# ENVIRONMENTAL GEOLOGY NOTES
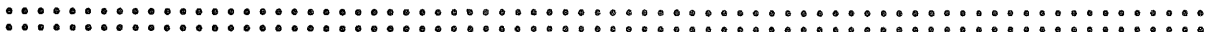
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# LAKE MARLS, CHALKS, AND OTHER CARBONATE ROCKS WITH HIGH DISSOLUTION RATES IN $SO_2$-SCRUBBING LIQUORS

Richard D. Harvey, Robert R. Frost, and Josephus Thomas, Jr.

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## ILLINOIS STATE GEOLOGICAL SURVEY

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# LAKE MARLS, CHALKS, AND OTHER CARBONATE ROCKS

# WITH HIGH DISSOLUTION RATES IN SO$_2$-SCRUBBING LIQUORS*

*Richard D. Harvey, Robert R. Frost, and Josephus Thomas, Jr.*

## ABSTRACT

Petrographic properties of carbonate rocks are useful guides to the utilization of these rocks in SO$_2$-scrubbing systems. High porosity and fineness of grain are thought to be the principal properties that contribute to high dissolution rates of the rocks in the scrubbing liquor. Lake marls and chalks are the major types of carbonate rocks that have these properties. Lake marls are composed mainly of equant grains of calcite (mean grain size usually less than 4 μm) weakly agglomerated into larger, porous particles. They commonly consist of 80 to 90 percent CaCO$_3$ as calcite and aragonite. Impurities are, for the most part, quartz silt and organic matter. The average pore volume for samples of lake marls (1 to 1.2 mm particles) is about 0.50 cc/g, which corresponds to a porosity of about 57 percent. The mean size of pores in these marls is usually between 1 and 2 μm in diameter. Surface areas of lake marls range from 0.8 to 6.8 m$^2$/g. Chalks have grain sizes and shapes similar to those of lake marls, but they generally have smaller amounts of quartz and organic matter and have minor amounts of clay minerals. Their pore volumes vary from one chalk formation to another, and their 1 to 1.2 mm particles average about 0.20 cc/g, which corresponds to a porosity of about 35 percent. The mean size of pores in chalks tested ranges from 0.15 to 0.76 μm in diameter. Surface areas of chalks range from 3.2 to 20.1 m$^2$/g.

In the United States lake marls are restricted largely to sediments of Pleistocene age that occur in the states around the Great Lakes. Chalk and chalky limestones are restricted mainly to the Upper Cretaceous and Tertiary strata in the Kansas-Nebraska-Colorado area and in the southeastern states, from Texas to Florida.

Results of a laboratory test of the relative dissolution rates of samples at pH 6 and 44° C indicate that, in addition to many lake marls and chalks, oolitic aragonite, pelecypod shells, and carbonate waste sludges from certain industrial plants also have high dissolution rates.

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INTRODUCTION

The reduction of $SO_2$ in flue gas emissions from industrial and electric utility plants is a goal shared by all persons concerned about air pollution. Disagreements arise when a decision must be made about how much reduction should be required and what is the most efficient method or process to achieve the desired reduction. This paper concerns the latter aspect of the problem and deals specifically with the question of what is the most efficient type of carbonate rock to use in one type of process, the limestone wet scrubbing process. This type of process has been the subject of a large number of major research projects within the last 6 years. As a result, the limestone (or lime) scrubbing process appears to be one of the more promising of the alternatives available to power plants in the near future.

Tests by Drehmel (1971) showed that a sample of lake marl had a higher $SO_2$ reactivity than the several limestones tested. A few other relatively incoherent and porous samples of chalk and a sample of oolitic aragonite sand were also found to be highly reactive. Since so few samples had been tested, detailed examination and testing of a representative number of these rock types were undertaken to evaluate how widely the previous results could be applied.

In that study (Harvey, Frost, and Thomas, 1973), samples were taken from a large number of deposits (fig. 1): 37 deposits of lake marl in the northeastern quarter of the United States, 30 deposits of chalks and chalky limestones, 3 samples of shells from coastal deposits, and 1 calcitic waste sludge from an industrial plant. Detailed petrographic and chemical studies were made of these samples and their calcines (the quicklimes made from the samples). The stratigraphic classification of all the deposits studied is shown diagrammatically in figure 2. In this figure, the column under each state shows formations from which samples were collected. In the areas where these formations occur, formations of other rock types and ages also are present but are not shown here. The present report summarizes the findings of the earlier study (Harvey, Frost, and Thomas, 1973) and gives new results of $SO_2$ reactivity tests on 10 lake marls and 8 chalks thought to be typical of these types; further, shells, waste sludge, and several common types of Paleozoic limestones were selected for this study (table 1).

Experimental Methods

Pore-Volume and Surface Area Measurements

The pore-volume distribution of the samples was measured by mercury porosimetry. A maximum pressure of 15,000 psi was applied to the mercury, which is sufficient to force it into pores as small as 0.012 μm in diameter. Representative crushed particles, 1 to 1.2 mm in size (16 by 18 mesh), were tested.

Surface area measurements were made by using a thermal conductivity cell to monitor the nitrogen adsorption and desorption curves on samples in a manner described by Thomas and Frost (1971). This procedure was used to determine the surface area from a single adsorption point for the calcined samples, and from multiple adsorption points for the rock samples.
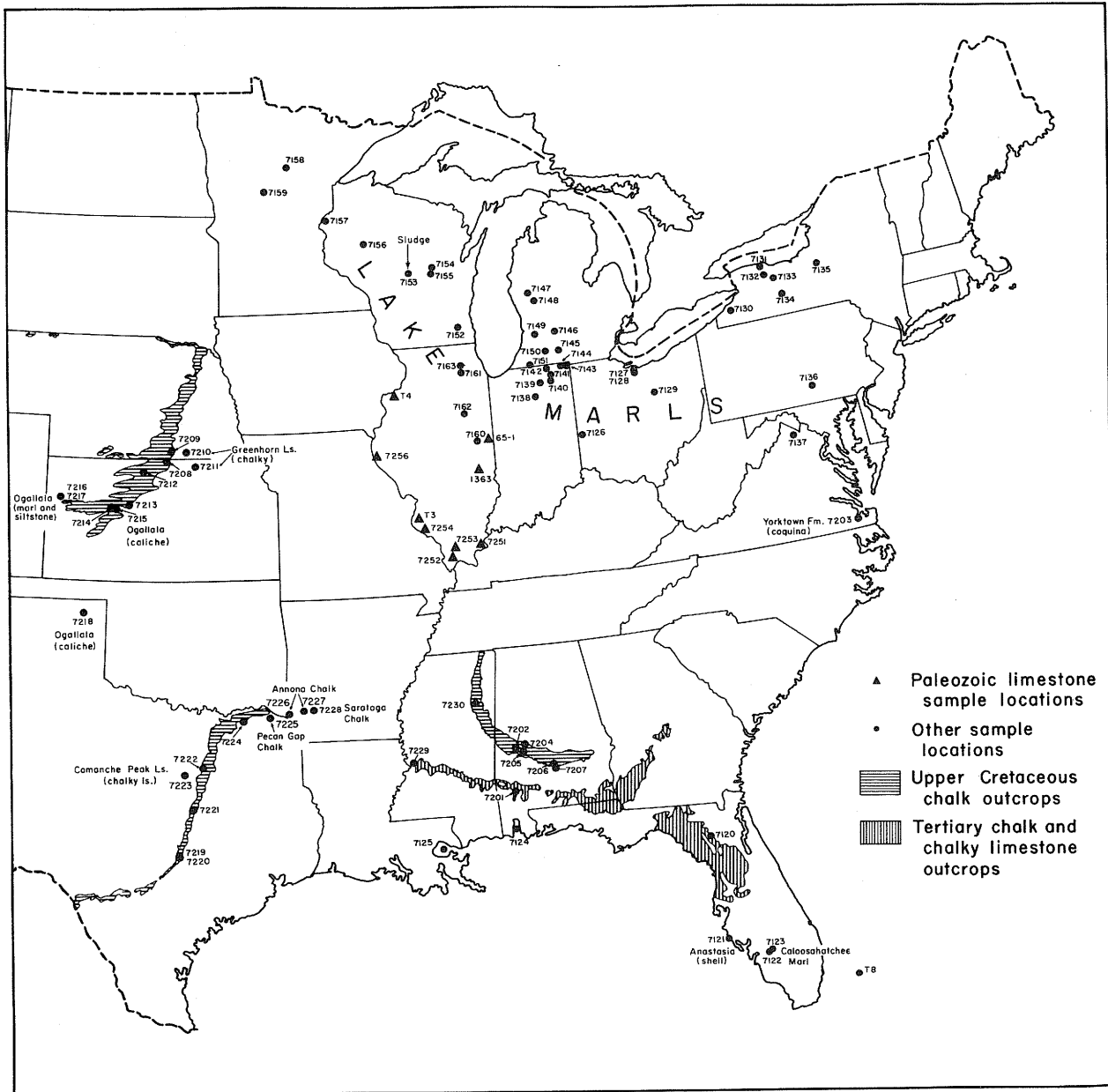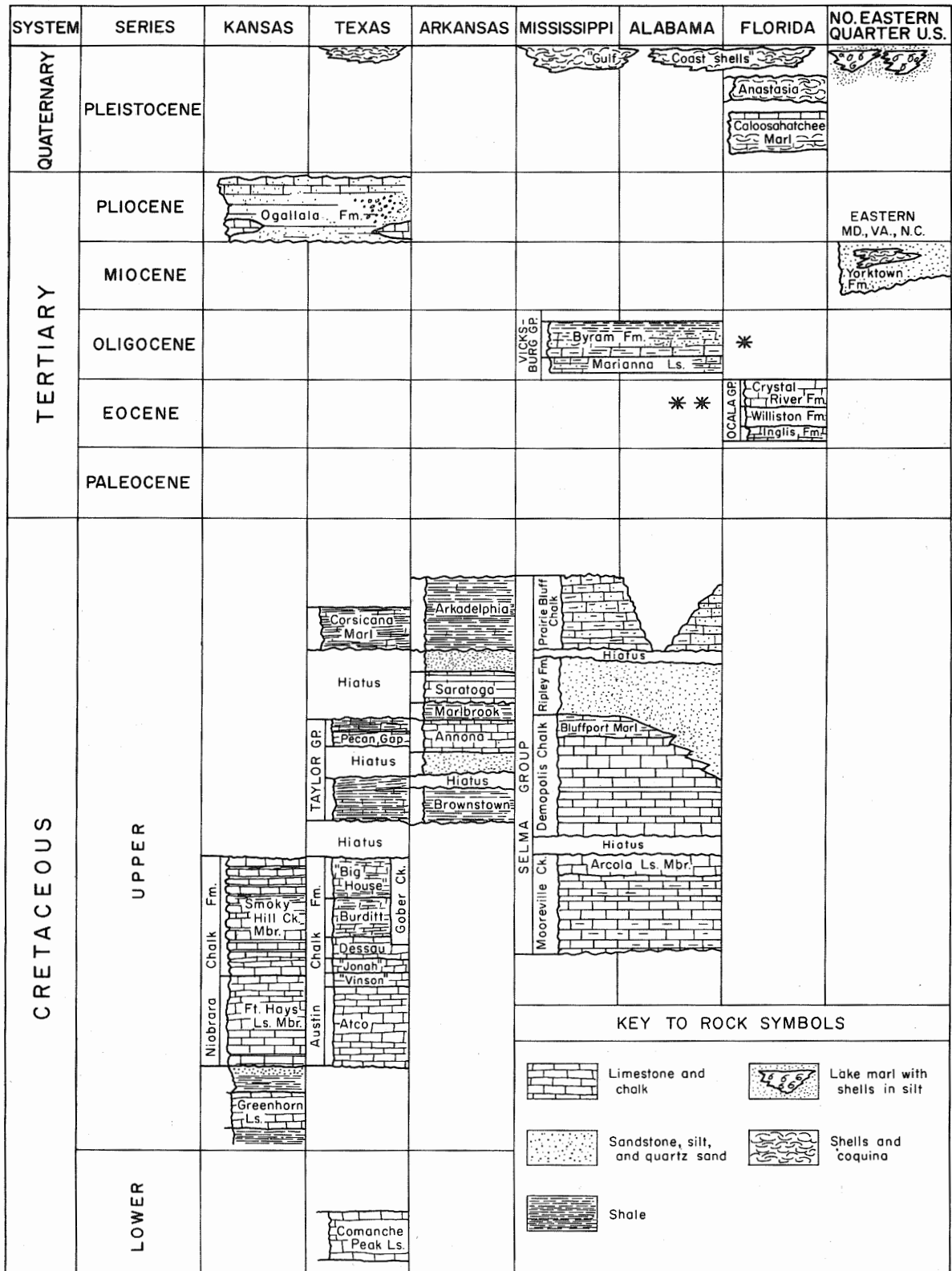
Fig. 1 - Localities of lake marls and other rocks sampled and the outcrop areas of principal chalk and chalky limestone strata. Sources: Alabama - Copeland (1968); Florida - Vernon and Puri (1965); Georgia - Georgia Division of Mines, Mining and Geology (1939); Kansas - Kansas Geological Survey (1964); Mississippi - Bicker (1960); Nebraska - Burchett (1969); Texas - Oetking (1959).

The conditions of calcination, i.e., temperature, time, and partial pressure of $CO_2$, are highly important variables that affect the surface area and pore-volume properties of calcines (quicklimes) of the carbonate materials. Highly reactive calcines were produced by calcining samples, crushed to 1 to 1.2 mm particles, at 850° C under a nitrogen flow rate of 100 cc/min. This provided a very low $CO_2$ partial pressure. The time of calcination was very rapid, less than 14 minutes. The details of these experimental methods and the procedures used are given in Harvey, Frost, and Thomas (1973).

| SYSTEM | SERIES | KANSAS | TEXAS | ARKANSAS | MISSISSIPPI | ALABAMA | FLORIDA | NO. EASTERN QUARTER U.S. |
|---|---|---|---|---|---|---|---|---|
| QUATERNARY | PLEISTOCENE | | | | "Gulf | Coast shells" | Anastasia / Caloosahatchee Marl | |
| TERTIARY | PLIOCENE | Ogallala Fm. | | | | | | EASTERN MD., VA., N.C. |
| | MIOCENE | | | | | | | Yorktown Fm. |
| | OLIGOCENE | | | | VICKS-BURG GP. Byram Fm. / Marianna Ls. | | * | |
| | EOCENE | | | | | ** | OCALA GP. Crystal River Fm. / Williston Fm. / Inglis Fm. | |
| | PALEOCENE | | | | | | | |
| CRETACEOUS | UPPER | Niobrara Chalk Fm. Smoky Hill Ck. Mbr. / Ft. Hays Ls. Mbr. / Greenhorn Ls. | TAYLOR GP. Corsicana Marl / Hiatus / Pecan Gap / Hiatus / Hiatus — Austin Chalk Fm. "Big House" / Burditt / Dessau / "Jonah" / "Vinson" / Atco — Gober Ck. | Arkadelphia / Saratoga / Marlbrook / Annona / Hiatus / Brownstown | SELMA GROUP Prairie Bluff Chalk / Hiatus / Ripley Fm. / Bluffport Marl — Demopolis Chalk / Hiatus / Arcola Ls. Mbr. — Mooreville Ck. | | | |
| | LOWER | | Comanche Peak Ls. | | | | | |

**KEY TO ROCK SYMBOLS**

- Limestone and chalk
- Sandstone, silt, and quartz sand
- Shale
- Lake marl with shells in silt
- Shells and coquina

\* The Marianna Limestone and the overlying Suwannee Limestone, both Oligocene in age, occur in the Florida panhandle and are in many places high-purity, fine-grained, porous, and chalky limestones (Reves, 1961).

\*\* The Ocala Limestone of southeastern Alabama (and southwestern Georgia) is composed of chalky and porous limestones very similar in character to the limestones of the Ocala in Florida.

SO$_2$ Reactivity Index Test Method

The SO$_2$ reactivity test was based on the time required for the pH of a slurry containing the carbonate sample (0.5 g in 200 cc water) at about 44° C (111° F) to decrease from 6.0 to 5.8 while a nitrogen gas stream containing about 5,000 ppm SO$_2$ was bubbled through the slurry at about 500 cc/min. The sample was pulverized to less than 44 μm (< 325 mesh). A schematic diagram of the test apparatus is shown in figure 3.

Fig. 3 - Diagram of SO$_2$ reactivity test appa-
ratus: 1 - digital pH meter; 2 -
constant-temperature bath; 3 - pyrex
350 cc medium-fritted Buchner funnel
cell; 4 - stirring motor; 5 - pyrex
glass delivery tube joined to funnel
with 18/9 ball and socket joints;
6 - pressure gauge; 7 - rotometer
flow meter and needle valve; 8 - gas
cylinder with about 5,000 ppm SO$_2$
with nitrogen balance.
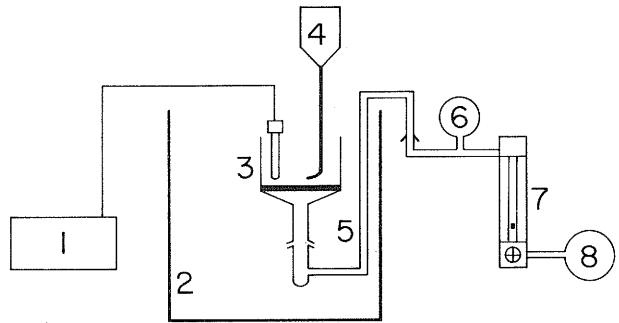
Sample 7208C was used as a reference material to obtain a relative reactivity index scale (time for sample X/time for sample 7208C). This approach for a reactivity test was taken because these test conditions are thought to more closely approximate the conditions in actual scrubbing systems than does the measurement of dissolution rates of particles of a narrower and coarser size range at constant pH. Also, the relative reactivity index scale eliminates the need to know exact values of the controllable variables (gas-flow rate and possibly the stirring rate) affecting the time for the pH change as long as these variables are held reasonably constant. However, even though the controllable variables were apparently held constant, some variables (partial plugging of the glass frits in the cell with use and/or changes in the SO$_2$ concentration supplied from the gas cylinder) could not be precisely controlled. Therefore, sample 7208C was tested repeatedly between tests of the other samples so that the observed reference time could be adjusted if these noncontrollable variables were to change.

The test procedure is as follows. The SO$_2$-nitrogen gas stream is made to flow through the cell just prior to the introduction to the cell of 200 cc of water preheated to about 50° C. The pH of the water is allowed to drop to about 3 before the 0.5 g sample is added. The pH of the slurry increases to about 7 and then slowly decreases as long as more SO$_2$ goes into solution than is neutralized by dissolution of the sample. The time required for the pH to decrease from 6.0 to 5.8 is measured. Several cells were used to obtain the test results, and they were back-flushed with dilute hydrochloric acid, rinsed thoroughly with distilled water, and dried before reuse.

Fig. 2 - Geologic time-rock classification of carbonate rocks studied, excluding Paleozoic
limestones from Illinois. Vertical scale does not represent true thickness of
rocks or duration of time.

TABLE 1 - MINERALOGY,

| Sample | Mineralogy* | | Chemical analyses** | | |
|--------|-------|-------|-------|-----|-------|
| | Minor | Trace | CaCO$_3$ | MgO | Al$_2$O$_3$ |
| **LAKE MARLS** | | | | | |
| 7126A | AR, QZ | none | 88.2 | 1.4 | 1.1 |
| 7132D | none | PY | 92.3 | tr† | 0.3 |
| 7138 | none | QZ, AR | 91.6 | 1.2 | 0.2 |
| 7140 | none | QZ | 90.8 | 1.4 | 0.1 |
| 7150 | QZ | DO, FS | 83.2 | 1.2 | 0.8 |
| 7158 | none | QZ, AR | 80.1 | 3.1 | 0.7 |
| 7162C | none | DO | 85.8 | 1.1 | 0.4 |
| 7163B | AR, QZ | DO | 79.8 | 1.1 | 1.0 |
| 7133 | none | PY | 91.9 | 0.5 | 0.5 |
| 7149A | none | QZ | 93.2 | 1.7 | 0.2 |
| **CHALKS** | | | | | |
| 7201 | CL | PY, MI | 84.5 | 2.0 | 1.8 |
| 7202 | CL | QZ, FS, PY, MI | 70.8 | 0.8 | 5.3 |
| 7208C | none | CL, QZ, PY, FS | 89.9 | 0.2 | 1.9 |
| 7212A | none | CL, QZ, FS | 93.4 | 0.2 | 0.5 |
| 7213 | none | CL, QZ, FS | 92.7 | 0.3 | 1.2 |
| 7221A | CL | QZ, FS | 86.1 | 0.2 | 1.4 |
| 7222B | none | QZ, CL, FS | 85.6 | 0.3 | 1.7 |
| 7227B | CL | QZ, FS, MI, PY | 87.5 | 0.2 | 1.4 |
| **LIMESTONES** | | | | | |
| 7120 | none | none | 99.1 | tr† | 0.0 |
| 7210B | CL | QZ, FS | 89.9 | 0.1 | 1.4 |
| 7252 | none | DO | 97.5 | 0.1 | 0.3 |
| T3 | DO (8) | QZ (?) | 95.3 | 1.9 | 0.0 |
| 7256 | DO (5) | QZ | 96.0 | 0.3 | 0.1 |
| 7251 | none | DO, QZ | 95.5 | 0.1 | 0.1 |
| 7253 | DO (16) | QZ | 89.8 | 4.0 | 0.1 |
| 7254 | DO (4) | QZ | 94.8 | 0.5 | 0.9 |
| 7260A | DP (5) | none | 96.7 | 1.0 | 0.0 |
| T4 | none | QZ | 97.8 | 0.0 | tr† |
| 65-1 | none | CL | 97.6 | 0.0 | 0.1 |
| 1363 | DO (3) | QZ, CL | 94.4 | 0.6 | 1.5 |
| **CALCITE SPAR** | | | | | |
| T2 | none | none | 99.1 | 0.0 | tr† |
| **OOLITIC SAND** | | | | | |
| T8 | none | none | 98.5 | 0.0 | 0.3 |
| **SHELL** | | | | | |
| 7124 | none | CL | 96.4 | 0.1 | 0.0 |
| 7125 | none | QZ, CL | 96.2 | 0.1 | 0.3 |
| 7203D | AR | QZ | 87.6 | 0.2 | 0.0 |
| **WASTE SLUDGE** | | | | | |
| 7153 | none | none | 96.0 | 0.5 | tr† |

* Major mineral component is calcite in all samples except T8 and 7124, which are both mostly aragonite. Minor = 1% to 20%, trace = < 1%. Symbols: AR, aragonite: DO, dolomite; CL, clay minerals; QZ, quartz; FS, feldspar; MI, mica; PY, pyrite. Numbers in parentheses indicate the percentage of the mineral determined by calculation of chemical analyses data.

CHEMISTRY, AND SOURCE OF SAMPLES

| Chemical analyses** | | | Location | | |
|---|---|---|---|---|---|
| $SiO_2$ | $Fe_2O_3$ | $Na_2O$ | (nearest town) | Geologic unit | Sample |
| | | | | | LAKE MARLS |
| 2.5 | 0.8 | 0.051 | New Madison, OH | Pleistocene | 7126A |
| 1.2 | 0.1 | 0.027 | Churchville, NY | Pleistocene | 7132D |
| 0.4 | 0.4 | 0.023 | Athens, IN | Pleistocene | 7138 |
| 0.9 | 0.3 | 0.025 | Kimmell, IN | Pleistocene | 7140 |
| 8.0 | 0.5 | 0.054 | Vicksburg, MI | Pleistocene | 7150 |
| 6.4 | 0.7 | 0.164 | Remer, MN | Pleistocene | 7158 |
| 3.4 | 0.9 | 0.046 | Strawn, IL | Pleistocene | 7162C |
| 6.7 | 1.1 | 0.130 | Batavia, IL | Pleistocene | 7163B |
| 1.6 | 0.2 | 0.041 | Caledonia, NY | Pleistocene | 7133 |
| 0.4 | 0.1 | 0.030 | Monterey, MI | Pleistocene | 7149A |
| | | | | | CHALKS |
| 6.5 | 0.7 | 0.08 | St. Stephens, AL | Marianna Ls. (Tert.) | 7201 |
| 14.2 | 2.0 | 0.14 | Demopolis, AL | Demopolis Ck. (Cret.) | 7202 |
| 4.8 | 1.0 | 0.07 | Superior, NB | Niobrara Ck. (Cret.) | 7208C |
| 3.0 | 0.7 | 0.06 | Cedar, KS | Niobrara Ck. (Cret.) | 7212A |
| 1.9 | 0.4 | 0.05 | Hays, KS | Niobrara Ck. (Cret.) | 7213 |
| 7.6 | 0.9 | 0.06 | Woodway, TX | Austin Ck. (Cret.) | 7221A |
| 6.6 | 1.3 | 0.09 | Midlothian, TX | Austin Ck. (Cret.) | 7222B |
| 5.5 | 0.6 | 0.07 | Okay, AR | Annona Ck. (Cret.) | 7227B |
| | | | | | LIMESTONES |
| 0.0 | 0.4 | 0.01 | Newberry, FL | Crystal River Fm. (Tert.) | 7120 |
| 3.4 | 0.4 | 0.10 | Gilead, NB | Greenhorn Ls. (Cret.) | 7210B |
| tr† | 0.1 | 0.04 | Jonesboro, IL | Ullin Ls. (Miss.) | 7252 |
| 0.0 | 0.2 | 0.015 | Valmeyer, IL | Kimmswick Ls. Subgroup (Ord.) | T3 |
| 1.1 | tr† | 0.02 | Quincy, IL | Burlington Ls. (Miss.) | 7256 |
| 1.0 | 0.2 | 0.02 | Cave-In-Rock, IL | Ste. Genevieve Ls. (Miss.) | 7251 |
| 1.2 | 0.1 | 0.02 | Anna, IL | Ste. Genevieve Ls. (Miss.) | 7253 |
| 1.3 | 0.0 | 0.01 | Prairie du Rocher, IL | Salem Ls. (Miss.) | 7254 |
| 0.0 | 0.1 | ----‡ | Ste. Genevieve, MO | Salem Ls. (Miss.) | 7260A |
| 1.5 | 0.3 | 0.047 | Milan, IL | Wapsipinicon Ls. (Dev.) | T4 |
| 0.0 | 0.8 | 0.03 | Fairmount, IL | Millersville Ls. M. (Pa.) | 65-1 |
| 2.0 | 0.5 | 0.01 | Casey, IL | Millersville Ls. M. (Pa.) | 1363 |
| | | | | | CALCITE SPAR |
| 0.0 | 0.2 | 0.015 | Rosiclare, IL | ———————— | T2 |
| | | | | | OOLITIC SAND |
| 0.2 | 0.0 | 0.53 | Bimini Isl. | Pleistocene | T8 |
| | | | | | SHELL |
| 0.9 | 0.1 | 0.34 | L. Pontchartrain, LA | Pleistocene | 7124 |
| 0.4 | 0.5 | 0.41 | Mobile Bay, AL | Pleistocene | 7125 |
| 7.3 | 1.6 | 0.43 | Chuckatuck, VA | Yorktown Fm. (Tert.) | 7203D |
| | | | | | WASTE SLUDGE |
| 0.0 | 0.2 | 0.85 | Nekoosa, WI | ———————— | 7153 |

** Weight percent, moisture-free basis.
† tr = trace amount.
‡ Not determined.

It is assumed that the higher the rate of dissolution of the carbonate material in our simulated scrubbing liquor, the higher the reactivity that the samples would have in a full-sized wet scrubbing system. At the present time we have no way to verify the correctness of this assumption. However, we think that it is a reasonable assumption and that the relative values obtained here will prove to be useful.

## THEORETICAL REMARKS ON DISSOLUTION RATE

The rate of dissolution of calcite or aragonite crystals into a surrounding aqueous solution depends primarily on the pH of the solution and to a lesser extent on the specific chemical activity of the crystal surfaces. Calcite is slightly less soluble than aragonite. In addition, the activities of calcite and aragonite surfaces vary theoretically according to their crystallographic orientation because both minerals are anisotropic. Calcite has been observed to dissolve much differently depending on the orientation of the crystal surface with respect to the c-axis (Rodgers, 1940). The activity will even vary from one specimen to another of the same mineral species if one has a much higher density of crystalline imperfections (dislocations, lattice vacancies, and interstitial impurities) than the other. These imperfections tend to promote dissolution.

The rate of dissolution is dominantly affected by kinetic factors regarding the effective surface area and the actual concentration of the solute in the layer of solution adjacent to the surface. The effective surface area is not necessarily equal to the surface area as measured by gas adsorption, for some of the internal surface may not be accessible to molecules of the solvent; moreover, the proportion of the surface which is accessible normally changes as the reaction proceeds. The concentration of the solute adjacent to the surface of the dissolving solid is partly dependent on the configuration of the pores within the material and on the agitation of the solvent since both affect the movement of the dissolved ions away from the surface of the solid.

The effective surface area of crushed materials is proportional to the size, roughness, and pore characteristics of the particles. The finer the particle size, the greater the effective surface area. The roughness of the particles is in large part due to the size of the grains making up the particles, but is also due to the nature of the fracture surface and the pores. The pores are important, independent of the roughness, in terms of the porosity or pore volume, the size distribution of the pores, and whether the pores are interconnected or isolated (permeability). In general, as the grain size decreases, as the porosity increases, as the size of the pores decreases, and as the permeability increases, the greater is the effective surface area. However, the fracture surface of carbonate rocks appears to be rougher for some types that have a mixture of fine and coarse grains than for those that are uniformly fine grained, and the pores must not be so small that the solvent cannot move in and out of the pores.

## RESULTS AND DISCUSSIONS

Mineralogical and chemical analyses of the samples are given in table 1. In table 2 the grain size, pore volume, mean size of pores, and surface area

## TABLE 2 - PHYSICAL PROPERTIES OF SAMPLES

| Sample | Grain size Mean (μ) | Grain size Distribution | Rock particles (1 to 1.2 mm) Pore volume (cm³/g) | Rock particles (1 to 1.2 mm) Mean pore size (μm) | Rock particles (1 to 1.2 mm) Surface area (m²/g) | Calcine (1 to 1.2 mm particles) Pore volume (cm³/g) | Calcine (1 to 1.2 mm particles) Surface area (m²/g) | Rock particles (less than 44 μm) Surface area (m²/g) | Rock particles (less than 44 μm) $SO_2$ reactivity index |
|---|---|---|---|---|---|---|---|---|---|
| **LAKE MARLS** | | | | | | | | | |
| 7126A | 3.8 | unimodal | 0.233 | 1.65 | ——* | ——* | 25.2** | 3.3 | 0.64 |
| 7132D | 3.1 | unimodal | 0.380 | 0.86 | 3.8 | 1.222 | 21.0 | 2.8 | 0.82 |
| 7138 | 2.4 | unimodal | 0.544 | 1.28 | 4.4 | 1.444 | 20.4 | 3.9 | 0.70 |
| 7140 | 3.2 | unimodal | 0.484 | 1.34 | 2.7 | 1.326 | 26.4 | 2.1 | 0.77 |
| 7150 | 4.4 | unimodal | 0.472 | 1.30 | 3.9 | 0.924 | 22.0 | 2.3 | 0.70 |
| 7158 | 2.4 | unimodal | 0.504 | 1.02 | 5.2 | 1.312 | 26.8 | 4.2 | 0.81 |
| 7162C | 4.0 | unimodal | 0.934 | 3.1 | 6.8 | 1.868 | 24.8 | 4.2 | 0.76 |
| 7163B | 4.0 | unimodal | ——— | ——— | ——— | ——— | ——— | 4.8 | 0.78 |
| 7133 | 4.1 | unimodal | 0.315 | 4.44 | 0.8 | 0.990 | 15.1 | 1.5 | 0.85 |
| 7149A | 2.8 | unimodal | 0.410 | 4.85 | 2.1 | 1.036 | 28.3 | 2.2 | 0.77 |
| **CHALKS** | | | | | | | | | |
| 7201 | 2.9 | bimodal | 0.302 | 0.76 | 8.8 | 0.729 | 24.1 | 3.6 | 0.91 |
| 7202 | 2.1 | bimodal | 0.212 | 0.15 | 17.6 | 0.547 | 13.5 | 10.4 | 1.18 |
| 7208C | 2.6 | bimodal | 0.216 | 0.35 | 7.0 | 0.593 | 15.4 | 8.0 | 1.00 |
| 7212A | 2.6 | bimodal | 0.217 | 0.39 | ——— | 0.638 | 15.0 | 3.4 | 1.04 |
| 7213 | 3.4 | bimodal | 0.183 | 0.47 | 4.7 | 0.686 | 16.5 | 2.7 | 0.93 |
| 7221A | 2.8 | bimodal | 0.132 | 0.20 | 10.8 | 0.477 | 16.8 | 5.7 | 1.00 |
| 7222B | 2.4 | bimodal | 0.152 | 0.18 | ——— | 0.505 | 11.4 | 6.2 | 0.92 |
| 7227B | 3.0 | bimodal | 0.121 | 0.20 | 8.0 | 0.502 | 10.8 | 5.2 | 1.13 |
| **LIMESTONES** | | | | | | | | | |
| 7120 | 4 | bimodal | 0.086 | 0.50 | .50 | 0.467 | 26.6** | 1.5 | 0.98 |
| 7210B | 4 | bimodal | 0.107 | 0.24 | 4.4 | 0.498 | 17.1 | 3.1 | 1.00 |
| 7252 | 10 | bimodal | 0.053 | 0.7 | ——— | ——— | ——— | 1.0 | 1.05 |
| T3 | 25 | mixed | 0.017 | 0.8 | —— | ——— | 34.5 | 0.5 | 0.78 |
| 7256 | 25 | mixed | 0.030 | 0.6 | —— | ——— | ——— | 0.85 | 0.80 |
| 7251 | 8 | mixed | 0.04 † | 0.3† | —— | ——— | ——— | 1.1 | 0.76 |
| 7253 | 8 | mixed | 0.038 | 0.3 | —— | ——— | ——— | 1.3 | 0.77 |
| 7254 | 8 | mixed | ——— | ——— | —— | ——— | ——— | 1.3 | 0.76 |
| 7260A | 8 | mixed | ——— | ——— | —— | ——— | ——— | 1.2 | 0.89 |
| T4 | 3 | unimodal | 0.004 | 0.4 | —— | ——— | 25.0 | 0.9 | 0.65 |
| 65-1 | 6 | bimodal | ——— | ——— | —— | ——— | ——— | 1.5 | 0.56 |
| 1363 | 6 | bimodal | ——— | ——— | —— | ——— | ——— | 2.1 | 0.55 |
| **CALCITE SPAR** | | | | | | | | | |
| T2 | 1000 | unimodal | 0.004 | < 0.1 | ——— | ——— | 24.1 | 0.6 | 0.57 |
| **OOLITIC SAND** | | | | | | | | | |
| T8 | 2 | unimodal | ——— | ——— | ——— | ——— | ——— | 3.0 | 1.3‡ |
| **SHELL** | | | | | | | | | |
| 7124 | 1 | unimodal | 0.014 | 0.15 | ——— | 0.394 | 0.6 | 3.4 | 1.3‡ |
| 7125 | 1 | unimodal | 0.023 | 0.15 | ——— | 0.429 | 0.6 | ——— | 1.3‡ |
| 7203D | 1 | unimodal | 0.039 | 0.56 | ——— | 0.410 | 0.9 | 2.9 | 1.12 |
| **WASTE SLUDGE** | | | | | | | | | |
| 7153 | 1.5 | unimodal | 0.270 | 0.15 | —— | ——— | 0.85** | 2.1 | 1.3‡ |

\* Dash (——) indicates not determined.
\*\* Particles tested were 74 to 88 μm in size.
† Estimate, based on another sample from the same geologic rock type and strata.
‡ Estimate; index is definitely greater than 1.2.

for the rock samples, and the pore volume and surface area for their calcines are listed. The mean grain (crystallite) size was taken to be equivalent to the mean chord length of a very large number of grains as measured by image analysis (Harvey and Steinmetz, 1971). The distribution of the sizes of the grains is described as unimodal (a more or less normal distribution of grain sizes), or bimodal, or mixed distribution. The latter contains a wide range of grain sizes, which have irregular, or multiple, modes of size of grains. The determination of the modes was made by visual examination of thin-sections of the samples.

## Petrography

Lake Marls

The term lake marl is used here as a petrographic term to describe a carbonate rock that is very soft and incoherent, is very fine grained, is composed largely of calcite, and occurs only in some freshwater lakes and bogs. Some lake marls have a pronounced sandy texture due to the presence of abundant tubular, calcitic particles ¼ mm to 1 mm in diameter and 1 mm to 10 mm long. These particles are fairly coherent; and when they are very abundant, the rock is called a tufaceous lake marl.

The basins of the lakes in which lake marl occurs may be small, occupying only a few acres, or as large as several hundreds of acres. Most deposits that are at present being mined are of the order of 50 to 100 acres and 10 to 30 feet thick. Current production is small compared with that of most limestone quarries and small compared with what could be produced, given a large market. Most lake marl is mined by dredging a channel through the deposit and stockpiling the marl along the bank, allowing the water to drain.

Lake marl deposits occur in the United States mainly in the glaciated areas around the Great Lakes (fig. 1). They are all Pleistocene in age. In some present-day lakes, marl appears to be forming today (Terlecky, in press).

Lake marls frequently contain organic remains of plants and scattered mollusk shells, the latter composed of aragonite. Lenticular stratification occurs by changes in the abundance of shells and by thin interlaminations of dark (organic) and light-colored marl material.

The major inorganic impurities in lake marls (table 1) are quartz as partly rounded grains of silt, 4 μm to 30 μm in diameter, and a few similar sized grains of feldspar. These impurities are scattered throughout the material rather than concentrated in certain layers. In some samples studied, clay and pyrite are trace constituents. Aragonite is present in some samples in amounts as much as 10 percent because of the abundance of mollusk shells. In many marls dolomite is present as individual rhombs, less than 10 μm across, in trace amounts.

Electron micrographs of lake marls (plate 1, A and B) show that they consist of more or less equant subhedral grains of calcite weakly agglomerated

Plate 1 - Textural characteristics of some highly reactive samples.
  A. Subhedral grains of calcite 0.5 to 7 μm in size loosely agglomerated in a lake marl, with a few broken pieces of diatoms (lace network) and an organic fragment (smooth, near center) scattered in the marl. Scanning electron micrograph, 7163C.
  B. Detail of calcite grains and particles in a lake marl. Scanning electron micrograph.
  C. Typical texture of chalks: Sparry calcite (coarse-grained, highlighted portions) in foraminifera tests surrounded by very fine calcite (dark) grains. Traces of clay and magnetite (opaque) occur with the fine grains of calcite. Photomicrograph of a thin section of 7208C in transmitted light.
  D. Detail of the very fine grains of calcite in chalk showing a coccolith and typical porous texture of the material. Scanning electron micrograph of a fractured surface of 7202.
  E. Interlaminated structure (cross-laminated in this case) of fibrous to bladed crystallites of aragonite on a fractured surface of a clam (Rangia) shell. Scanning electron micrograph, 7124.
  F. Grains of precipitated calcite from an industrial waste sludge disposal lagoon. Scanning electron micrograph, 7153.
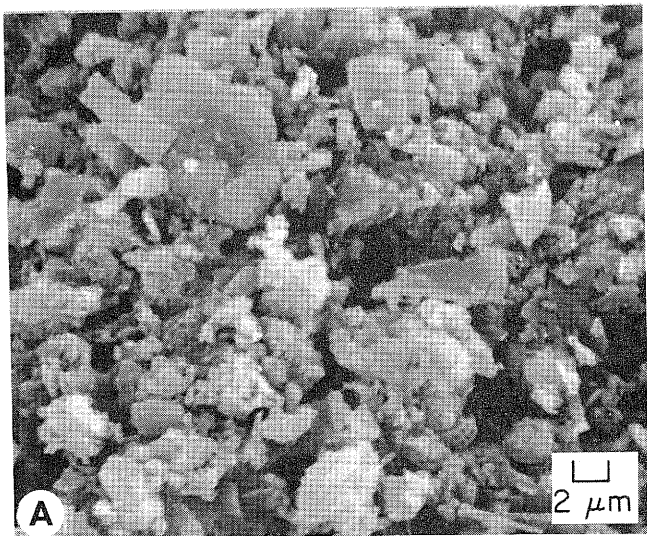
A

B

C

D

E

F
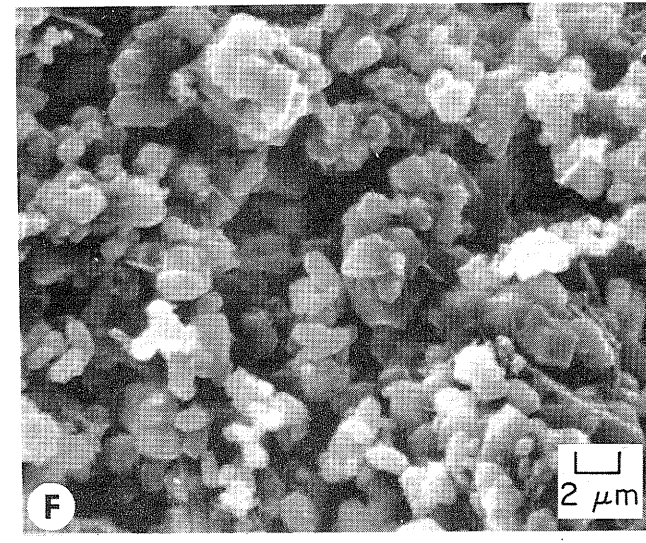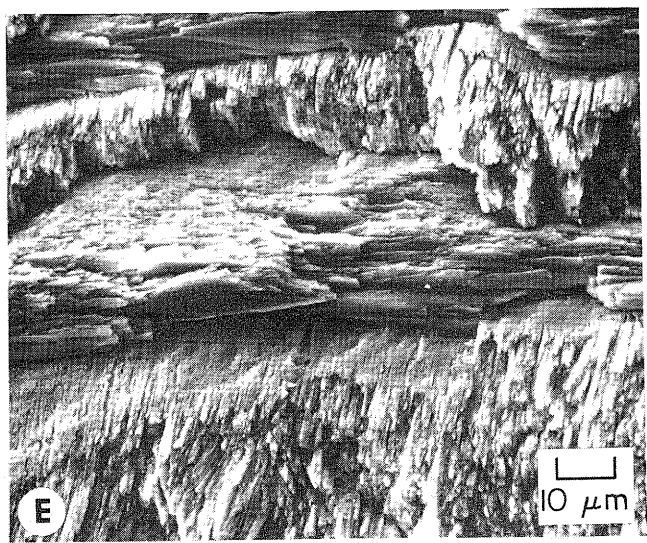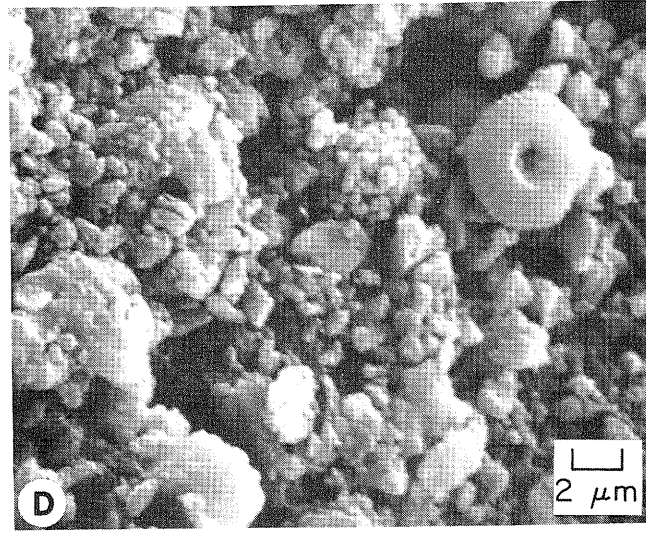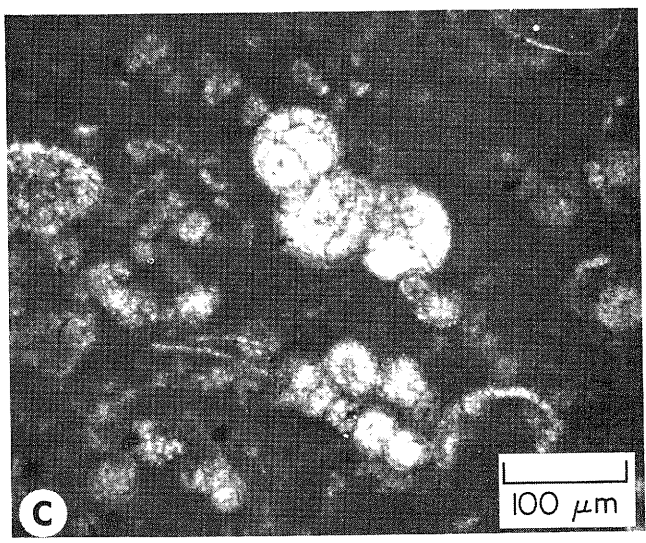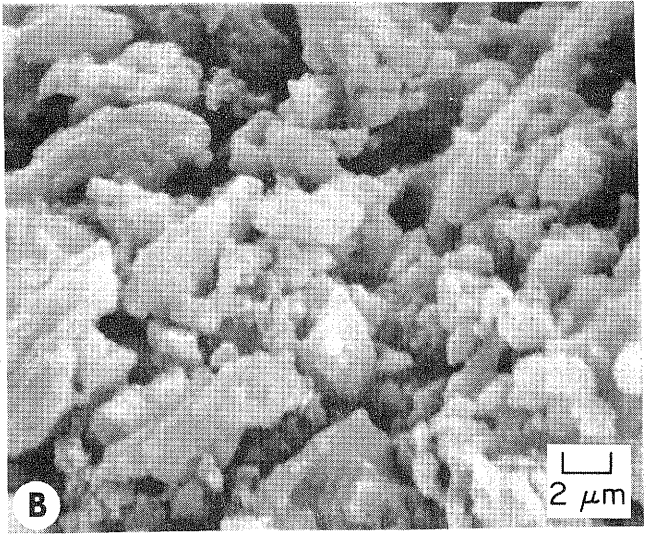
Plate 1

into porous particles. The grains themselves range in size mainly from about
0.1 µm to 4 µm. A small percentage of grains ranges up to about 15 µm across.
The mean grain size of all marls tested is about 3 µm across. The range of
grain sizes in lake marls is small compared with that of most other types of
carbonate rock materials—it is about the same as that of sublithographic
limestones.

Chemical analyses of lake marls sampled from active and discontinued
pits show $CaCO_3$ values ranging mainly from 83 to 93 percent (table 1). Mag-
nesia ($MgO$) is generally 1 to 2 percent, occurring mostly in dolomite and pos-
sibly in some clays. Alumina ($Al_2O_3$) is commonly about 1 percent or less; most
of it occurs in feldspar grains, and thus the clay mineral content of lake marls
is remarkably low, probably less than 0.5 percent. Soda ($Na_2O$) is usually less
than 0.15 percent; it probably occurs in soluble salt crystallites or in feld-
spar grains and in the clay mineral impurities. The difference between 100 per-
cent and the total of the oxides reported for the marls in table 1 is mostly
the organic carbon content. It varies mainly from 1 to 6 percent, but one
sample tested in our previous study—a very peaty marl sample—has more than
13 percent.

The pore volume of lake marls ranges from 0.21 to 1.08 cc/g. Typical
values are shown in table 2. Pore-volume distribution curves of lake marls are
shown in figure 4. The pore-volume distribution curves of the calcines of many
lake marls usually show enlargement of pores over those of the marl material in
the size range larger than 0.1 pore diameter (samples 7132D and 7133 in fig. 4).
Some calcines of marl samples show a pore-size distribution nearly identical
with that of the marl throughout this range (sample 7162C, fig. 4). The large
number of pores in the size range less than 0.1 µm diameter in the calcines is
due to the creation of new pores within the original grains of calcite during
calcination of the marl. Some particle shrinkage apparently occurs on calci-
nation, as the observed increase in pore volume after calcination is usually
somewhat less than the theoretical increase, which is based on calculations of
the data in table 2 and the $CaCO_3$ content of the samples. However, this shrink-
age is negligible for the marls and chalks examined in this study.

The mean size of the pores in lake marls varies from about 0.9 to
1.3 µm in diameter, and it remains about the same in calcined marl because of
enlargement of the larger pores in the marl and the formation of a large number
of very fine pores (< 0.1 µm) during calcination. The mean size of these fine
pores is about 0.04 µm in diameter. Thus the distribution of the size of pores
is distinctly bimodal in the calcines.

The surface area of lake marls (excluding tufaceous ones) is mainly
in the range from 2.7 to 6.8 $m^2$/g marl; and their calcines range from 20.4 to
26.8 $m^2$/g calcine, which represents an increase of surface area upon calcina-
tion of from 5.9 to 13.6 $m^2$/g marl.

Chalks

Chalk occurs principally in the Niobrara Chalk of Kansas and Nebraska
and adjacent states, the Austin Chalk in central and northeastern Texas, the
Annona Chalk in southwestern Arkansas, and the Demopolis Chalk (Selma Group) in
Alabama and Mississippi (fig. 1). Each of these units is Upper Cretaceous in
age (fig. 2). A high proportion of the commercial production of chalk from
these formations is used as raw material for cement manufacture. Some chalks
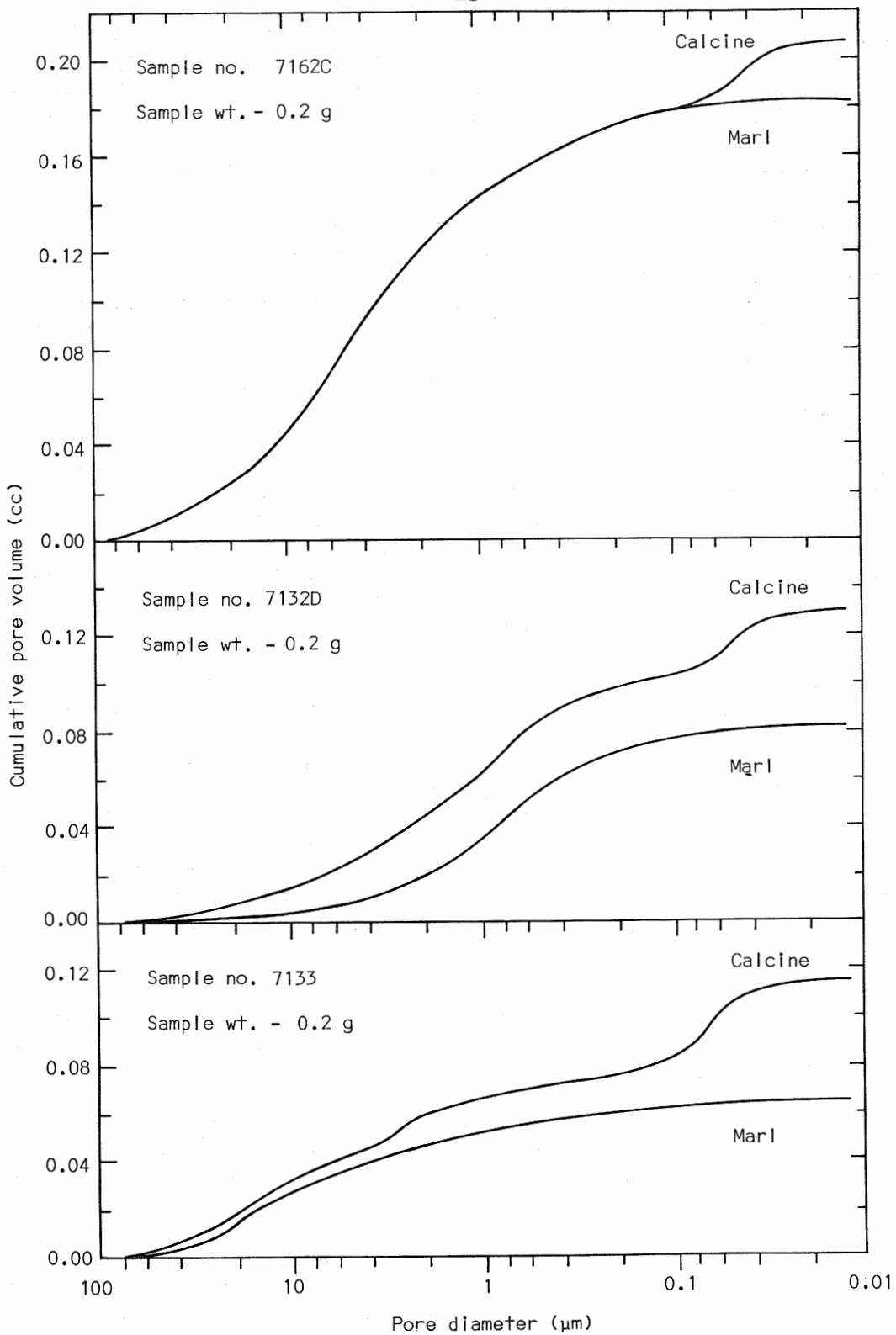
Fig. 4 - Typical pore-volume distribution curves for lake marls and
their calcines. Sample 7133 is a tufaceous lake marl. 1
to 1.2 mm particles tested.

and chalky limestones occur in Tertiary strata—especially in the Marianna
Limestone in Alabama and in the Ocala Group in Florida and Georgia (fig. 2).
Also the Harrodsburg Member of the Ullin Limestone (Mississippian) in southern
Illinois contains a thick unit of chalky limestone (sample 7252, tables 1 and 2).

Chalks are composed primarily of micritic calcite (grains < 4 µm in
diameter), but all samples studied contain more than 5 percent of sparry calcite
(clear grains > 10 µm diameter) in the form of foraminifera tests (plate 1, C)
scattered throughout the micrite. The average sparry calcite content of the
chalks studied is 10 percent. The mean grain size of chalk material varies
from 2.1 to 3.0 µm in diameter. The very fine grains of calcite in chalks are
broken pieces of fossil coccoliths (plate 1, D). The grain-size distribution
is bimodal; the sparry calcite has a grain-size mode of about 10 to 15 µm in
diameter while the finer and more abundant micritic calcite has a grain-size
mode of nearly 1.5 µm in diameter.

The calcite ($CaCO_3$) mineral composition of chalks has a considerable
range (table 1). Minor mineral impurities are quartz as silt grains, and clay
as less than 2 µm flakes. The clay is principally montmorillonite, with lesser
amounts of illite (10 Å, non-expandable) and kaolinite minerals. The illite,
observed microscopically, has the form of green glauconitic pellets that are
scattered through the chalk material. Traces of feldspar, mica, pyrite, mag-
netite, and limonite are also present in nearly every sample tested.

The pore volume of chalks ranges from 0.12 to 0.30 cc/g and averages
about 0.2 cc/g, which are somewhat lower than in most marls. The mean size of
pores in chalks has a rather narrow range, 0.2 to 0.8 µm in diameter (table 2).
The small size of the pores results in chalks having a relatively large surface
area, in the range of 5 to 18 $m^2$/g (table 2), although those samples with sur-
faces greater than about 9 $m^2$/g have these high values because of the greater
abundances of clay in these rocks. Typical pore-volume distribution curves of
chalks and their calcines are shown in figure 5. As in the case of the marls,
some chalks appear to experience no pore-size enlargement during calcination
(7208C, fig. 4) while others do show various amounts of pore enlargement.

Limestones and Other Carbonate Materials

Many of the limestone samples selected for study are high-calcium
limestone (≥ 95 percent $CaCO_3$) (table 1). Samples 7120, 7210B, and 7252 are
chalky limestones. 7210B contains minor amounts of clay. Several of the re-
maining limestones contain minor amounts of dolomite. The pore volumes of the
chalky limestones range from 0.05 to 0.11 cc/g, whereas the non-chalky limestones
range from 0.004 cc/g to 0.04 cc/g. Typical pore-volume distribution curves are
shown: two chalky limestones (fig. 6, A and B), two coarse-grained crinoidal
limestones (fig. 6, C and D), and a very fine grained, dense limestone (fig. 6, E).

The calcite spar sample (tables 1 and 2) is a vein type of calcite
from a fluorspar mine in southern Illinois and it is very coarsely crystalline,
is milky colored, and represents one end-member of limestone types in terms
of coarseness of grain size.

Shell deposits are represented in this study by samples of the cal-
citic type (oysters, 7125), aragonitic type (clams, 7124), and a mixture of these
two mineralogical types (7203D). The latter is a processed shell material pro-
duced from the coquina facies of the Yorktown Formation (Miocene) in Virginia.
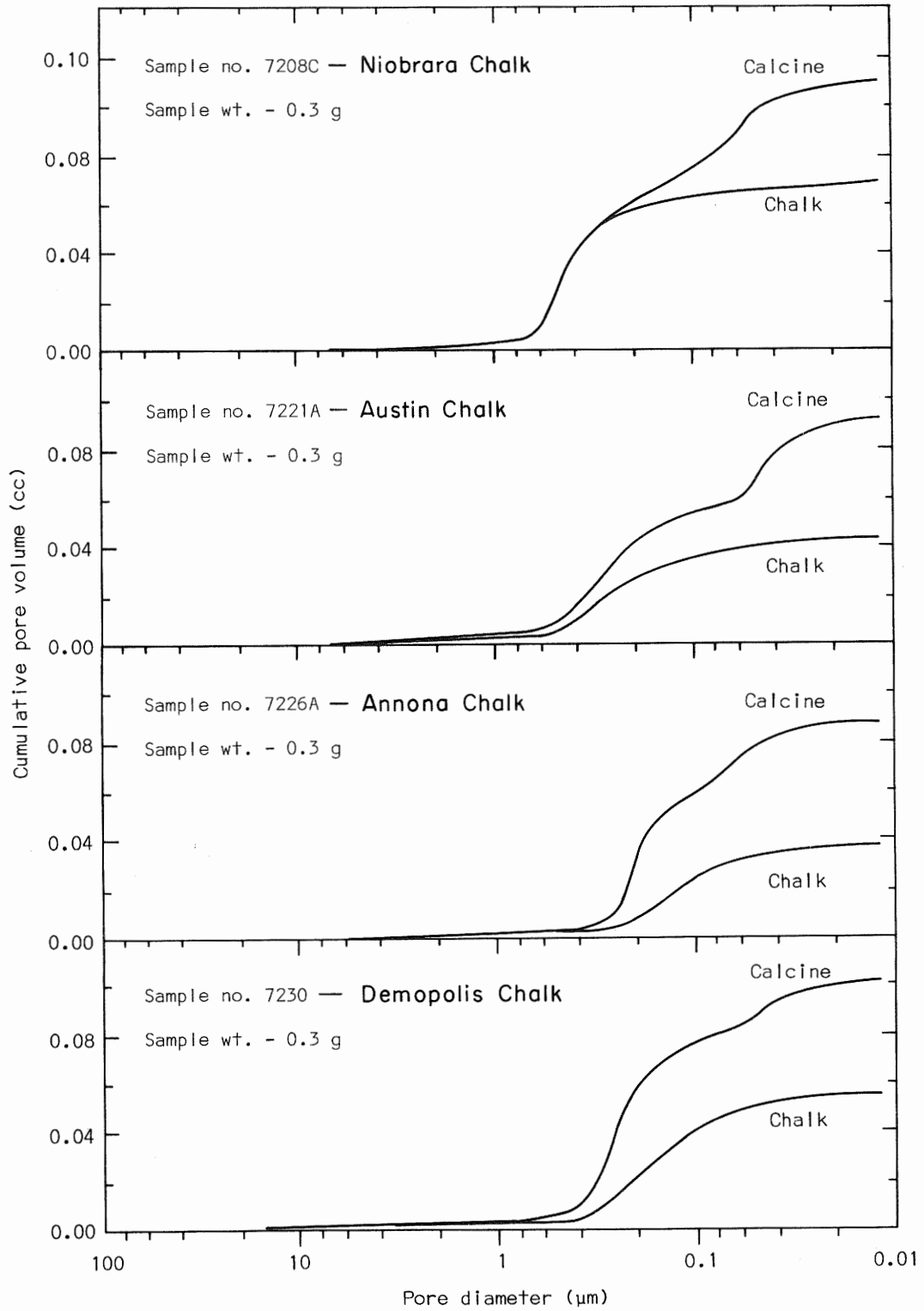
Fig. 5 - Typical pore-volume distribution curves of chalks and their
calcines.  1 to 1.2 mm particles tested.
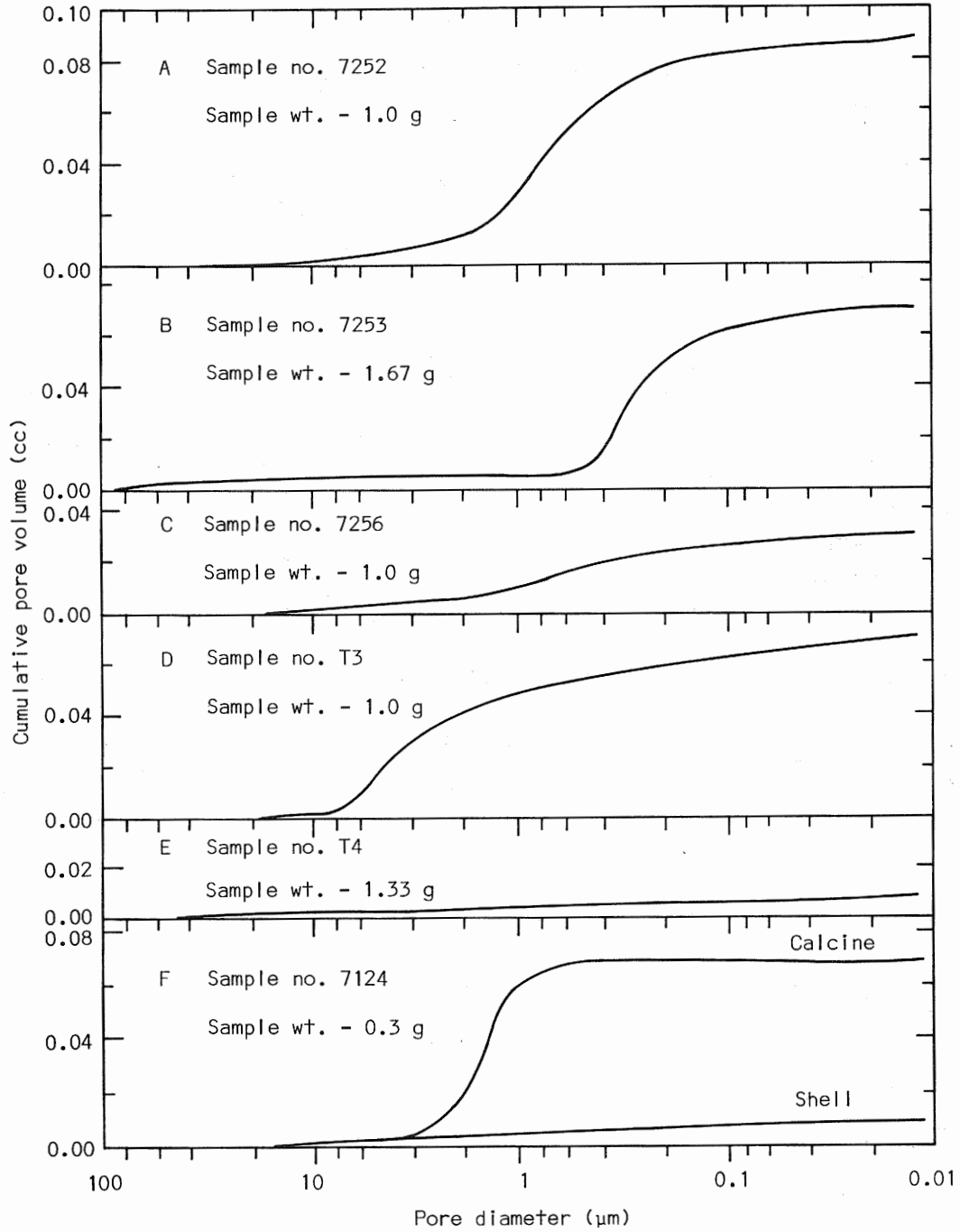
Fig. 6 - Typical pore-volume distribution curves of chalky limestones, A and B; limestones, C to E; and a shell sample and its calcine, F. 1 to 1.2 mm particles tested.

The shells all have an interlaminated structure typically represented by that shown in plate 1, E. Both calcite and aragonite in the shells take the form of fibers or blades, most of them less than 1 $\mu$m wide and 10 to 30 $\mu$m long. These are oriented parallel to one another, each with nearly identical crystallographic orientation within each lamella.

Shells typically are very dense and have small pore volumes (fig. 6, F); however, calcines of shells tested have pore volumes of near 0.40 cc/g, slightly greater than the theoretical amount (0.36 cc/g) for $CaCO_3$. The mean size of the pores in calcined shells is approximately 1.5 $\mu$m in diameter.

The remaining carbonate sample is a waste sludge from a paper manufacturing plant (Nekoosa Edwards Paper Company, Port Edwards, Wisconsin). It is a precipitated calcite of high purity (table 1). The trace amount of soda ($Na_2O$) present in this sample is relatively high compared with that in the other samples. Theoretically, soda can occur within the rapidly precipitated crystals of calcite or can occur as a soluble salt. The grain size of the sludge has a very narrow range and averages about 1.5 $\mu$m in diameter (plate 1, F). The sludge has a fairly high pore volume and surface area compared with the other carbonate materials. Waste calcitic sludge from many water treatment plants and other types of industrial plants is likely to have physical properties very similar to those of this sample.

## $SO_2$ Reactivity Results

The results of the laboratory tests of the relative dissolution rate of each sample, pulverized to less than 325 mesh (< 44 $\mu$m), in the simulated scrubbing liquor are given in table 2. Attention should be called to the fact that four samples entirely dissolved and dissolved so rapidly in the test that no absolute index for them could be determined; however, it is our best estimate that these samples—the oolitic aragonite sand, two of the shell samples, and the waste sludge—have an index of approximately 1.3. For the purpose of this discussion, this estimate is quite adequate.

The index values range from 0.55 for one of the dense, fine-grained algal limestones tested (sample 1363) to an estimated 1.3 for the samples just mentioned, more than 2.2 times the index of the least reactive sample. The other fine-grained algal limestone (65-1) tested similarly low, 0.56, and the very fine grained limestone (T4) tested 0.65. Coarse-grained crinoidal limestones (T3 and 7256) tested 0.78 and 0.80. The chalky (porous) crinoidal limestone (7252) tested the highest of all the limestones, 1.05.

The marls ranged from 0.64 to 0.85 and averaged 0.76; the chalks ranged from 0.92 to 1.18 and averaged 1.01. The shell samples averaged 1.24; and the oolitic aragonite and the waste sludge tested high, as discussed above.

It is difficult to predict with assurance from a study of pore-volume data, mean pore size, and surface area measurements from gas adsorption on dry samples just what the effective surface area of a given sample will be in the reactivity test. However, consideration of these data explains to a great extent the observed reactivities of all the samples except the shells. As most limestones have relatively small pore volumes, they have relatively small effective surface areas and consequent low reactivity indexes; this is especially true for the dense limestones. Further, particles of lake marls have larger pore volumes than those of chalks, but the mean pore size of the pores in chalks is smaller than in marls, thus giving rise to larger surface area values in chalks than in marls. The pores are not so tiny as to inhibit penetration by

water in the reactivity test, and thus the effective surface area is also larger. The relatively high reactivities of the chalks and marls are in agreement with these considerations.

The high reactivities found for the shells are higher than anticipated from their relatively low pore-volume and surface area values. It is possible that the true pore volume is larger than observed, because there may be numerous pores in the shells in a size range less than 0.012 μm in diameter, the lower limit of the measurements. There also may be many isolated pores within the shells forming a closed pore system that is not reflected in the surface area measurements. However, neither of these possibilities is readily supported by electron microscopic analyses. Other factors may contribute to the reactivity of the shells. There is a high degree of preferred orientation of the fine crystallites in the shells. The orientation and fracture behavior of shells may be such as to expose the most reactive crystallographic surfaces of calcite and aragonite crystals to the scrubbing liquor. In addition the effect of the high soda content of the shells may be a very important factor, as discussed below.

Graphical analyses of the properties of the samples in relation to their $SO_2$ reactivity indexes are shown in figures 7 through 10. The grain-size graph indicates a general trend of increasing index with decreasing size (fig. 7).
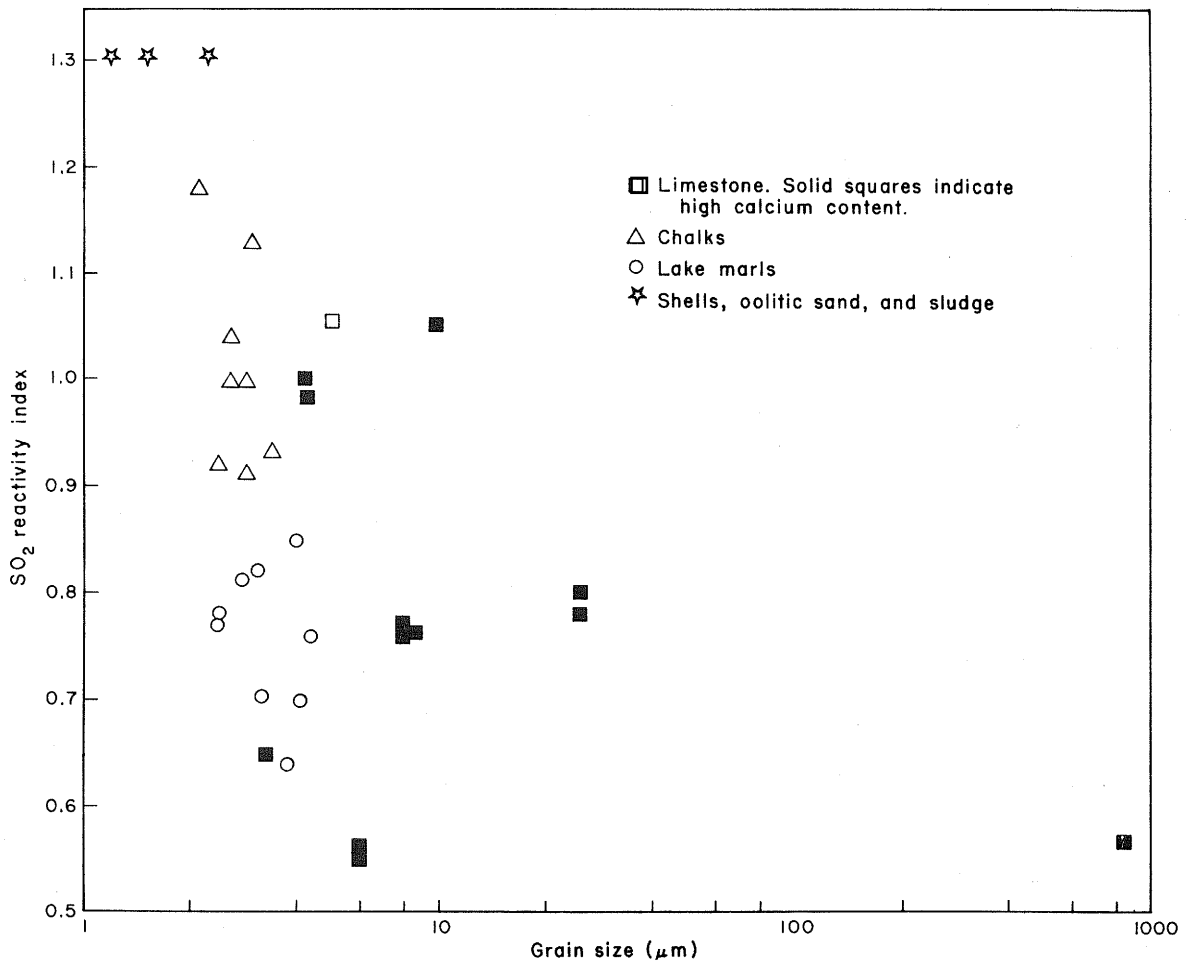


Fig. 7 - Relation between the $SO_2$ reactivity index, as measured on the rock ground to less than 44 μm, and the mean grain size (crystallite size) of the rock.

The fine-grained and dense limestones have an anomalously low index according
to this trend.  The calcite spar, coarse-grained limestones, chalks, shells,
and sludge fit this trend moderately well.

The pore-volume graph (fig. 8) shows little overall correlation al-
though the different rock types plot in separate areas of the graph; and for
the limestones and lake marls, considered apart from the others, increasing $SO_2$
reactivity index is accompanied by increasing pore volume.  However, the rate
of increase is decidedly different for these two rock types.  The data of the
chalks appear to be an extension of the general trend shown by the limestones.
The shells, with their very low pore volumes, are not in agreement with this
trend but the behavior of the waste sludge sample is.  Lake marls have a lower
reactivity than expected when considering only their high pore-volume values.
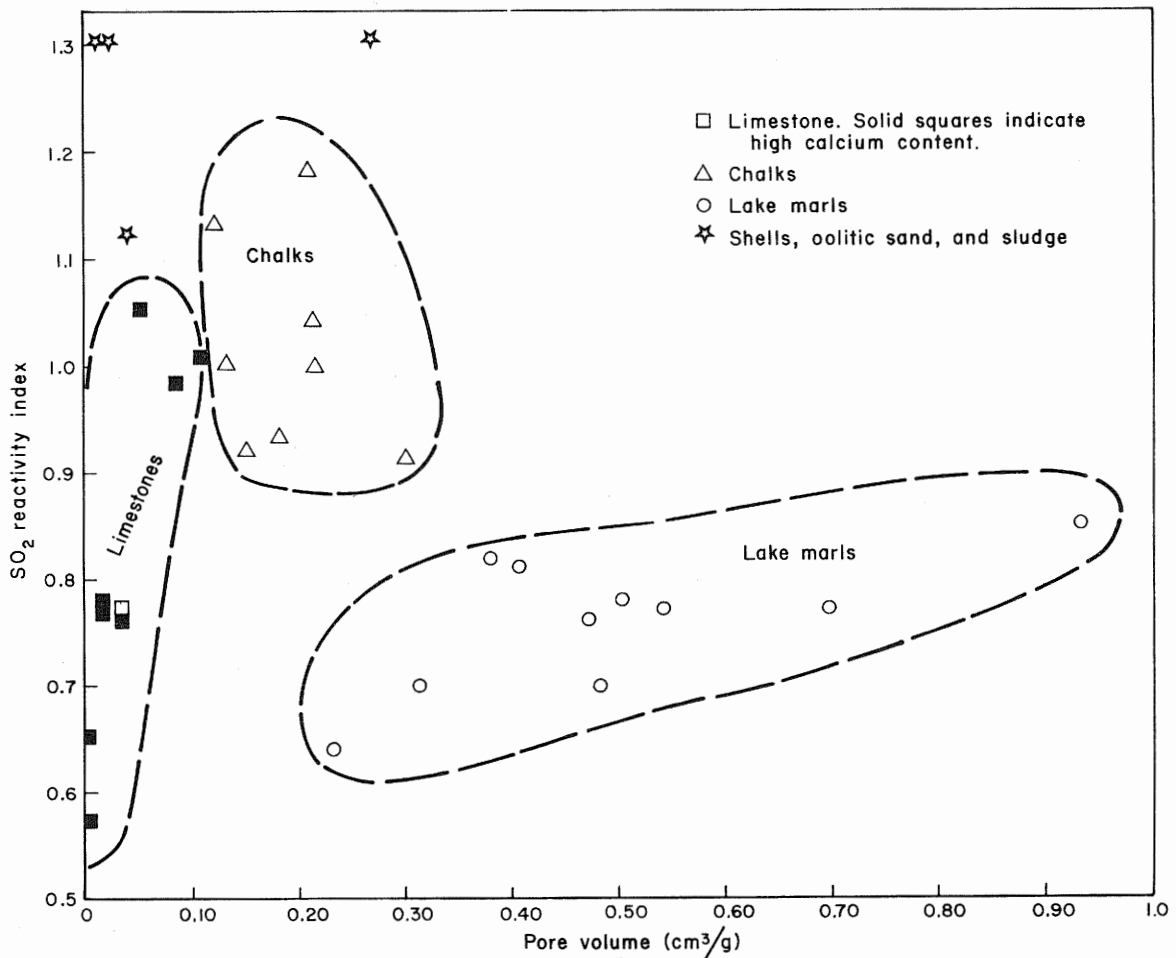


Fig. 8 - Relation between the $SO_2$ reactivity index, as measured on the rock
ground to less than 44 μm, and the total pore volume, as measured
on 1 to 1.2 mm particles.

The relation of the surface area to the $SO_2$ reactivity index, both
measured on samples pulverized to minus 325 mesh, is shown in figure 9.  Some
similarities exist between this graph and figure 7, but the lake marls are
grouped in a random pattern while the chalk samples appear to show a trend of
increasing index with increasing surface area.
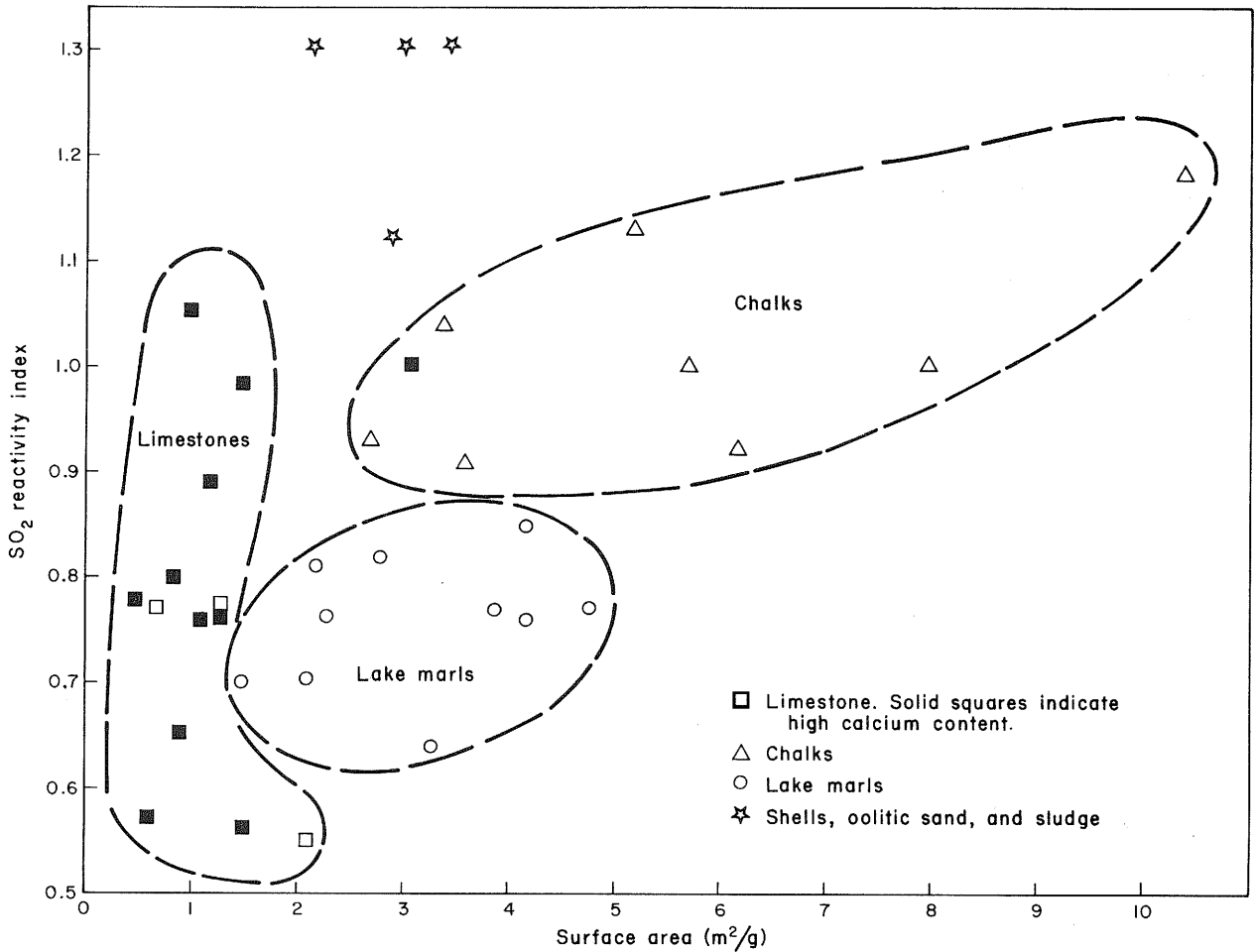
Fig. 9 - Relation between the SO₂ reactivity index and surface area.  Less
than 44 μm particles were tested for both properties.

The relation of the soda, as determined analytically on the whole rock
material, to the SO₂ reactivity index (fig. 10) shows a general trend of increas-
ing index with increasing weight percentage of soda.  The various types of rocks
are not grouped into any distinct pattern on this graph.  Other chemical results
do not correlate with the reactivity index.  The apparent correlation of index
with soda is not fully understood.  Ions of sodium that occur as interstitial
ions within the crystal structure of calcite and aragonite, or as an inclusion
within grains, or as a soluble salt along grain boundaries would probably act
to increase reactivity.  However, it is difficult to understand how other occur-
rences of soda in the rocks, whether in clay or in feldspar mineral impurities,
would enable it to act to increase reactivity.

## CONCLUSIONS

Conclusions drawn from these data indicate that pulverized shells from
deposits along the coasts have good potential for high rates of dissolution in
SO₂-scrubbing liquors, as does oolitic aragonite sand.  Our results show a very
high rate of dissolution for a calcitic waste sludge material; this may be es-
pecially significant for certain areas in the country where limestone resources
are limited and where calcitic waste sludge is available from paper, water
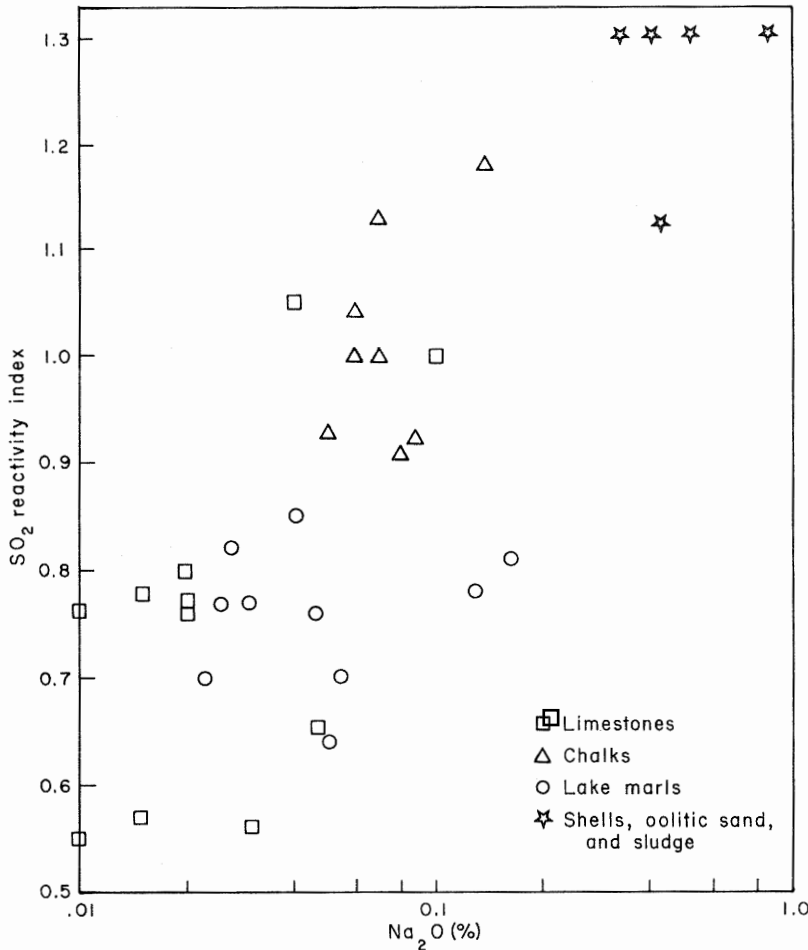
Fig. 10 - Relation between the $SO_2$ reactivity index, as measured on the rock ground to less than $44 \, \mu m$, and the sodium oxide content of the rock.

treatment, and other types of industrial plants. Such waste material is likely to be very reactive in wet scrubbing systems. Chalks appear to be more reactive than most limestones, and lake marls are likely to be more reactive than dense, fine-grained limestones, no matter how finely such limestones are pulverized.

Lake marl, because of the ease of its production (no blasting and little or no crushing), together with its high degree of disaggregation when mixed with water, should be given important consideration for use in limestone scrubbing systems at power plants near lake marl deposits.

The soda $(Na_2O)$ and the grain size (crystallite size) of a carbonate material, as well as the pore-volume distribution and surface area properties, appear to be useful guides to the $SO_2$ reactivity index of the material.

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