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**HANDLING, TRANSPORT AND DISPERSION OF SORBENT POWDER
FOR IN-FURNACE INJECTION**

Third year final report

by

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FEB 22 1994

DEPARTMENT OF DEVELOPMENT
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September 1993

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This project was funded in part by Ohio Coal Development Office,
Department of Development, State of Ohio.

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EXECUTIVE SUMMARY

The purpose of this study is to explain, using fundamental theories of interparticle forces, the difference in transport and dispersion between various sorbents. This project is closely tied with 1.1 through the focus of maximum utilization of sorbent materials used in the LIMB process. Interparticle forces lead to agglomeration or removal to transport tube walls of the sorbent fine particles, reducing sulfur removal capabilities.

In the first and second years, the pneumatic transport of sorbent powders was investigated for four typical sorbent materials, calcium carbonate, dolomite, dolomitic hydrate and hydrated lime. Results indicate that hydrated lime has the best dispersion and flowability. Studies in the third year involved investigating improving the performance of hydrated lime with additives. Studies have revealed an improvement in sulfur capture when calcium lignosulfonate is added to the water of hydration when reacting lime with water to form a hydrate.

The effect of the additive calcium lignosulfonate, added to the water of hydration, on the resulting hydrate's properties is investigated in the third year. The addition of calcium lignosulfonate to the water of hydration appears to improve both the dispersibility and reactivity of the resulting product hydrate. Increased reactivity is closely tied to available surface area for reaction, as expected. However, in applications where powder flowability becomes important, such as in the use of hydrate in flue-gas desulfurization, a balance between the flowability and surface area must be considered. If the powder has poor flowability, the added surface area may not be utilized. Powder dispersion and the high-temperature are used to determine the dispersibility of the modified and unmodified sorbents at room temperature and at typical furnace temperatures. Results verify that an increase in dispersibility is realized with the lignosulfonate-modified hydrate. Phase 1 results show this increased dispersibility to be due to electrostatic repulsion between lignosulfonate molecules on the surface of the dry powder.

The effect of high temperature on the unmodified sorbent is to increase the agglomeration of the powder due to the increase in van der Waals forces. This increase is due to the morphological change in the hydrate due to the calcination process.

I. INTRODUCTION

A. Background and Scope

The focus of this project is on sorbent injection technologies using dry, calcium-based sorbents for high-sulfur coal flue gas desulfurization. The goal is to provide research findings on handling, transport and dispersion of sorbent powder, aimed at improving SO₂ (to at least 90%) removal and increasing sorbent utilization in a cost-effective fashion. With this goal, the purpose of this project is to investigate the fundamental aspects of powder technology relevant to the fine sorbent powders, and to provide means of improving sorbent performance through superior dispersion and reduced dispersed particle size. Particular attention will be paid to the case of in-furnace injection.

It is well known through reaction studies that the sorbent reactivity and structural properties play an important role in sulfur removal and sorbent utilization, and that small particle size is favorable. However, in the furnace dispersed particle size may be different from the primary particle size due to agglomeration or attrition. Another key to improving the technology is to minimize the dispersed particle size and to effectively disperse the particles in the reactive environment. The forces acting on the agglomerate (hydrodynamic, impact) must be great enough to overcome the force holding the particles together. The effect of sorbent powder properties in achieving these conditions remains relatively unexplored in spite of its significance.

Typical particle sizes for furnace injection are less than 50 μm , and for such small particles, interparticle forces are significant. These forces depend on the material of the solid, and for both carbonated and hydroxide sorbents these forces are particularly strong. Under the action of these forces, primary sorbent particles tend to agglomerate or become "sticky". Studies on the fundamentals of particle-particle interaction, as they apply to desulfurization processes, are virtually non-existent. Relevant conceptual considerations are discussed below.

Agglomerate formation between primary particles may be due to the influence of several forces (Pietsch, 1984): (1) Short range forces such as van der Waals, electrostatic,

or magnetic forces: Decrease in particle size increases the magnitude of these forces. These forces are significant in the sorbent conveying systems. (2) Capillary pressure and interfacial forces: These forces may be due to the formation of a liquid bridge between individual particles or due to the effect of an adsorbed layer of gas or organic material on the particle surface. These forces play a role for the case of injection with humidification and when the sorbent contains moisture, for example, hydrated lime. (3) Solid bridges: These are formed due to coalescence between primary particles at elevated temperatures, and therefore, are very important for sorbents injected into the furnace. This project is to study the particle-particle interactions of sorbent powders under the effect of these forces. In addition, the effect of entrance geometry and sorbent powder nozzle type on the dispersibility of the particles are studied.

Agglomeration can affect the overall sulfur capture efficiency in several ways:

(1) The powders have poor flowability. The powder tends to accumulate on the walls of the transport system, which can impede the flow, and if high velocities are used, the sorbent flow rate becomes unsteady (Solt and McElroy, 1988).

(2) Dispersion of the injected sorbents is affected. The agglomerates behave like larger particles with lower density. When sorbents are present as both primary particles and agglomerates, a much wider size distribution results. This can cause nonuniform distribution of the sorbents over the cross section of the furnace. An additional effect is that a number of sorbent particles may attach to the fly ash produced from combustion. Thus, sorbent particles will be concentrated in the region surrounding the as particle, resulting in poor dispersion.

(3) Reactivity of the injected sorbent decreases due to the addition of a diffusional resistance term - the reactant has to diffuse through the agglomerate structure to reach the reactive pore surface within the primary particles (Gullet and Blom, 1987). For the same primary particle size, they showed that the reactivity decreases with agglomerate size. Laboratory kinetic studies cannot be directly applied to process conditions since the results are reported based on the primary particle size.

(4) For sorbents injected into the high-temperature environment, effects of sintering can become more pronounced. Sintering is the process which causes the solid grains or particles

in contact to coalesce. In the case of agglomerates, the solid material flows to the points of contact between primary particles, forming a solid bridge. This may effectively close the pores mouths at the regions of the primary particles surface where coalescence takes place. This phenomenon is magnified for typical sorbent particles used because of their non-spherical shape. If the local radius of curvature is large (i.e., flat), as in the case of sorbent particles, contact between primary particles is promoted, enhancing the effect of sintering. Since high solid concentration promotes agglomeration, their formation is inevitable during storage and handling. It is important that the agglomerates are broken up at least after injection into the furnace.

This project focuses on the techniques for improving sorbent injection. Injection systems should not only disperse the sorbent rapidly and uniformly, but also break up agglomerates. High shear from the carrier gas is an effective method, but care should be taken to ensure that the feed rate does not become unsteady. Type of injector used, its location in the furnace, and the flow conditions at the entrance can all affect sorbent dispersion.

In the past studies in literature, it is believed that the role of additives is to increase the intrinsic sorbent reactivity. But, an important aspect that has received very little attention is the effect of additives on dispersion of sorbent powder. In a binary mixture of particles, particles with smaller primary size act as "spacers" (Visser, 1989): they tend to adhere to the larger particles, thus preventing contact between them. Therefore, for additives which are known to increase the intrinsic reactivity of the sorbent, proper selection of their particle size prior to mixing with the sorbent powder can also improve the dispersion characteristics.

Thus, the project aims to study an important, yet unexplored, area of research for improving sorbent performance; the project goal can be achieved through guidelines for improved particle dispersion and smaller particle size for reaction.

B. Long Term Objectives

Specific long-term objectives of this research project is to deliver results of the following:

(1) pneumatic transport of sorbent powders and its effects on sorbent dispersion and agglomerate size,

(2) effect of entrance effects (e.g., nozzle size and geometry, flow conditions) on sorbent dispersion and agglomerate size,

(3) characterization of agglomerate size and strength under the influence of various interparticle forces,

(4) effects of furnace conditions (e.g., high temperature, presence of fly ash) on powder behavior,

(5) role of additives and sorbent preparation on powder properties in the furnace,

(6) a comprehensive set of guidelines based on this study for achieving the project goal.

This project will interact closely with Project 1.1, where fundamental kinetic and structural evolution studies are performed.

II. FUNDAMENTAL POWDER CHARACTERIZATION

A. Introduction

Studies on the effect of particle size on the reactivity of calcium hydroxide sorbents reveals a relationship between the measured particle diameter and conversion. The reactivity is found to increase inversely with particle diameter to the 0.22-0.32 power in the sulfation reaction at high temperature (Gullet, 1987). This increase in reactivity is thought to be mainly due to the increase in surface area per volume for the smaller particles and the lower resistance to diffusion of SO_2 through the pores. The formation of agglomerates decreases the reactivity though the size of the constituent particles influences the effect. Smaller constituent particles is found to decrease the intra-agglomerate diffusion of SO_2 .

Calcium hydroxide powders are formed when limestone is calcined to CaO and subsequently hydrated. The reaction involves a change from the cubic structure of CaO to the hexagonal close packed structure of Ca(OH)_2 (See Figure 1). Accompanying hydration is a strong exothermic, reversible reaction (Boynton, 1980):

An excess of moisture over the theoretical amount is essential to achieve complete hydration since some water will be lost through evaporation due to the heat of hydration. Also, to some extent, there is free water that is not chemically combined but that envelopes the hydrate particle as a film of adsorbed water. The purity of the lime and the method of hydration will effect the physical properties of the resulting hydrate. High chemical purity and smaller particle size abets rapid hydration as do higher temperatures. Excess water retards the rate of hydration and improves the dispersion of the hydrate particles, contributing to finer particle size. Insufficient water causes an irreversible agglomeration of fine hydrate particles with lower chemical reactivity.

Studies have shown that surfactant-modified hydrates have 15-20% more reactivity to sulfation compared to the unmodified hydrates (Jozewicz and Kirchgessner,

Figure 1 : Unit cell of calcium hydroxide.

1989; Kirchgessner and Lorrain, 1987). Modified hydrates are produced by dissolving sufficient calcium lignosulfonate, an anionic surfactant, in the water of hydration to yield up to 4.0% on a mass basis of lignosulfonate in the product hydrate. Reactivity of the hydrates to SO_2 is determined in a flow reactor at nominal temperature of 1000°C and a sorbent residence time of 1 second. Results show an optimum sorbent reactivity at approximately 1.0% lignosulfonate. The increased reactivity is thought to be due in part to both a decrease in the primary crystal size combined with a decrease in the particle (agglomerate) size. The result of smaller crystallites is to decrease the primary particle size and increase the surface area. A decrease in agglomerate size indicates greater dry dispersibility with the modified sorbents.

The dispersing properties of a surfactant enable it to adsorb onto a solid particle and to produce by this adsorption energy barriers of sufficient height to disperse the particle. The properties of the surfactant, medium and the solid particle determine the best combination for maximum dispersion. Ionic dispersing agents having ionic groups distributed over the entire surfactant molecule and hydrophobic groups containing polarizable structures such as aromatic rings or ether linkages are best for dispersing polar solids such as calcium hydroxide in an aqueous medium (Rosen, 1987). Lignosulfonate salts are surfactants that fulfill these requirements.

Lignosulfonate is a waste product from the pulp and paper industry. In the Kraft pulping process, wood chips are cooked at elevated temperatures and pressures, using a mixture of sodium hydroxide and sodium sulfide. In this process, phenolic hydroxyl groups and carboxyl groups are inserted into the lignin structure, which is made up of phenylpropane units. Sulfonate groups are introduced into the alpha positions of the phenylpropane units (Sjöström, 1981). The resulting ionic molecule contains many sulfonate groups (See Figure 2).

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 surfactant molecule into the aqueous phase thus creating a steric barrier to coalescence. Whether the

Figure 2: A Sodium Lignosulfonate Molecule.

adsorption takes place on the crystal faces or edges seems to depend on the prevailing pH conditions (Theng, 1979). Under acidic conditions, studies with clays have shown that adsorption occurs at cations exposed at crystal edges. In alkaline media, adsorption of lignosulfonate occurs predominately at the external basal surfaces of the crystals by hydrogen bonding with between hydroxyl groups on the polymer and water molecules in the primary hydration shell of the exchangeable cation.

From electrophoretic mobility measurements of adsorption of lignosulfonate onto $\text{Ca}(\text{OH})_2$ solid showed that adsorption occurred strongly at the solid calcium hydroxide/water interface through mutual electrostatic attraction and by specific adsorption (Nyman, Rose and Ralston, 1986). Qualitative electrophoretic measurements indicate that even in an acid medium the electrostatic surface forces are predominantly repulsive (Beeckman, 1962). The effect of a decrease in pH should, therefore, favor the adsorption process by increasing the number of available unionized sulfonic acid groups in the polyelectrolyte capable of hydrogen bonding with oxygen atoms in the surface of the solid, by reducing the mutual repulsion between polyelectrolyte segments and by making the zeta potential of the adsorbent more positive.

Beeckmans (Beeckman, 1962) conducted adsorption isotherm experiments of lignosulfonates/kaolin and lignosulfonate/titanium dioxide systems. Adsorption was found to be rapid, irreversible and independent of temperature in the range 25°C to 35°C. Isotherms were linear when plotted according to the Langmuir or modified Langmuir equation. The mechanism of adsorption was considered to be basically similar to that of the adsorption of a non-ionic polymer but modified by the presence of electrostatic forces between the polyion and the solid surface, and by the intra- and inter-molecular forces between the charges on the polyions. An estimate of the quantity of lignosulfonate adsorbed at surface saturation was made based on the assumption of spherical, impenetrable spheres of molecules of radius R and molecular weight M of total projected area per unit area of surface of θ from:

$$\frac{\Gamma_m}{A} = \frac{M\theta}{4R^2N_o} \quad (2)$$

N_0 being Avogadro's number and A the specific surface area of the adsorbent. If the value of R^2 is taken as the root mean square distance of the polymer segments from the center of gravity of the molecule, $\bar{S}^2$, the ratio of M to $\bar{S}^2$ was found to be a constant value of $21.9 \times 10^{16} \text{ g cm}^2 \text{ mole}^{-1}$ for lignosulfonates in the molecular weight range 4,000-19,000 when checked by means of intrinsic viscosity-number-average molecular weight data. Substitution of this value and $\pi/4$ for θ in Eqn. (2) leads to a constant value 7.15×10^{-8} for Γ_w/A .

The entrance geometry for sorbent injection affects the dispersibility of the sorbent powder as well as the agglomerate size in the reactor. The proper design of a powder injector is dependant on an understanding of the interactions of powders with the turbulent flow structure. In the LIMB process, sorbent powders are stored in a feed silo before being injected into furnace. Powder interparticle cohesion forces lead to the formation of agglomerates. The problem in dispersing powders in a gas stream lies in the re-dispersion of these agglomerates. The mechanisms of powder de-agglomeration in a gas stream are uncertain. Thomas (1964) investigated the turbulent disruption of floc in a liquid suspension and indicated that the pressure difference on opposite sides of the floc is the main mechanism leading to floc rupture under turbulent conditions. Assuming that an aggregate is spherical, Bagster and Tomi (1974) analyzed the stresses within a spherical particle in simple flow fields, specifically the stress arising from a simple uniform flow and an induced shear field. They found that the maximum stresses in a simple shear flow field are $\sigma_{y1max} = 5\mu\gamma$ for tension and $\tau_{y1max} = 8.5\mu\gamma$ for shear. However their analysis is based on a viscous liquid. A gas-fine particle mixture is usually dispersed by forcing the mixture through a nozzle or wound tube. Yamamoto et al. (1977) measured the agglomerate size change in an air stream through a small pipe by using a cascade impactor. Masuda et al. (1977) investigated the de-agglomeration of metallic silicon and calcium carbonate in a mixer type disperser, a fluidized bed and a capillary pipe. Their results showed that in such a flow, agglomerates are disrupted mainly by acceleration or deceleration of powders. Kousaka et al. (1979) explored the disruption mechanisms of aerosol agglomerates by analyzing the disruption forces. They claimed

that impaction of powder on obstacles and acceleration or deceleration of the powder are effective ways for powder dispersion in an air stream. It appears that the key to powder dispersion, from the hydrodynamics point of view, is to organize the flow structure so that a strong turbulent eddy can be created.

In these experiments, the effect of mass % calcium lignosulfonate in the final product on the structure and surface area of laboratory-made crystallized Ca(OH)_2 from solution is investigated. Also, the reactivity of the resulting hydrates to carbonation is tested. Bulk properties of the hydrates as a function of lignosulfonate are tested using four commercial hydrates obtained from Dravo Lime Company. Experiments of powder dispersion are conducted with Black River hydrate (BRH) and 1.3% calcium lignosulfonate Black River hydrate obtained from the Dravo Lime Company using the powder dispersion system developed in the second year. The expansion nozzle with two booster air jets is used in these experiments. The primary air velocity is varied from 5 to 18 m/s, and the booster air velocity is varied from 20 to 70 m/s. The solids feeding rate is maintained at a constant (fixed screw revolution). The air humidity is monitored by a humidity probe. All the images of the powder dispersion are recorded on video tapes. The shutter speed used is 20,000 1/sec, and the magnification is varied from 50 to 100X. The same procedure and operating conditions are repeated with the 1.3% Lignosulfonated Black River Hydrate also obtained from Dravo Lime Company. The results are compared to study the effect of additives on the powder dispersion.

B. Experimental

B.1 Powder Characterization

Hydrates are made in the laboratory using reagent-grade (high purity) CaO and distilled water. In making the hydrates, a pre-measured amount of CaO powder is placed in a beaker and excess distilled water in the range 70-80°C is added in one batch. The resulting mixture is found to bubble violently due to the exothermic reaction and is placed on a hot plate to boil off the excess water. After most of the excess water is boiled off, the cake is then dried in a vacuum oven at 50°C for 24 hours. The dried cake is then ground in a mortar and pestle.

The calcium lignosulfonate used in these studies is made by Pfaltz & Bauer, Inc. and 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 the CaO. Mass percentages investigated are 0.0%, 0.38%, 0.75%, 1.13%, 1.5%, 3.7% and 7.1%.

Differences in the morphology of the dried powders are determined using a scanning electron microscope. A chemical surface analysis of the dried powders (ESCA) is also performed. Surface areas of the resulting hydrates are measured using nitrogen adsorption/desorption BET method.

The reactivity of the resulting hydrates is tested at room temperature using the carbonation reaction. Carbonation is chosen as the reaction due to the ease and safety of the experiments. It is suspected that sulfation will yield similar results. To conduct the experiments, the powdered hydrates are placed in petri dishes and set in an evacuated chamber at room temperature. Carbon dioxide from a gas cylinder is bubbled through water before entering the chamber. The pressure in the chamber is adjusted to equal atmospheric. The hydrates are exposed to the CO₂ 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.

B.2 Powder dispersion system

In the LIMB process, sorbent powders are stored in a feed silo before being injected into the furnace. Powder interparticle cohesion forces lead to the formation of agglomerates. The problem in dispersing powders in a gas stream lies in the re-dispersion of these agglomerates.

For the examination of entrance geometric effects on powder dispersion, a fine powder dispersion system was designed and constructed last year. The schematic diagram of the system is shown in Fig. 3. The system consists of a powder feeder, transport column, a powder separation sub-system and a powder re-circulation device. In the system, an interchangeable entrance is used for the study of entrance geometric effects on the powder dispersion. A cylindrical column, 6" in diameter, equipped with

Figure 3.
Schematic Diagram of Powder Dispersion System

viewing windows is used for the bottom section. The entrance, 2" in diameter and about 12" long, is connected to the bottom section of the column. The sorbent powders are fed into the system by a powder feeder through the entrance. The viewing window at the entrance is made of PYREX glass. Dispersion of the powders is observed throughout the flow field inside the entrance. The powder entrained by the stream is separated from the gas by a two-stage filter and then collected in the powder hopper. To prevent powder from accumulating, coaxial horizontal tubes are used in the powder feed line. Powder fed into the tip of the feeder discharge tube will be directly carried away by air, and a uniform feed rate is obtained. Air from the central air system is used as the carrier and booster air. Both air flow rates are measured by a rotameter and relative humidity and temperature obtained from a humidity probe (Vaisala, Model HNI 32). An AccuRate Model 602 dry material volumetric feeder with standard construction and 1/2 inch helix is used. This feeder uses the massaging action of double external paddles on the flexible hopper walls to provide accurate feeding of cohesive powders. The powder feeding rates are obtained from the calibration curve of powder feeder rate against the revolution of the screw for a given powder which is obtained by collecting powders for timed intervals. To minimize electrostatic charging generated during handling, the sorbent powders are stored in the powder feeder at least 24 hours before the experiments are run to allow for discharging to ground.

In the visualization measurements, the flow field is illuminated by a laser sheet. A 4 Watt Argon Ion laser is used to generate the laser sheet with a thickness of about 2 mm. The tube wall curvature will cause some distortion of the laser sheet but this problem is minimized by reducing the tube wall thickness. Also, due to the small size of the sorbent powders investigated, the distortion of the particle image can be neglected. The continuous laser sheet is used in combination with a CCD (Charge Coupled Device) camera which controls the exposure time by an adjustable shutter. The laser sheet, parallel to the direction of the main flow, can be shifted to focus on various planes along the radial direction and the pictures of powder motion at various planes are recorded.

Powder visualization software is developed to identify particles on the images, determine solids concentration, calculate agglomerate sizes and locate centroids.

Additionally, statistical flow information such as concentrations and sizes at specified locations is obtained. Note that the time interval between two consecutive frames is 1/30th of a second and each frame consists of two (even and odd) fields with a time interval of 1/60th of a second. The powder dispersion image processing technique utilizes the field of sequentially recorded frames, instead of one frame, as a processing unit. An image enhancement and filtering technique is used to remove the background and electronic noise in an effort to improve image quality. Details of this technique can be found in last year's report.

The experimental results obtained last year showed that the expansion nozzle with two booster air jets type entrance provides good powder dispersion. This system is used to study additive effects on the powder dispersion this year. The experiments are conducted under the same operating conditions for both of the modified and unmodified sorbents. As an example, figure 4 gives a filtered image and the processed results from this image. To find out the additive effects, results obtained for both limestone powder and modified powder are compared under the same operating conditions (i.e., loading and gas velocity).

We have been communicating extensively with Professor Kadambi, the PI for Project 3.1, regarding the general applicability of the laser measurement technique. We have benefitted considerably from this interaction. The PIV (Particle Image Velocimetry) system developed in this project is intended for the in-situ measurement of particle (or powder) dispersibility including particle size and size distribution, concentration and velocity. The technique, however, is limited by the frame-grabber speed and VCR speed to flow conditions with particle velocities less than 2 m/s. In Professor Kadambi's experiments, considerably higher particle velocities (> 10 m/s) are encountered. For our system, it will require a new frame-grabber and VCR system to be developed to accommodate such high velocities. The costs will be very high and it will require considerable length of time for such development. We have thus recommended to Professor Kadambi to continue adoption of LDV system which is currently in use in his research for high flow velocity measurements.

(a) Field view of the magnified powder image

(b) Concentration and size distributions of the agglomerates

Solid concentration=1.4 %, Average agglomerate size= 33 μm
 Jetting velocity=4.2 m/s, Booster air velocity=12.5 m/s, Solid/gas mass flow=10,
 Limestone diameter=5-100 μm , Air relative humidity=14%

Fig. 4. Concentration and size distributions of the agglomerates
 in a nozzle with a two booster air jet.

C. Results and Discussion

C.1 Powder Characterization

Scanning Electron Microscopy.

Scanning electron micrographs of the laboratory-made non-filtered hydrates are shown in Figures 5-10. Comparing the micrographs between the pure hydrate and the modified hydrate, a change in the crystal morphology is noted. The hydrates formed in the presence of lignosulfonate (Figures 6-10) show the formation of hexagonal single crystals. The pure hydrate shown in Figure 5, however, looks to be made up almost entirely of tiny spherical crystals fused together into agglomerates. The hexagonal-shaped particles, on the other hand, appear as single crystals, that is, not agglomerated to other particles. Also noted is an increase in the size and quantity of the hexagonal single crystals with an increase in the % lignosulfonate in the final product.

This change in morphology indicates that the basal planes of the developing crystallites have been "poisoned." In other words, the lignosulfonate molecules have preferentially adsorbed to the basal planes, thereby preventing further growth in this crystal direction. The increase in number of the hexagonal single crystals with increase in % lignosulfonate is the result of more surfactant available to adsorb to the developing crystallites.

The laboratory-made filtered hydrates show more agglomeration than the unfiltered samples (See Figure 11). At high magnification (See Figure 12) these agglomerates show the presence of the hexagonal crystals as thin sheets but no longer as dispersed particles. There seems to be more attraction between the particles.

ESCA Analysis.

ESCA is used to provide information on the elemental and chemical distribution of the near surface region, the region where a surfactant material will exist in the greatest concentration since it has the property of adsorbing onto the surfaces of the system. The spectrum is displayed as a plot of electron binding energy versus the number of electrons in a fixed, small energy interval. The results from the ESCA analyses on the three laboratory-made hydrate powders and the pure lignosulfonate

Figure 5 : SEM micrograph of pure laboratory-made Ca(OH)_2 .

Figure 6 : SEM micrograph of laboratory-made 0.38 %
lignohydrate.

Figure 7 : SEM micrograph of laboratory-made 0.75% lignohydrate.

Figure 8 : SEM micrograph of laboratory-made 1.13 % lignohydrate.

Figure 9 : SEM micrograph of laboratory-made 1.5% lignohydrate.

Figure 10: SEM micrograph of laboratory-made 3.7 % lignohydrate.

Figure 11: SEM micrograph of filtered 1.5% lignohydrate, low magnification.

Figure 12: SEM micrograph of filtered 1.5% lignohydrate, high magnification.

powder are shown in Figure 13(a)-(d). Each powder disc was ion sputtered for 5 minutes prior to analysis to remove impurities.

Figure 13(a) shows the ESCA surface spectrum of pure lignosulfonate. The spectrum shows a strong oxygen peak at 531 EV. This oxygen exists in both the lignin hydrophobic portion of the molecule and the sulfonate anionic portion of the molecule. The sulfur peak occurs at 165 EV corresponding to the sulfur in the sulfonate surfactant tail. However, the magnitude of this peak is small corresponding to the relatively low mass of sulfur in the lignosulfonate molecule. The carbon peak occurs at 287 EV, lower in magnitude to only the oxygen peak, on the lignosulfonate spectrum and is due to the lignin portion of the molecule. Figure 13(b) shows the spectrum of pure laboratory-made $\text{Ca}(\text{OH})_2$. In this spectrum, a strong oxygen peak is again observed and expected. The three calcium peaks are also present at 353, 440 and 29 EV. Only a very small carbon peak is detectable, probably due to a slight surface contamination. With the 4% addition of lignosulfonate, the relative magnitude of this carbon peak increases. With 10%, this carbon peak is quite pronounced probably due to the greater concentration of surfactant at the hydrate crystal surfaces. These results seem to indicate that the lignosulfonate adsorbs to the surfaces of the $\text{Ca}(\text{OH})_2$ crystals during hydration. However, the relative concentrations are slight compared with the hydrate. The sulfur peak is not present in the hydrate spectra even at the higher lignosulfonate concentration. The relatively low amount in the sample is probably responsible for the lack of detection.

The infrared spectra of the four samples are shown in Figure 14(a)-(d) and are plotted as % Transmittance versus Wavenumber (cm^{-1}). The IR adsorption spectra are recorded in the region 400 to 4000 cm^{-1} . The samples are prepared using the KBr disc technique by pressing disc-shaped pellets. The pure lignosulfonate spectrum in Fig. 14(a) shows two large, diffuse regions of adsorption. These bands correspond to the complex lignin molecule. The OH stretching and bending vibrations occur at about 3400 and 1200 to 1000 cm^{-1} , respectively. The stretching OCH_3 vibration occurs at about 2900, 2840 and bending at about 1420 to 1260 cm^{-1} . The weak shoulder at about 1715 cm^{-1} represents the $\text{C}=\text{O}$ stretching vibration.

The infrared spectrum of the pure $\text{Ca}(\text{OH})_2$ in Fig. 14(b) is much simpler showing

(a) Calcium Lignosulfonate

(b) Calcium Hydroxide

(c) 4% LignoHydrate

(d) 10% LignoHydrate

Figure 13:
ESCA Results of Laboratory-Made Hydrates and Calcium Lignosulfonate

(a) Pure Lignosulfonate

(b) Pure Calcium Hydroxide

(c) 4% LignoHydrate

(d) 10% LignoHydrate

Figure 14. IR spectra of pure lignosulfonate and hydrates.

a sharp hydroxyl stretching vibration at about 3650 cm^{-1} . The broad peak at 1500 cm^{-1} and sharp peak at around 880 cm^{-1} correspond to the presence of carbonate in the samples. The addition of lignosulfonate results in changes to the IR spectrum of the pure hydrate. The most significant changes occur in the low frequency range. The OH bending vibration shows a significant broadening with addition of lignosulfonate. For the 10% lignosulfonated hydrate, the spectrum shows other bond vibrations not present in the pure spectrum. These vibrations are thought to correspond to the lignosulfonate molecules adsorbed to the surface.

BET Analysis.

Results of the surface area analyses are listed in Table 1. The BET results are shown graphically in Figure 15 for the filtered and unfiltered hydrates up to 1.5% lignosulfonate. The surface area steadily increases with an increase in % lignosulfonate for both the filtered and unfiltered hydrates up to 1.5%. For the lignohydrates of higher than 1.5% lignosulfonate, the surface area of the unfiltered hydrates then decreases. There appears to be a critical percentage of lignosulfonate that leads to an increase in surface area. The increase in surface area is thought to be due to the lignosulfonate molecules adsorbing to the surfaces of the forming $\text{Ca}(\text{OH})_2$ crystals. The large molecule sterically hinders the close approach of other crystallites in the solution that would otherwise agglomerate and eventually sinter as seen in the pure hydrate. Another factor that may be occurring is the electrostatic repulsion between lignosulfonate molecules adsorbed on separate crystals acting to prevent agglomeration.

ESCA has verified the presence of the lignosulfonate on the dry product. The factors responsible for keeping the particles apart in the aqueous environment appear to be acting in the dry state as well. This is indicated by comparing the filtered and unfiltered hydrates. Not only do the surface areas decrease with filtration, the SEM show increased agglomeration for the filtered hydrates.

Carbonation Experiments.

The results of the carbonation experiments are shown in Table 1. For the

Table 1: BET and Reactivity Results for Laboratory Hydrates.

% Lignosulfonate	Surface Area (m ² /g)	% carbonation
0	5.60	23.0
0.38, unfiltered	7.70	25.1
0.38, filtered	4.27	16.6
0.75, unfiltered	11.81	24.2
0.75, filtered	8.60	22.7
1.13, unfiltered	26.17	30.5
1.13, filtered	17.42	29.4
1.5, unfiltered	32.46	39.8
1.5, filtered	20.63	31.6
3.7, unfiltered	25.47	25.3
7.1, unfiltered	27.09	25.6

Figure 15: Surface Area versus Mass % Lignosulfonate added to final product hydrate.

unfiltered hydrates, the % carbonation shows little change until 1.13% 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%. At percentages of 3.7 and 7.1%, the reactivity returns to a value similar to the lower percentages.

The filtered hydrates showed lower reactivity than the unfiltered with a similar trend. This effect appears to follow, at least to some extent, the changes in surface area. It is expected that a loss in surface area will lead to lower reactivity.

Figure 16 shows both the changes in surface area and conversion with the % lignosulfonate in the product hydrate. This graph indicates the direct relationship between these two factors.

C.2 Powder Dispersion

The Sedigraph distributions of the two sorbents are shown in Fig. 17 for comparison. The Sedigraph distributions correspond to the primary particle size distributions, or the most dispersed size distributions experimentally possible, of the two sorbents. The Sedigraph analyses show a slight decrease in primary particle size with the addition of the lignosulfonate. The BRH has a median diameter of about 5 μm and m-BRH a median diameter of about 4.5 μm .

Figures 18 and 19 show typical results obtained from the instantaneous images for BRH and 1.3% lignosulfonated BRH at various operating conditions. Due to the turbulent nature of the flow, a wide distribution of agglomerate sizes is observed. The dispersion results are represented by a histogram of the agglomerate size. The size histogram is plotted as Counts, or number of agglomerates, versus their size.

Figure 18(a) shows the histogram of BRH obtained at the primary air velocity of 5.6 m/s and booster air velocity of 34.7 m/s. In this instantaneous image, the most frequent agglomerate size is 11 μm and the largest size is 82 μm . The experimental results for m-BRH obtained under the same operating conditions are shown in Fig. 18(b). The most frequent agglomerate size is 8 μm and the largest size is 60 μm . Figure 19 shows the results at a greater primary air velocity. The agglomerate size distributions become narrower and finer at the higher gas velocity indicating greater dispersion.

Figure 16: % Conversion and Surface Area versus Mass % Lignosulfonate for the unfiltered hydrates.

Figure 17 : Sedigraph results for Black River and 1.3% Lignosulfonated Black River Hydrates.

Average Diameter : 33.14 microns
 Total Particle Area : 0.00031 cm²
 Total Window Area : 0.07 cm²
 Percent Area Occupied : 0.4493 %
 Number of Particles : 35

SIZE HISTOGRAM

Primary air velocity=5.58 m/s, booster air velocity=34.8 m/s

(a) Black River hydrate

Figure 18. The histogram of the agglomerate size obtained from the instantaneous image.

Average Diameter = 27.41 microns
 Total Particle Area = 0.00051 cm²
 Total Window Area = 0.10 cm²
 Percent Area Occupied = 0.51016 %

Number of Particles = 86

Primary air velocity=5.58 m/s, booster air velocity=34.8 m/s

(b) 1.3% Lignosulfonated Black River hydrate

Figure 18. The histogram of the agglomerate size obtained from the instantaneous image.

Primary air velocity=10.9 m/s, booster air velocity=34.8 m/s

(a) Black River hydrate

Figure 19. The histogram of the agglomerate size obtained from the instantaneous image.

Primary air velocity=10.9 m/s, booster air velocity=34.8 m/s

(b) 1.3% Lignosulfonated Black River hydrate

Figure 19. The histogram of the agglomerate size obtained from the instantaneous image.

The instantaneous powder dispersion results are essential to the understanding of powder dispersion, since these results are directly associated with flow structure inside the nozzle. These results, however, are difficult to be used for comparison due to the turbulent fluctuations. To examine the additive effects, the instantaneous results were averaged over about 20 images at a fixed condition. These 20 images were sampled randomly on the video tape. Figure 20 gives the comparisons of the powder dispersion quality between the BRH and 1.3% Lignosulfonated BRH at various operating conditions. Comparing these two types of sorbent, it appears that the dispersion of the 1.3% BRH is better than that of BRH.

We believe that an even greater relative dispersion would be found for the m-BRH at higher total gas velocities. In our dispersion system, due to the low velocities used, the agglomerate size is smaller than the energy dissipating (Kolmogorov) eddies, and, therefore, the powder dispersion quality is dominated by viscous forces. Under this circumstance, shear stresses exerted on the agglomerates are dominant factors in dispersion. De-agglomeration occurs when the hydrodynamic forces exceeds the cohesive forces. Based on the theory of the simple shear flow, this criterion can be translated as

$$\frac{5}{2} \pi R \mu \gamma \sin^2 \psi_0 \geq H N_b \quad (3)$$

Obviously, for very fine sorbent powders, high air velocities are required. Due to the limitations of our visualization system, the gas velocities can not be very high. However, even under these limited conditions, an improvement in dispersion is realized with the lignosulfonate-modified hydrate. It appears that an even greater relative increase in dispersion will occur with the modified sorbent at the higher gas velocities used in industrial situations.

Figure 20. The effects of total air flow rate on powder dispersion

III. POWDER MECHANICAL PROPERTIES

In this phase, completion of solids testing equipment assembling and refurbishing has been accomplished. The Hosokawa powder tester, which is the last piece of equipment received from Shell Development Company, has been tested and proved to give reliable and repeatable results for powder flow properties such as angle of repose, angle of fall, dispersibility, and other fundamental flow properties.

Preliminary flowability analyses were conducted on two calcium-based sorbents in two different sets of testing. The sorbents examined were the Pennsylvania Delta Carbonate and the Dravo Black River hydrate. In the first set of tests, the Ajax cohesion tester was used to measure the cohesion of each powder and to study how the cohesive strength of the powder changes with its bulk density. The procedure of testing was detailed in the last quarterly report. Figure 21 shows the results of this set of tests. As expected the cohesive strength of each powder increases in a linear fashion with the increase of bulk density. Scattering of the data points about the fitted lines in Fig. 21 may be due to instrument sensitivity to minor differences in sample preparation. It was found also from this set of tests that the carbonate is more cohesive than the hydrate and, consequently, more likely to plug the flow especially if the sorbent is transported in a dense phase.

The second set of tests was conducted on the Jenike compressibility tester to determine how the bulk densities of the two sorbents, Black River hydrate and Delta carbonate, change when the powders are subjected to static compacting loads. Results of these tests determine the compressibility of each sorbent. Compressibility is an important flow property and is defined as,

$$\% \text{ Compressibility} = \frac{100 (P - A')}{P}$$

where P is the packed bulk density, and A' is the aerated bulk density. Typical range of

Figure 21:
Results of AJAX Cohesion tests

compressibility for powders is 5 to 45%. The higher the compressibility of a powder, the lower its flowability will be.

The testing procedure can be described as follows. A sample container, 2.5" inner diameter and 0.75" depth, is filled carefully with the powder without packing. The powder is leveled with the top of the container by scrapping of any excess powder with a spatula. The sample then is weighed to determine the "loose" bulk density of the powder by subtracting the weight of the empty container from the weight of the sample and dividing by the volume of the container. A stainless steel cover, 2.5" in diameter, is placed on top of the sample. A combination weight hanger is placed on the cover together with a dial indicator mounted on a stainless steel holder which has a counter-bored bottom that fits over the container. The indicator is calibrated such that it reads the exact height of the powder inside the container. The first indicator reading is recorded when it has stabilized and it corresponds to a vertical load of 1.5 pounds (weight of powder + weight of cover + spring resistance of the gage). Different levels of vertical loads are then applied to the sample by placing weights on the weight hanger. These load levels are: 3.5, 11.5, 21.5, 41.5, 61.5, 81.5, and 91.5 pounds, respectively. For each load level, the indicator reading is recorded and the corresponding new bulk density is calculated. Results of this set of tests are shown in Fig. 22 as bulk density versus compacting load. Both of the two tested sorbents have high compressibility (46% for the Delta Carbonate and 54% for the Black River Hydrate) and accordingly flow problems are expected during transportation. It should be noted that the procedure followed in this set of tests is not the standard method to measure the compressibility of a powder, yet the results were consistent and repeatable. The standard procedure of measuring compressibility of powders can be followed by using the Hosokawa powder tester which will be used, as reported in the fourth year plan, to measure compressibility as well as other flow properties.

Fig. 22 Compressibility Tests for Pennsylvania Delta Calcium Carbonate & Dravo Black River Hydrate

IV. HIGH-TEMPERATURE EFFECTS

A. Introduction

The objective of this phase is to study the effect of high temperature on agglomeration/dispersion characteristics of the sorbent powder. Specific tasks are operation of the high-temperature reactor system with injection and sampling of sorbent powders with the cascade impactor to determine particle size distribution changes with high temperature.

One effect of temperature on the van der Waals forces is the changes in Hamaker constant with temperature. This change is reflected in the effect of temperature on the refractive indices, used in the Hamaker constant calculation. The following relation describes the effect of temperature on the index of refraction:

$$\frac{dn}{dT} = -0.0004 \quad (4)$$

Solving Eq. (4) gives:

$$n_T = n_{T_0} - 0.0004 (T - T_0) \quad (5)$$

Using Eq. (5), an increase in temperature from 25°C to 850°C results in a decrease of refractive index of approximately 22%. This will result in a significant decrease in the Hamaker constant and, correspondingly, the van der Waals forces.

The Hamaker constant is a material property and any morphological changes at high temperature will result in a change in the Hamaker constant. Since the calcium-based sorbents calcine above 480 °C, the structure changes from hexagonal closed-packed to a cubic structure. The Hamaker constant at room temperature for the hydrated lime used in these experiments is 6.39 whereas the value for lime at room temperature is

12×10^{-20} J. Though these values will be lower due to the temperature effect, the difference in values will not change. The effect of calcining is to increase the van der Waals forces between the powder particles significantly.

In this phase the high-temperature reactor set up from project OCRC/91-1.1 was utilized. The objective of this phase is to study the effect of high temperature on agglomeration/ dispersion characteristics of the sorbent powder. The sorbent materials to be investigated in the third year are the Black River hydrate and the 1.3% calcium lignosulfonate BRH.

B. Experimental

B.1 High-temperature Reactor System

The high-temperature, short contact time reactor system used to accomplish the kinetic study is shown schematically in Figure 23. The reactor set up consists of a furnace, the reactor tubes, a particle feeder with solenoid valve for pulse injection, an injection probe, a collection probe and a particle separation/classification system. Various components of the experimental system are discussed below in detail.

B.2 The Powder Feed System

The sorbents powders used in furnace sorbent injection, due to their small particle size and adhesive nature, belong to Geldart's Group C category. Transportation of this powder to obtain a steady and stable flow is quite a difficult task. Furthermore, for this project, the sorbent powders need to be injected in high enough quantity to be easily detected by the optical techniques employed (detailed below) for their residence time measurement. In the first year of this project, initially, various feeder designs were tried from the literature. While one design could not produce a stable flow of the powders, the other provided powder concentrations too low to be detected by the optical systems. Eventually, a novel feeder design was worked out which performed quite satisfactorily in providing stable flow of powder when operated under pulse injection mode.

The feeder used in the high-temperature reactor system is similar to the one developed during first year of this project. It is a plexiglas column with cylindrical top

Figure 23:
Schematic of experimental apparatus used in Phase 3.

and conical bottom. At the bottom of the conical section, is a 1.2 cm ID tube fitted with a porous disc at its top. At the center of this tube is a capillary tube (1.6 mm OD, 0.5 mm ID) extending about 1 cm into the vessel above and through the porous disc, for creating a jet. Located above the jet tube is an off-take tube extending outside the column and attached to a vibrator. The jet and off-take tubes form an ejector system that can transport particles out of the feeder vessel. The annular flow through the porous disc maintains the powder in the vicinity of the ejector at a "loosened" or locally fluidized state, and the vibrator which provides irregular vibration to the vessel, prevents channeling of fluidizing gas in this region. Part of the incoming gas is vented separately at the top of the feeder.

The sorbent particles are fed as pulses into the reactor by means of a modified solenoid valve. The outlet from this valve is connected to the injection probe at the reactor (see Figure 23). When the solenoid is open, the powder is ejected from the feeder into the valve chamber and swept by the transport gas to the reactor. When the solenoid is closed, the transport gas flushes the valve as well as the transport tube connected to the reactor, preventing powder accumulation. At the same time, accumulation in the off-take tube from the feeder is eliminated by the purge line which causes a reverse flow back into the feeder. Thus, as the solenoid opens and closes, a pulse of sorbent powder is injected into the reactor. The powder is injected as a train of pulses during experiments. Duration of a pulse and frequency of pulsing are controlled by a timer connected to the solenoid.

B.3 The High-Temperature Reactor

The high-temperature reactor consists of two concentric alumina tubes (5.08 cm and 7.62 cm OD respectively) which are housed within a 3-zone, 1500°C, Lindberg vertical furnace. Furnace heating is controlled for each zone separately by a control console. The reactant gas enters from the bottom into the annular region between the two alumina tubes. While travelling upwards through a heated length of 91.4 cm (36 inches), it is heated up to the desired reaction temperature, and at the top makes a 120° turn to enter into the inner tube as two hot jets. Pulses of sorbent particles are

introduced into the reactor by the injection probe, whose tip is located just above the incoming jets. Thus the sorbent stream from the injection probe is impacted by the hot reactant gas jets.

C. Results and Discussion

Figure 24 shows the particle size distribution exiting the feed system that injects sorbent into the furnace compared to the Sedigraph or primary particle size distribution. The size distribution exiting the feeder shows a more bimodal nature than the primary size distribution.

Figure 25 compares the size distributions of BRH from the feeder and exiting the furnace at room temperature. The hydrate shows considerable agglomeration or loss of fine particles as it is transported through the furnace. Agglomeration may occur as particle contact each other in the furnace. The loss of fine particles is probably due to adherence to the walls of the furnace during transport.

Figure 26 compares the size distributions of the BRH exiting the furnace at room temperature and high temperature (825°C). The results indicate even more agglomeration and/or loss of fines at high temperatures. This result may be due to the effect of calcination of the hydrate on the van der Waals forces. As noted, the Hamaker constant for lime is double in magnitude the value for hydrated lime. With higher van der Waals forces, the probability of agglomeration with contact between particles would increase. Also, the van der Waals forces acting between the wall material and particle would increase with increasing particle Hamaker constant. The increase in these forces may explain the observed increase in particle size with transport.

Figure 27 shows the results for the 1.3% Lignosulfonated BRH at low (30°C) and high temperature conditions (839°C). The effect of temperature on the size distribution is not as significant as with the unmodified hydrate. The lignosulfonate molecules adsorbed on the surface of the solid particles, as verified in Phase 1, appear to act to keep the particles from agglomerating at both high and low temperature. The de-agglomerating effect of the lignosulfonate molecules overshadows the increase in van der Waals forces at high temperatures (above the calcination temperature).

Figure 24: Sorbent size distribution of Black River Hydrate from gravity sedimentation (*) and the feeder using the inertial impactor (Δ).

Figure 25: Comparison of Black River Hydrate size distributions from the feeder (Δ) and the furnace ($\square$) at $T=25^{\circ}\text{C}$.

Figure 26: Comparison of Black River Hydrate size distributions from the furnace at 21°C (□) and 825°C (○).

Figure 27: Comparison of 1.3% Lignosulfonated Hydrate size distributions from furnace at $T = 30\text{ }^{\circ}\text{C}$ (Δ) and $T = 839\text{ }^{\circ}\text{C}$ ($\square$).

Figures 28 and 29 compare the low and high temperature distributions for the unmodified and modified Black River hydrates exiting the furnace. From the sedigraph results (See Figure 17), the size distributions between these two commercial hydrates is similar. Therefore, making direct comparisons between size distributions to determine extent of agglomeration is valid.

As seen in Figure 28 for the low temperature results, the unmodified Black River hydrate shows a coarser size distribution. However, the amount of fine particles ($< 2 \mu\text{m}$) is similar for both hydrates. At high temperature (See Figure 29), the unmodified hydrate shows consistently more agglomeration throughout the distribution. The modified hydrate appears to provide the best dispersion for SO_2 contact, especially at the high temperature condition.

Figure 28: Comparison of size distributions for 1.3% Lignosulfonated Black River Hydrate (▲) at 30°C and Black River Hydrate (○) at 25°C.

Figure 29: Comparison of size distributions from the furnace for 1.3% Lignosulfonated Black River Hydrate (□) at 839 °C and Black River Hydrate at 825 °C (○).

V. CONCLUDING REMARKS

The purpose of this study is to explain, using fundamental theories of interparticle forces, the difference in transport and dispersion between various sorbents. This project is closely tied with 1.1 through the focus of maximum utilization of sorbent materials used in the LIMB process. Interparticle forces lead to agglomeration or removal to transport tube walls of the sorbent fine particles, reducing sulfur removal capabilities.

The addition of calcium lignosulfonate to the water of hydration appears to improve both the dispersibility and reactivity of the resulting product hydrate. Increased reactivity is closely tied to available surface area for reaction, as expected. However, in applications where powder flowability becomes important, such as in the use of hydrate in flue-gas desulfurization, a balance between the flowability and surface area must be considered. If the powder has poor flowability, the added surface area may not be utilized. The lignosulfonate appears to increase the surface area at a critical concentration, depending on CaO and surfactant purity. However, above this critical concentration the dispersibility continues to rise which may offset the effect of the decrease in surface area at the higher concentrations.

Powder dispersion and the high-temperature studies verify the increased dispersibility of the lignosulfonate-modified hydrate. The benefit of the modified hydrate toward decreasing agglomeration appears to be the greatest for the high-temperature application. It is also shown to increase dispersion at low temperature applications.

The effect of high temperature on the unmodified sorbent is to increase the agglomeration of the powder due to the increase in van der Waals forces. This increase is due to the morphological change in the hydrate due to the calcination process.

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VII. NOTATION

A	Area of surface
A'	Aerated bulk density of the powder
d_p	Particle diameter
H	Adhesive force
N_0	Avogadro's number
N_c	Number of contact points
M	Molecular weight
P	Packed bulk density of the powder
$\bar{S}^2$	Root mean square distance of the polymer segments from the center of gravity of the molecule
T	Temperature
U_s	Gas velocity

Greek letters

Γ_m	Quantity of lignosulfonate adsorbed at surface saturation
ρ_p	Particle density
γ	Velocity gradient
μ	Viscosity
$\sigma_{r_{1max}}$	Normal stress
$\tau_{r_{1max}}$	Shear stress
λ	Light wavelength
η	Index of refraction

θ Total projected area per unit area of surface

Ψ . Angle between a peripheral from sphere center and the central normal

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