ILLINOIS STATE GEOLOGICAL SURVEY
John C. Frye, Chief   Urbana, Illinois 61801
October 1969

INDUSTRIAL MINERALS NOTES 39

ALUMINA CONTENT OF CARBONATE ROCKS AS AN INDEX TO SODIUM SULFATE SOUNDNESS

A Preliminary Report

James W. Baxter and Richard D. Harvey

ABSTRACT

Core samples from the upper part of the St. Louis Limestone near Alton, Illinois, were subjected to physical tests, chemical analyses, and mineralogical study to seek chemical and/or mineralogical indices that would be useful in preliminary evaluation of limestone deposits that are possible sources of aggregate for concrete.

A correlation coefficient of 0.79 was obtained between alumina content and sodium sulfate soundness for the rocks examined, a variety of fine-grained limestones and a few dolomites. Sodium sulfate soundness tests are widely used for aggregate evaluation. The correlation appears to be significant and is notably better than correlations between sulfate soundness and other major chemical oxides or mineral constituents.

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INTRODUCTION

The upper part of the St. Louis Limestone is extensively quarried in western and southwestern Illinois, principally in the vicinity of Alton in Madison County and East St. Louis in St. Clair County. The chemical composition and gross physical characteristics of the stone produced are fairly well known.

The Illinois State Geological Survey worked in cooperation with the Illinois State Department of Mental Health on a core drilling and testing program designed to determine the extent, chemical composition, and physical properties of the St. Louis Limestone under certain property of the Alton State Hospital near Alton. As a result, detailed data became available, offering the opportunity to explore the relation between the physical, chemical, and mineralogic properties of the carbonate rock strata. The aim of this study was to seek chemical or mineralogic properties that could serve as indices to certain physical properties on which quality specifications of aggregates are based. Such indices would be of great value in initial evaluation of limestone and dolomite deposits. Statistical analysis of the data revealed a significant relation between the sodium sulfate soundness of the rock and its total alumina content—the latter being the Al_2O_3 content of the whole rock in weight percent.

The sodium sulfate soundness test is one of several used to measure the resistance of an aggregate to processes simulating freeze-thaw conditions. These tests are designed to accelerate splitting, flaking, and other types of disintegration involved in the deterioration of aggregate when it is exposed to natural conditions. The sodium sulfate soundness test involves alternately soaking a sample in a saturated solution of sodium sulfate in water and drying it at moderate temperature in an oven. In other similar tests, magnesium sulfate and sodium chloride solutions are used. The growth of salt crystals in the pores of the rock during drying exerts a force that is thought to be similar to that exerted by the growth of ice crystals but is more rigorous and tends to accelerate the splitting of the aggregate particles. The "A-freeze test" is an accelerated test in which a water-alcohol solution is used. These accelerated tests are thought to be indicative of freeze-thaw durability, although correlations with laboratory freeze-thaw soundness tests have not been widely publicized.

The sodium sulfate soundness test (ASTM C 88) is one of three main acceptance tests used for many years by the Illinois Division of Highways to determine the quality of aggregate to be used in road and bridge construction. The test sample is a specified amount of aggregate of a certain size gradation, and it is subjected to five cycles of immersion and drying. The results of the test are given in terms of a weighted percentage loss, high loss values being indicative of a high degree of disintegration of the aggregate particles during the test. The sulfate soundness test has, with few exceptions, proved to be satisfactory for judging the durability of Illinois limestone and dolomite aggregates used for construction in Illinois.

The correlation of sodium sulfate test results with the basic mineralogical and chemical properties of carbonate rock samples has not been determined. Related studies of natural sands by Adams and Pratt (1945) and Mather (1947) showed that an increase in absorption by the sand sample results in an increase in the percentage loss during magnesium sulfate soundness tests. A survey of the literature revealed no direct relation of absorption to sulfate soundness of carbonate rock aggregates. Verbeck and Landgren (1960) and Powers (1955), using direct freezing and thawing tests, showed that pore-size distribution, permeability, and degree of saturation had great influence on the freeze-thaw durability of various types of aggregate. Dunn and Hudec (1966) concluded from a study of the disintegration of stone particles during alternate soaking in water and oven drying that temperatures below 0° C are not necessary to disrupt rocks and that the expansive force exerted by water adsorbed on clay surfaces is sufficient. Experience in Illinois suggests that, with some exceptions, the clayey or argillaceous material in a limestone contributes greatly to the loss in soundness. The relations of sulfate soundness to shaly argillaceous material appear to be worth study.

The sodium sulfate soundness tests reported in this paper were made by personnel in the Bureau of Materials, Illinois Division of Highways. We gratefully acknowledge their cooperation, especially the efforts of Richard Kiel.

LITHOLOGIC CHARACTER OF THE UPPER PART OF THE ST. LOUIS LIMESTONE

The St. Louis Limestone is approximately 220 to 225 feet thick in the Alton State Hospital area. Its lithologic composition varies vertically and, to some extent, laterally; however, the upper and lower subdivisions recognized in the bluffs of the Mississippi River at Alton by Collinson, Swann, and Willman (1954), Collinson and Swann (1958), and Baxter (1965) are also recognizable in the cores from the Alton State Hospital property. The chemical and physical properties of only the upper part of the limestone are considered in this report.

The upper part of the St. Louis Limestone is approximately 115 feet thick. It has a quite variable lithology (fig. 1), but stratigraphic relations

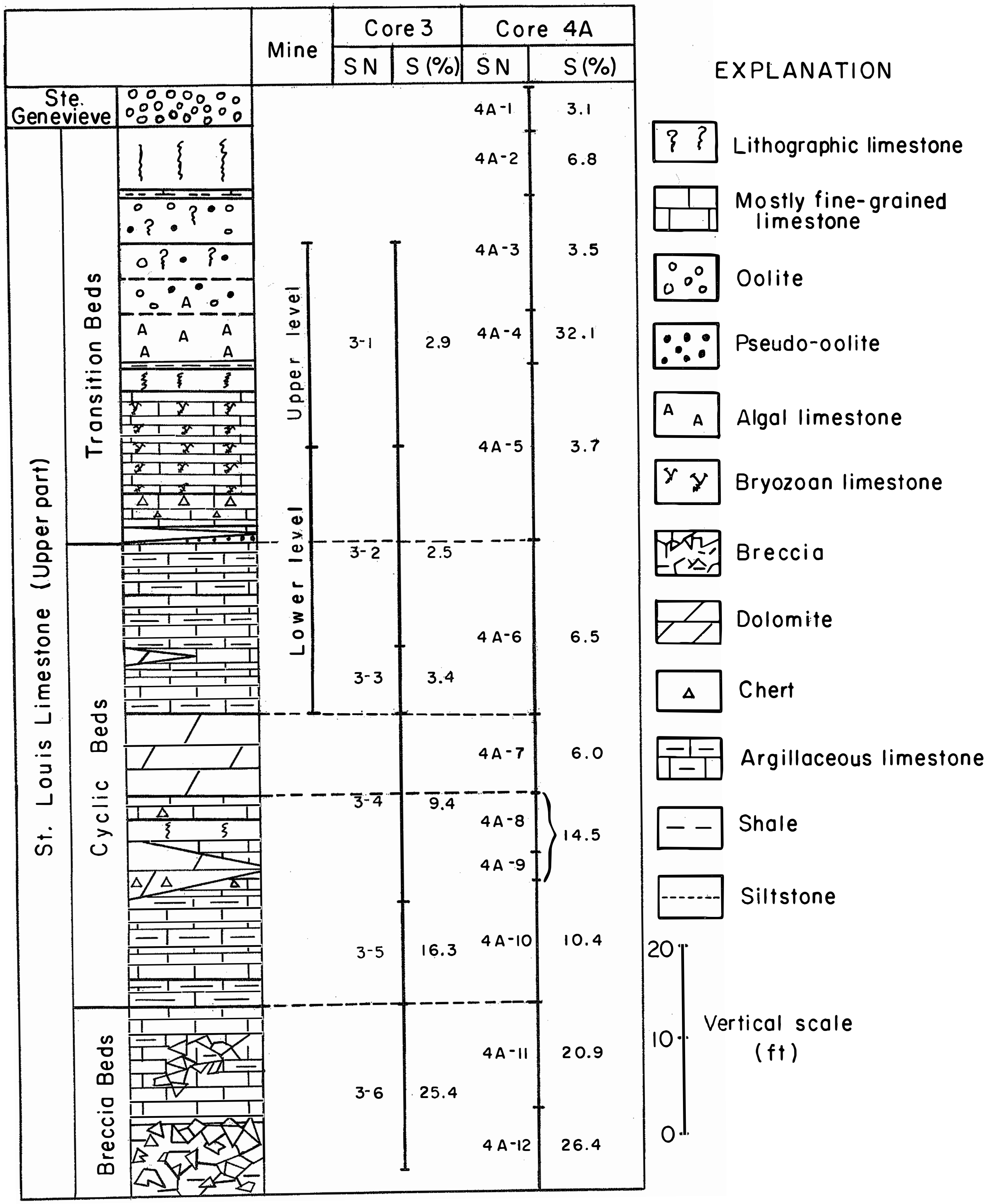

Fig. 1 - Columnar section, sample numbers (SN), and soundness test results (S).

are similar to those seen in exposures in the bluffs near Alton. Three units with different characteristics are recognized in each of five diamond drill holes—the transition beds at the top, cyclic beds, and breccia beds at the base.

Transition Beds

The transition unit, approximately 45 feet thick, at the top of the St. Louis Limestone (fig. 1) shares some of the lithologic characteristics of the overlying Ste. Genevieve Limestone. The unit, especially its upper portion, is partly oolitic and/or pseudo-oolitic limestone. In contrast to the sandy oolitic limestones of the Ste. Genevieve, the oolitic zones of the St. Louis are relatively pure limestone, with the major portion of clastic impurities—shale, quartz silt, and quartz sand—restricted to about four beds, each 0.1 to 0.9 of a foot thick, in the upper part of the unit.

Four types of limestone dominate the lithology of the transition beds—lithographic limestone at the top; pseudo-oolitic to oolitic limestone in the upper half; slightly argillaceous, algal limestone near the center; and bryozoan limestone with a basal cherty zone in the lower half.

Lithographic Limestone

Lithographic limestone occurs at the top of the transition beds and its characteristic light gray to almost white color and stylolitic partings make it a prominent marker in the Alton area. Lithographic to semilithographic limestone also occurs 0.4 to 0.9 of a foot below the algal beds and at or near the base of the transition unit in the hospital property drill cores. The lithographic marker bed at the top of the St. Louis is from 5 to 8 feet thick, the bed below the algal limestone is from 2 to 3 feet thick, and that at the base of the transition beds is 0 to 2 feet thick.

Oolitic Limestone

Oolitic to pseudo-oolitic limestone is largely restricted to an interval 4 to 12 feet thick in the upper part of the transition unit in the hospital property drill cores. The limestone consists of light brownish gray, fine- to medium-grained, oolitic to pseudo-oolitic limestone with variable amounts of lime mud and clear, sparry calcite cement. Some of the beds grade to an almost lithographic texture. A discontinuous lens of crossbedded pseudo-oolite occurs at the base of the transition beds.

Algal Limestone

Algal limestone near the middle of the transition unit has a total thickness of 9 to 14 feet and is somewhat argillaceous, partly silty, and fine to oolitic. The algal material ranges from vague, curdy mottling and pseudo-oolites to 1½- to 2-inch nodules of concentrically banded lithographic limestone that look like conglomerate. Shale partings and clay pockets, the latter associated with the algal conglomerate, are common.

Bryozoan Limestone

The bryozoan limestone, 15 to 17 feet thick, is light gray and relatively pure except for a basal cherty zone. It is composed of very fine to semilithographic limestone with thin bands of fossils, most of them bryozoans. The cherty stone at the base is less fossiliferous than the higher beds.

Cyclic Beds

The middle unit of the upper part of the St. Louis Limestone, the cyclic beds (fig. 1), is about 52 feet thick and consists of brownish gray, fine- to medium-grained limestone and dolomite with cyclic intercalation of thin, continuous clay partings and shaly layers up to half an inch thick. Fine-grained dolomite occurs in a persistent 9-foot bed near the middle of the cyclic beds and in discontinuous lenses approximately 5 feet above and 5 feet below the persistent band. A bed of semilithographic limestone 1½ to 2 feet thick and 0 to 2 feet below the middle dolomite is another persistent marker bed. Small amounts of secondary chert and silicified solitary corals are present in the lower part of the cyclic beds.

Breccia Beds

The breccia beds that form the basal unit of the upper part of the St. Louis (fig. 1) are 18 to 22 feet thick and show various degrees of fracturing, brecciation, and reworking of limestone. The breccia is composed of angular pebbles and boulders of lithographic limestone, pseudo-oolitic calcarenite, and, more rarely, stromatolitic, algal limestone with a silty, oolitic matrix. Brecciation in the upper part of these beds is less intense than in the lower 8 to 10 feet, which has been strongly reworked and has conspicuous interstitial green silty clay.

RESULTS OF PHYSICAL TESTS

Cores 3 and 4A (fig. 1) were subjected to detailed physical testing to determine the suitability of the strata for use as concrete and other types of aggregate. Samples tested were selected from the upper part of the St. Louis Limestone, six samples from core 3 and 13 from core 4A. From core 3, the uppermost three samples were taken from strata equivalent to strata mined in the vicinity, sample 3-1 corresponding to the upper workings in a nearby mine and samples 3-2 and 3-3 corresponding to those in the lower level. Deeper samples in core 3 were taken to reflect major lithologic changes. Core 4A was sampled at closer intervals to evaluate the physical properties of more precise lithologic units throughout the entire upper part of the St. Louis Limestone. Tests for specific gravity, absorption, sodium sulfate soundness, and the Los Angeles test for abrasion were run by the Bureau of Materials, Division of Highways, Illinois Department of Public Works and Buildings. The soundness results are reported in table 1 and opposite the sample numbers in figure 1.

TABLE 1--SULFATE SOUNDNESS, INSOLUBLE RESIDUE, SILICA, AND ALUMINA DATA

Sample	Soundness loss[a] (%)	Insoluble residue (%)	Silica[b] (SiO_2) (%)	Alumina[b] (Al_2O_3) (%)
4A-1	3.1	2.2	1.25	0.5
4A-2	6.8	6.2	4.86	0.8
4A-3	3.5	1.5	0.85	0.4
4A-4	32.1	14.0	9.85	2.5
4A-5	3.7	3.6	2.30	0.5
4A-6	6.5	4.1	3.02	0.9
4A-7	6.0	6.3	6.77	0.9
4A-8 & 9	14.5	7.9[c]	6.38[c]	1.5[c]
4A-10	10.4	5.0	3.95	0.9
4A-11	20.9	4.0	3.68	0.8
4A-12	26.4	10.0	7.87	1.6
3-1	2.9	4.7	3.67	0.7
3-2	2.5	8.0	7.14	0.6
3-3	3.4	3.4	2.00	0.6
3-4	9.4	2.5	3.21	0.7
3-5	16.3	5.4	3.78	0.9
3-6	25.4	6.2	4.68	0.9

[a] Sodium sulfate soundness loss (ASTM C 88-63), 5 cycles.
Test results by the Bureau of Materials, Illinois Division of Highways, Springfield, Illinois.

[b] Analyses by the Analytical Chemistry Section, Illinois State Geological Survey, Urbana, Illinois.

[c] Weighted according to thickness of samples 4A-8 and 4A-9.

The results of sodium sulfate soundness tests (fig. 1, table 1) show losses of from 2.5 to 32.1 percent for predominantly limestone units and losses of 6 to 9.4 percent for calcareous dolomite units. Three samples of the breccia beds that occur at the base of the upper part of the St. Louis Limestone (samples 3-6, 4A-11, and 4A-12) had soundness losses from 20.9 to 26.4 percent. Sample 3-5 from the base of the cyclic beds had a soundness loss of 16.3 percent. Sample 4A-4, representing the 177.3- to 183.0-foot interval of the argillaceous algal beds, showed a soundness loss of 32.1 percent, the highest of all the samples tested.

The results of soundness tests on samples of the commercial product from a nearby mine range from about 5 to 9 percent loss; the higher loss values are from tests of the upper level in areas within the mine where shaly beds thicken. In the north half of the mine, selective mining is necessary to meet state specifications that limit shale to 1 percent for quality A coarse aggregate. The average soundness for core samples 3-1, 3-2, and 3-3, weighted according to thickness, is 2.8 percent, which is less than the lower range observed from the commercial mine product. The soundness for samples 4A-3, 4A-4, 4A-5, and 4A-6, also weighted for thickness but representing more precise lithologic units, is 7.6 percent and thus agrees more closely with results from the mine than did tests of core segments selected on the basis of thickness only. Definitive conclusions as to the most useful sampling procedure cannot, however, be made on the basis of these tests alone. Additional data from other core samples should be obtained.

CORRELATION OF MINERALOGY AND SOUNDNESS

Representative samples of the cores were examined for their mineral content. The amounts of the insoluble residues (table 1) of the St. Louis Limestone obtained by digestion of the limestone in 1N HCl warmed to less than 90° C are approximately equal to the sum of the quartz (including chert) and clay content of the limestone. The quartz content was determined from X-ray diffraction data obtained for the whole, undigested sample by comparing them with X-ray calibration curves drawn from known mixtures of quartz in calcite and quartz in dolomite. The clay content was taken to be the percentage difference between the total insoluble residue and the quartz. The calcite-dolomite ratios also were determined by comparisons with X-ray calibration curves and corrected for the percentage of insoluble residue observed in the sample. A plot of soundness versus the calcite-dolomite ratio, as expected, indicates soundness is independent of the carbonate mineralogy. The correlation coefficient of the soundness and the percentage of clay present was 0.47. The coefficient of soundness and the percentage of quartz was 0.62, and that between soundness and insoluble residue was 0.69.

CORRELATION OF SILICA AND ALUMINA WITH SOUNDNESS

Representative samples of the cores were analyzed for the major oxides—calcium oxide, magnesium oxide, silica, alumina, and iron oxide. Only the results for silica and alumina indicate any notable correlation with sodium sulfate soundness (table 1). The correlation coefficient of soundness to silica is 0.62 (identical to the value for quartz), and for soundness to alumina it is 0.79. The latter value is the highest coefficient obtained and indicates the sulfate soundness is better related to or predicted by the alumina content of the stone than by any of the other chemical and mineralogical properties examined. The alumina and soundness data are shown graphically in figure 2. As clays are the only aluminum-bearing minerals observed in the rocks, the amount of aluminum, expressed as alumina, indicates the relative amount of clay in the samples. Aluminum very likely does not react chemically with the sulfate solution. The fact that the correlation of soundness with alumina is better than that with clay content suggests that the method used to determine the clay content is not sufficiently accurate for comparison with results of the soundness test.

SUMMARY AND CONCLUSIONS

The St. Louis Limestone, an important source of limestone products in the Alton - East St. Louis area, was drilled on Illinois State Department of

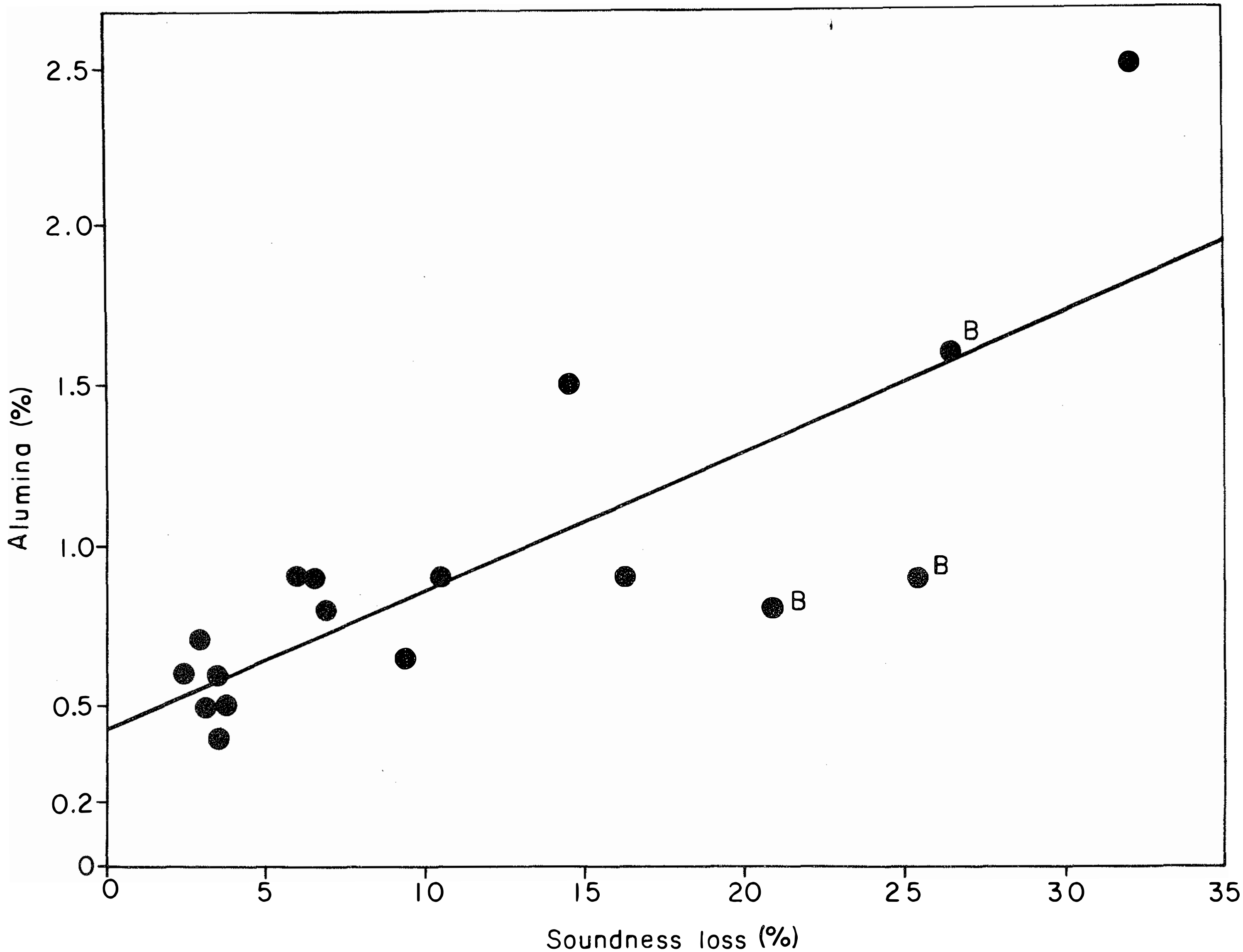

Fig. 2 - Relation of alumina to sodium sulfate soundness. Samples from breccia beds indicated by B. The regression line shown has a slope of 0.0823.

Mental Health property, Alton, Illinois, for exploratory purposes. Physical tests were made of the limestone strata and detailed descriptions and sample studies allowed a comparison of the stone's soundness with its other properties. Little or no correlation of the sodium sulfate soundness test was observed with the calcite-dolomite ratio or the total clay content measured by the difference between the percentage of insoluble residue and the quartz content (determined by X-ray diffraction methods). The linear correlation coefficient of the soundness related to the quartz content was 0.62 and to the 1N HCl insoluble residue was 0.69. The alumina content of the samples correlates better with the soundness values than all other parameters measured. The correlation coefficient of the alumina with soundness was 0.79.

If the principal mechanical factors governing freeze-thaw deterioration of carbonate rocks are the pore size distribution and rates of saturation, as postulated by Verbeck and Landgren (1960) and Powers (1955), and/or the clay-water adsorption advocated by Dunn and Hudec (1966), then these factors appear to be statistically related to the amount of alumina present in the samples examined. Thus the alumina may serve as a useful guide to sulfate soundness for fine-grained limestone deposits even though the aluminum ions may not be causally and directly related to failures of stone in the soundness test. On the other hand, consideration of the results reported here suggests that the argillaceous or shaly beds in the samples are not the sole governing property effecting sulfate soundness. The correlation with alumina is not perfect and soundness test results are no doubt related to other factors, one of the most significant of which may be the orientation of the clay material.

Comparison of the alumina content and the sulfate soundness of other carbonate rock formations, such as the Silurian dolomites in northern Illinois, may or may not yield similar correlations. Investigations based on a carefully controlled sampling program would provide helpful data that might allow more meaningful interpretation of sulfate soundness tests.

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