A FEASIBILITY STUDY OF THE CENTRIFUGATION METHOD FOR OBTAINING MINUS 0.5 MICRON SIZE CALCITE PARTICLES

A Thesis

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by

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INTRODUCTION

The purpose of this work is to obtain particles of essentially pure calcite ($CaCO_3$) no greater than 0.5μ in diameter from a suspension of calcite in water. The technique utilized involves centrifugation of the suspension, as opposed to the more unagitated method of simply allowing the suspended particles to drop out of the medium due only to gravitational acceleration. The centrifugation method of particle size separation was chosen to speed up the collection process and to learn the factors involved in this procedure. Calculations are based on an integrated form of Stoke's Law of Settling Velocities which considers centrifugal acceleration in its formulation (Jackson, 1956). Scanning electron micrographs will verify particle size. Ultimately, after calcite particles of the desired size are retrieved, X-ray study and quantitative analysis of particle size are planned.

EXPERIMENTAL PROCEDURE

Initially, pure calcite powder, $CaCO_3$ (Mallinckrodt Primary Standard Analytical Reagent), was mixed with water in a 6% (ie., 30 g $CaCO_3$ in 500 ml H_2O) suspension. After stirring the suspension, the particles appeared to settle quickly. This was the first sign of flocculation.

In an attempt to eliminate flocculation, 5 ml increments of a 10% Calgon solution were added to the suspension. Only a small improvement was seen, even at the point where the suspension medium appeared to be blue in color from the addition of the Calgon.

To verify the presence of 0.5μ size particles, some of the dry calcite was examined under the Cambridge Scanning Electron Microscope. A micrograph revealed that 0.5μ size particles were indeed present (although only a small amount), and that most of the particles were clinging together (see Plates A and B).

The next step was to grind the calcite dry for 20 minutes with an automatic mortar grinder. A trial suspension of 8.8 g calcite in 147 ml water exhibited no flocculation.

Grinding of dry calcite to be used in subsequent suspensions continued. The calcite was ground in approximately 3-5 g increments for 20 minutes. A new 6% (30 g $CaCO_3$ in 500 ml H_2O) was formed. The grinding appeared to decrease flocculation. Thus, the next step of centrifuging the suspension seemed to be in order. At this point, had the particles been permitted to quietly drop out of suspension due only to gravitational acceleration, the problem of flocculation may have been minimal and the yield may have been increased somewhat.

Before the actual centrifugation of the calcite in water, observations of times for the centrifuge to reach certain desired speeds and to come to rest after being turned off were recorded. A photographic timer, accurate to the nearest second was employed. The load in the centrifuge used for these observations was 40 ml of water in each of eight test tubes (55 ml maximum capacity per test tube) for a total of a 320 ml load (see Tables I, II, III).

Excess water was poured off the most recently prepared 6% suspension (after the calcite was thoroughly settled) and was saved. Particle residue was rinsed off the sides of the suspension beaker. This

remaining suspension was stirred and each of the eight metal centrifuge test tubes was filled with 40 ml of the calcite in water. The suspension was spun for 23 minutes, 02 seconds (not including spin-up and spin-down times). The supernatant was poured off of each tube into a beaker. Theoretically, this supernatant held the desired 0.5μ size particles. The calcite remaining in the tubes as a white, gluey substance was rinsed with water and poured into another 600 ml beaker. The supernatant was poured into evaporating dishes and heated in an oven at 112 ^{o}C until evaporation of the water was complete. After heating, the calcite remaining in the bottom of the evaporating dishes was scraped off with a toothbrush and was transferred to a small glass vial (initial dry vial weight was 21.75 g). Water was added to the calcite which remained after the first spinning and the new suspension was stirred and centrifuged again for the same amount of time to assure that the maximum amount of the desired particle size was obtained. The supernatant of this settling was also poured into evaporating dishes and heated at 112 ^{o}C.

Since the yield from the dishes seemed small, an additional small suspension (8.75 g $CaCO_3$ in 146 ml H_2O) was made from the remaining dry ground calcite. This suspension was also centrifuged twice and each time the supernatant was poured into evaporating dishes and heated at 112 ^{o}C. The yield was still negligible. Fifteen additional grams of calcite were then ground for 25 minutes on the automatic grinder. Another 6% (15 g $CaCO_3$ in 250 ml H_2O) suspension was centrifuged and the supernatant heated for evaporation.

The result of the above procedures yielded 0.4823 g of 0.5μ size calcite particles (see Plate C).

DISCUSSION OF RESULTS

Observed times for the centrifuge to reach various desired speeds and to come to rest after the power was shut off were recorded. The following tables list these values at several different practical percentages of full power which the machine is capable of achieving:

TABLE I. Centrifuge initially set at 20

RPM	Spin-Up Time	Spin-Down Time
750	1 min 02 sec	0 min 37 sec
1000	1 min 44 sec	0 min 50 sec
2500	9 min 38 sec	2 min 28 sec
2750	28 min 29 sec	2 min 56 sec

TABLE II. Centrifuge initially set at 30

RPM	Spin-Up Time	Spin-Down Time
750	0 min 06 sec	1 min 10 sec
1000	0 min 18 sec	1 min 18 sec
2500	0 min 35 sec	2 min 16 sec
2750	0 min 37 sec	2 min 19 sec
5000	2 min 08 sec	4 min 06 sec
6000	4 min 45 sec	4 min 57 sec
7000	greater then 15 min	-

TABLE III. Centrifuge gradually set to 40

RPM	Spin-Up Time	Spin-Down Time
7000	1 min 47 sec	5 min 28 sec

Several problems encountered in the experiment prohibited optimum results. First and foremost is the undesirable occurrence of flocculation. This phenomenon results from electrostatic charges on the surface of the particles which facilitates the attraction of many particles to each other, and causes a clump of smaller particles to cling together and drop out of the suspension as a larger aggregate. Therefore the settling of these aggregates is not indicative of individual particle size. As mentioned above, the addition of Calgon did not alleviate this problem.

Grinding of the calcite used in suspension appeared to break up the aggregates since rapid settling did not seem to occur after the grinding. But evidence of flocculation remained since such a small yield of 0.5μ size particles was recovered.

Another reason for such a small yield may be that the lower grinding limit of the automatic mortar grinder was at least no less than the desired 0.5μ size, causing only a small percentage of that size to be initially present.

Another possible reason for the small yield may be caused by errors in the pouring off of the supernatant of the test tubes which were spun in the centrifuge. Some larger particles may have escaped from the bottom into the liquid as the tubes were tilted and the supernatant was poured down the stirring rod. Evidence for this was seen under the scanning electron microscope, since only about half of the calcite on the specimen stub was less than or equal to 0.5μ in diameter (see Plate C).

An additional possible source of such a small yield may have occurred after the evaporation of the water in the oven. The calcite remaining in the evaporating dishes seemed to take on a platey form, probably from the

collection of water vapor from the highly humid air in the laboratory facilities. The calcite was difficult to brush off of the dishes, as it hardened and stuck to the bottom and sides of the evaporating dishes. Therefore the amount recovered may have been slightly increased, although still probably negligible.

CONCLUSIONS

The calcite I used in an attempt to obtain a minus 0.5μ fraction presented difficulties, notably flocculation in a water suspension, which could not be overcome. The use of Calgon as a dispersing agent seemed ineffective. I gained some expertise with the method of centrifugation as a means of collecting particle size fractions.

CALCULATIONS FOR CENTRIFUGE
(Jackson, 1956)

$$t = \frac{63 \times 10^8 \times n \times \log(\frac{R}{S})}{N_m^2 \times D_\lambda^2 \times \Delta s}$$

where

t=time in minutes
n=viscosity in poises
R=radius in cm of rotation of the top of the sediment in the tube (9.62 cm)
S=radius in cm of rotation of the surface of the suspension in the tube (6.72 cm)
N_m=revolutions per minute
D_λ=particle diameter in microns
Δs=difference in specific gravity between solvated particle and suspension liquid

(a) at 20 °C

n=.01005 poises
s=2.71 - .99823 = 1.712

(b) at 25 °C

n=.008937 poises
s=2.71 - .99707 = 1.713

(c) Laboratory temperature = 25 °C

PLATE A
10 kV
1 cm=1 micron

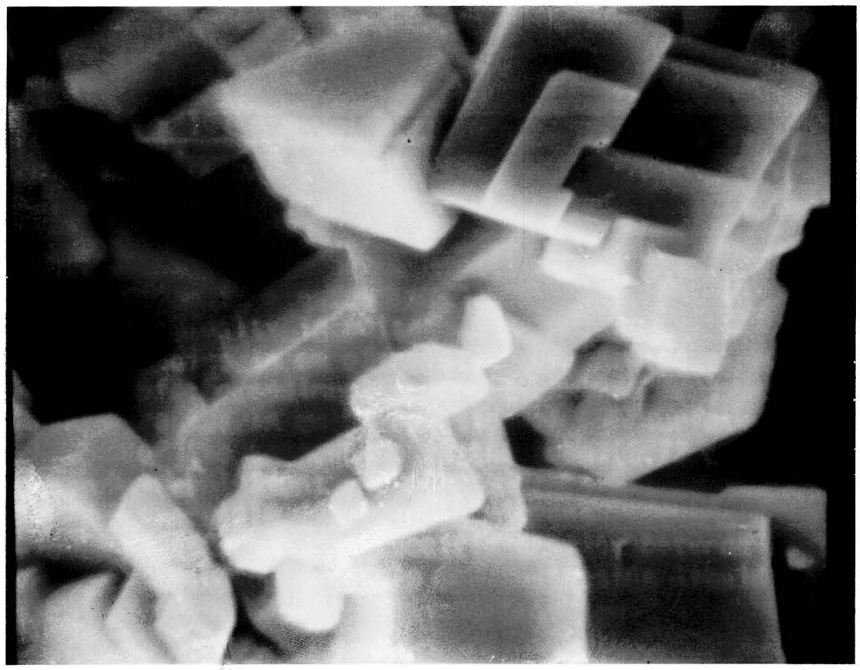


PLATE B
10 kV
1 cm=1 micron

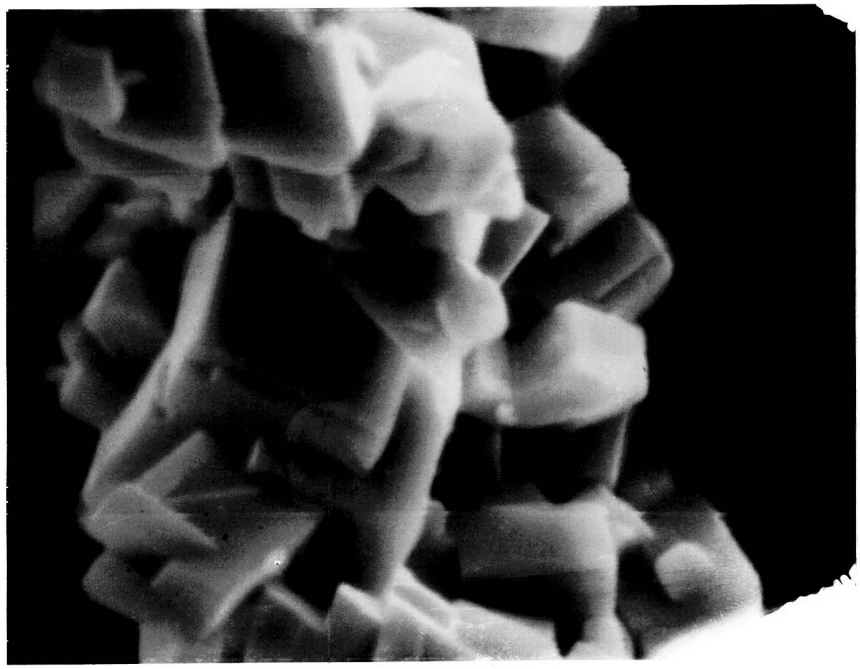
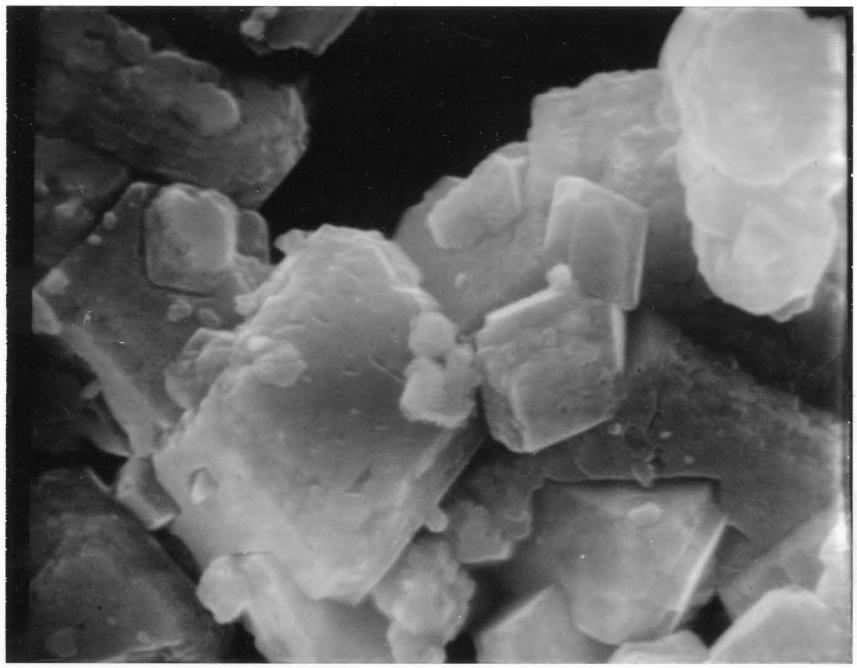


PLATE C
10 kV
1 cm=1 micron



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