final surface area.

Hydrated lime powders are used in sulfation and carbonation solid/gas reactions, formed by hydration of CaO powders. Hydration involves a change from the cubic structure of CaO to the hexagonal close-packed structure of $Ca(OH)_2$. Since hydration of lime is a strong exothermic, reversible reaction, an excess of moisture over the theoretical amount is essential to achieve complete hydration.

Studies have shown that calcium hydrates precipitated in the presence of lignosulfonate salts have 15-20% more reactivity to sulfation compared to the unmodified hydrates (Jozewicz and Kirchgessner, 1989; Kirchgessner and Lorrain, 1987). Results show an optimum powder reactivity at approximately 1.5 wt. % calcium lignosulfonate. The increased reactivity is thought to be due to a decrease in the primary particle size combined with a decrease in the tendency to agglomerate.

Lignosulfonate salts are ionic-dispersing agents, having ionic groups distributed over the entire surfactant molecule and hydrophobic groups containing polarizable structures such as aromatic rings and ether linkages (Rosen, 1987). The dispersing action of lignosulfonate can be due to a number of factors. The molecules adsorbed to the solid surface may cause the formation of electrical barriers to aggregation due to the repulsive force felt between the ionic charges of similar sign on adsorbed molecules. The ionic groups also permit extension of the molecule into the aqueous phase thus creating a steric barrier to coalescence.

This study uses electron optics to characterize the hydrated lime powders which are formed in the presence of lignosulfonate salts. Discussion will concentrate on the crystal morphology and agglomeration tendency of the powders. Experimental results are interpreted in terms of crystal nucleation and growth plus steric effects between crystals. Additionally, the results are shown to support one of the mechanisms previously proposed (Jozewicz and Kirchgessner, 1989; Kirchgessner and Lorrain, 1987).

Experimental Studies

Calcium hydrates are made in the laboratory using 2 g of reagent-grade (high purity) CaO and 20 mL of distilled water per sample. This volume of water gives 30 times the stoichiometric amount needed for complete hydration. In making the hydrates, the CaO powder is placed in a beaker and the distilled water in the temperature range 70-80°C is added. The beaker is placed on a hot plate to boil off the excess water. After most of the excess water has evaporated, the beaker is placed in a vacuum over at $T=50°C$ for 24 hours. Finally, the dried cake is lightly ground in a mortar and pestle.

The calcium lignosulfonate (by Pfaltz & Bauer, Inc.) used contains 80% calcium lignosulfonate, 9.2% sugars, and 1% insolubles. For the modified hydrates, the necessary mass of calcium lignosulfonate to equal the final product mass percent is dissolved in the water of hydration prior to adding it to CaO. The weight of calcium lignosulfonate in the final product investigated are 0.0, 0.38, 0.75, 1.13, 1.5, 3.7, and 7.1%. A portion of the powder samples up to 1.5 wt. % are filtered after the drying process with distilled water ($T=70$-$80°C$) and redried.

Differences in the morphology of the dried powders are examined under a scanning electron microscope (SEM). The powders are sprinkled onto double-sided conductive tape and pressed down to ensure good electrical contact. The samples are placed on aluminum stubs and gold-coated. Surface areas of the resulting hydrates are measured using the nitrogen adsorption/desorption BET method.

The reactivities of the hydrates are tested at room temperature using the carbonation reaction. To conduct the experi-

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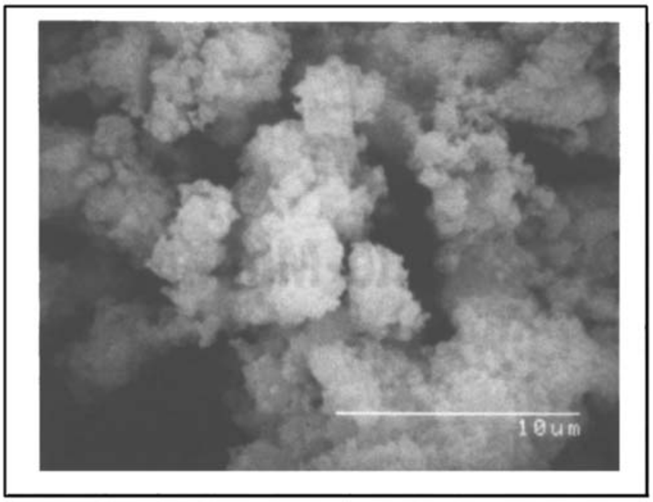

Figure 1. SEM micrograph of pure, as-hydrated $Ca(OH)_2$ sample.

The hydrate is composed of numerous ill-defined solid crystals.

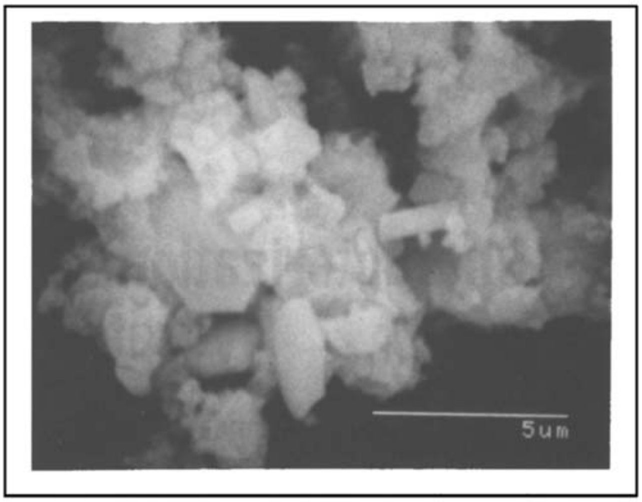

Figure 2. SEM micrograph of 0.38 wt. % lignosulfonate-modified sample.

Large, hexagonal single crystals are clearly observed.

ments, the powdered hydrates are placed in petri dishes and set in an evacuated chamber at room temperature. Carbon dioxide from a gas cylinder is first bubbled through distilled water before entering the chamber. The pressure in the chamber is adjusted to 1 atm. The hydrates are exposed to the CO_2 and moisture for 12 hours. The extent of carbonation of the hydrates is measured using thermogravimetric analysis (TGA) with a Perkin-Elmer TGA 7 instrument.

Results and Discussion

Scanning electron microscopy

CaO powders have a NaCl crystal structure and are cubic in shape under the SEM. Originally, the average CaO particle size of the powder used in these experiments is about 7×7 μm. After hydration, micrographs of the pure $Ca(OH)_2$ product (Figure 1) indicate a much finer crystal size compared to its precursor and a loss of particle distinctness due to agglomeration of the fine crystals. For a given amount of mass, a high nucleation rate will result in a large number of small crystals while a low nucleation rate will generate fewer crystals but larger in size. By comparing the sizes between pure CaO and $Ca(OH)_2$, it is reasonable to conclude that the hydration reaction must have involved a large degree of nucleation and low growth of the $Ca(OH)_2$ crystals.

Figure 2 shows the formation of hexagonal $Ca(OH)_2$ plate-like single crystals in the 0.38 wt. % lignosulfonate-modified hydrate. These single hexagonal crystals are observed in all modified hydrate samples. In addition to the "normal nucleation and growth" process as in the pure $Ca(OH)_2$ sample, the lignosulfonate-modified samples seem to have a second mechanism which generates the hexagonal single crystals. It is well known that the presence of additives in a precipitating solution will alter the crystal morphology or the habit of crystal growth (Tadros and Meyes, 1964; Sarig, 1974). As reported by Smith and Alexander (1970), adsorbed impurities can lower the transport from solution to the solid by: (1) reducing the area of exposed crystal; (2) generating electric fields which repel ionic species; or (3) affecting the growth steps on the solid crystal surfaces. In addition, polymeric molecules have relatively long chains which can adsorb on a solid surface at more than one site, increasing adsorption stability.

Observed SEM results for lignosulfonate-modified hydrates can be explained as follows. In the early stages of hydration, the water content is high, the degree of supersaturation is low, and therefore the nucleation rate is low. Moreover, the presence of lignosulfonate molecules in the solution may interfere with the nucleation process. Relatively large plate-like hexagonal single crystals seen under the SEM in all modified samples indicate not only preferential crystal growth in the a-axes directions of the developing single crystals but also both a retarded growth in the c-axes directions and an overall low nucleation rate. The plate-like structure of the hexagonal single crystals indicates that the basal planes of the developing crystallites may have been "poisoned." In other words, the lignosulfonate molecules preferentially adsorb on the basal planes of the developing single crystals, thereby retarding growth in the c-axes directions. As water evaporates, the degree of supersaturation increases significantly and forms the tiny $Ca(OH)_2$ crystallites. The final product is therefore a mixture of large well-defined plate-like hexagonal single crystals and many small crystals.

SEM observations also indicate an increase in the number of hexagonal single crystals with an increase in wt. % lignosulfonate. This effect is probably the result of a larger amount of lignosulfonate available for developing crystallites at higher lignosulfonate weight percentages.

Figure 3 shows a low magnification micrograph of the pure $Ca(OH)_2$ powder as an example of the severe agglomeration noted in this powder. When modified by lignosulfonate, agglomeration is still observed at all percentages but to a lesser extent. Figure 4 shows a typical agglomerate of a modified hydrate. Note that the agglomerate size is smaller than the pure hydrate and the pressing action of sample preparation broke the agglomerate apart. This breakage indicates that the modified hydrates are less cohesive.

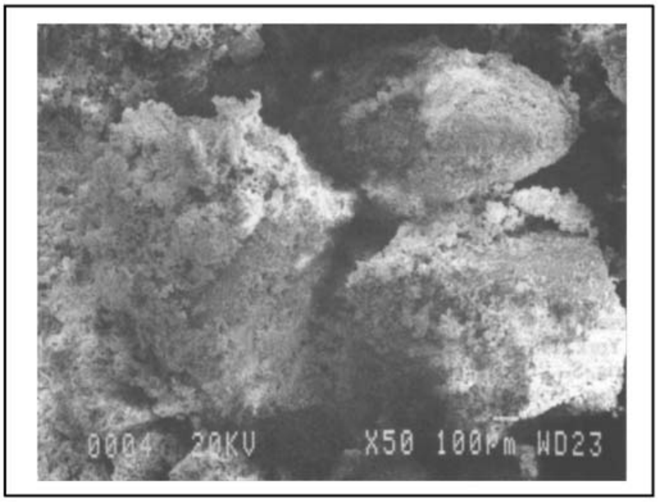

Figure 3. SEM micrograph of pure hydrate.

The ill-defined, tiny crystals appear to form large agglomerates after drying.

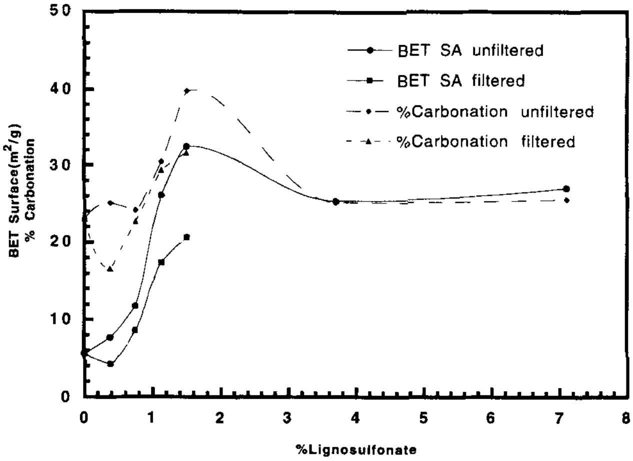

Figure 5. BET surface area and % carbonation as a function of wt. % lignosulfonate for filtered and unfiltered hydrates.

When the lignosulfonate-modified hydrate samples are washed with boiling distilled water and redried, large, cohesive agglomerates are observed as in the pure hydrate sample. This behavior indicates that the adsorption is reversible at these conditions and the presence of lignosulfonate reduces agglomeration in the dried solid as well as changes the crystallization process in solution.

BET analysis and carbonation experiments

Surface area analyses and carbonation experiments are plotted in Figure 5 as a function of wt. % lignosulfonate. The surface area steadily increases with increasing wt. % lignosulfonate for unfiltered hydrates up to 1.5%. The surface area decreases for wt. % lignosulfonate greater than 1.5%. There appears to be a critical concentration below which the surface area increases with % lignosulfonate. The increase in surface area is thought to be due to the presence of lignosulfonate molecules in the solution. The large molecules sterically hinder the close approach of other crystallites in the solution that would otherwise agglomerate as seen in the pure hydrate sample. Another contributing factor is the electrostatic repulsion between lignosulfonate molecules adsorbed on the separate crystals acting to prevent agglomeration. The decrease in surface area at the higher lignosulfonate concentrations is probably due to the combination of lower nucleation rate caused by the increasing interference of the lignosulfonate molecules and the formation of a greater number of hexagonal single crystals.

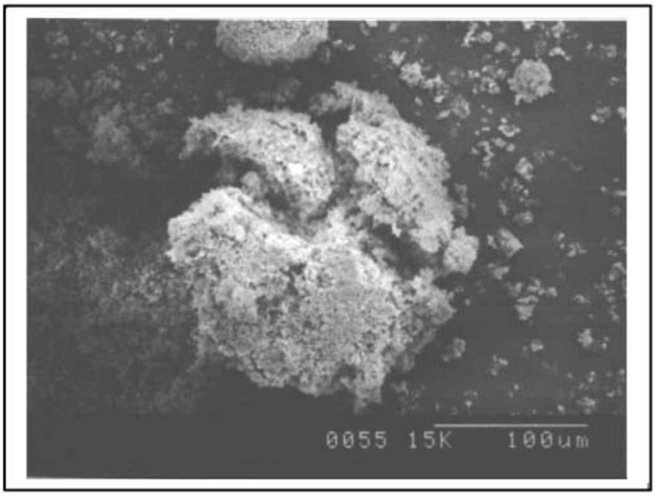

Figure 4. SEM micrograph of 1.5 wt. % lignosulfonate-modified hydrate sample.

This breakage of agglomerates is not observed in the pure, unmodified hydrate sample.

The filtered modified hydrates show a decrease in surface area from unfiltered samples. This observation supports the proposal that the samples reagglomerate to some extent after filtering and redrying. Interestingly, the 0.38 wt. % sample shows an even smaller surface area than the pure (0%) hydrate after filtering. This result indicates even more severe agglomeration occurred in this sample than the pure sample.

As shown in Figure 5, for the unfiltered hydrates, the % carbonation shows little change until 1.13 wt. % lignosulfonate in the final product. At this percentage, the % carbonation shows a large increase indicating a much greater reactivity with 1.13 and 1.5 wt. %. At 3.7 and 7.1 wt. %, the reactivity returns to a value similar to lower percentages. The filtered hydrates have a lower reactivity than the unfiltered with a similar trend. The surface area and % carbonation show some degree of correlation though there appears to be other factor(s) influencing the reactivity.

Concluding Remarks

Calcium lignosulfonate modifies the crystallization process of $Ca(OH)_2$ during its formation from CaO in water. Lignosulfonate molecules appear to adsorb on the basal planes of the hydrate crystals and hinder growth in the c-axes directions. In addition, the lignosulfonate molecules seem to retard the nucleation process, resulting in significant growth of some crystals. BET surface area of $Ca(OH)_2$ increases with wt. % lignosulfonate up to 1.5 and then decreases. A possible explanation is the competing factors of dispersive action, interference with nucleation, and alteration of the growth habit to produce a large number of low surface area hexagonal crystals in the final product. At low concentrations, the dispersive action dominates but a critical concentration exists where other factors become significant.

In the solid hydrates, the lignosulfonate reduces the size of agglomerates and the binding energy between the particles. The filtration process shows that the adsorption is reversible and lignosulfonate molecules influence the interaction (agglomeration) between $Ca(OH)_2$ crystals not only in liquid but in solid as well. The present results support the hypothesis (Jozewicz and Kirchgessner, 1989; Kirchgessner and Lorrain, 1987) that lignosulfonate is capable of reducing the size of agglomerates. However, their speculation that lignosulfonate addition reduces the primary crystal size still needs to be proven by further experimentation.

Acknowledgment

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