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## CHEMICAL AND PHYSICAL STABILITY OF CALCAREOUS SANDS USED FOR PUTTING GREEN CONSTRUCTION

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### Executive Summary November 2000

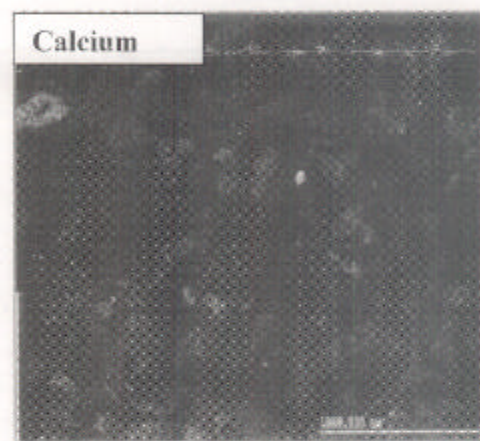
A calcareous sand can be defined as any sand that contains at least 1% CaCO<sub>3</sub> (calcium carbonate, or calcite) by weight. These sands exist in various places around the U.S. and the world, and are often used for construction of golf course putting greens and other sand-based root zone media. However, their use is discouraged because of suspected yet unconfirmed problems associated with their long-term stability. It is suspected that calcareous sands may break down, resulting in restricted or plugged pore space. The result of this is poor drainage, restricted rooting due to root zone saturation, and eventually severe thinning or death of the turf. To date, there are no reported systematic investigations into the occurrence or cause of this problem. Two primary approaches are being used in this project: controlled studies using simulated golf green profiles to study the weathering process of these sands; and a field survey which involves collection of intact cores from putting greens constructed with calcareous sands, with subsequent examination of the physical and chemical properties of these soil cores. Our objectives are to determine (1) if the use of calcareous sands results in eventual failure of the putting green to support healthy plant growth and playability, and (2) to determine the mechanism of this process, and if current management practices contribute to the problem.

Work during the past year has focused on examining the mineralogical properties of calcareous sands. Samples have been collected from across North America over the past three years. Through laboratory analysis, it has been determined that the samples collected range in calcite content from 0 to 100%. The majority of the samples contain less than 10% calcite by weight. Examination by scanning electron microscopy (SEM) reveals two different categories of calcite structure in these sands. Highly calcareous sands (70% calcite or greater) consist of discrete grains of calcite, mixed with silica particles. Sands with less than 10% calcite are comprised of quartz or silica grains with small deposits or coatings of calcite on the grains. Samples containing 30 to 40% calcite have a combination of the two. This may be significant because the two different forms of calcite may react and weather differently in the field. Future experiments will test this theory.

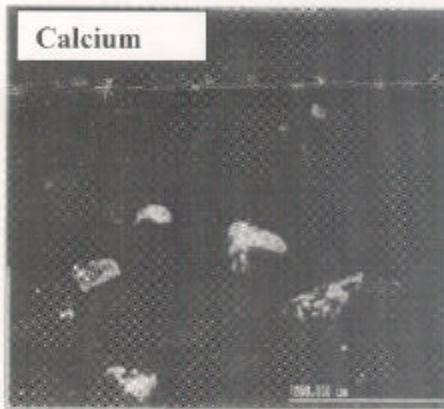
A series of laboratory experiments have been conducted using PVC columns to simulate putting green profiles. In the most recent one, the effect of phosphorus on calcium carbonate chemistry was evaluated. Phosphorus is involved in many chemical reactions in the soil, some of them resulting in the formation of highly insoluble calcium phosphate minerals. Sand amended with phosphorus was packed into columns, and the sand was treated to mimic the results of soil acidification due to fertilization in the field. Results indicate that calcite is dissolving due to acidification, as has been shown in previous experiments. However, we did not see differences between an unamended sand and sands amended with phosphorus. This will be explored further by analyzing specifically for calcium phosphate minerals and testing sands with different calcite contents.

### Mineralogical Investigations

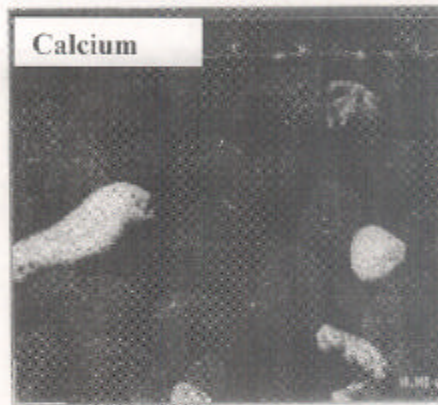
Since the November 1999 annual report, significant progress has been made in SEM analysis of sand samples. This type of analysis can reveal the varying mineralogy of calcareous sands, which may lead to an understanding of the weathering mechanism. Prior to this past year, progress in this area has been limited due to instrument access and several long periods of instrument malfunction. Samples were analyzed by scanning electron microscopy (SEM) and by energy dispersive spectroscopy (EDS) at the Utah state University SEM Facility. EDS scans, or "electron dot maps," provide a map of the elemental content of the sand grains imaged by SEM. Electron dot maps were created for calcium (Ca) and silica (Si). In the dot maps, white areas represent presence of the respective mineral. Depending on the sand, a particular grain in the SEM image may appear completely white in the Ca dot map, and black in the Si map. This would indicate that this grain is composed primarily of a calcium mineral (most likely calcium carbonate). Conversely, a grain that is black in the Ca map and white in the Si map is a silica mineral. For some samples, a grain may appear white in both the Ca and Si maps. These grains are probably silica minerals with surface deposits of calcium carbonate. Images and descriptions of several samples follow. Values given for calcium carbonate (calcite) content were determined by acid digestion.



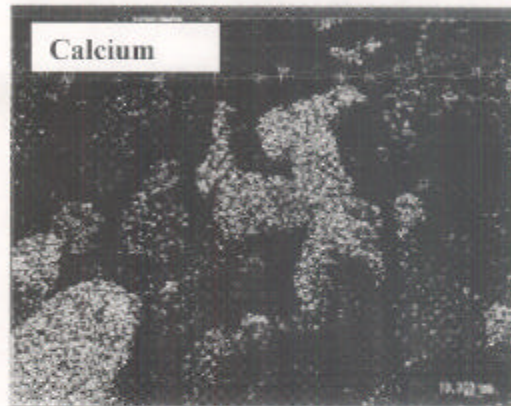
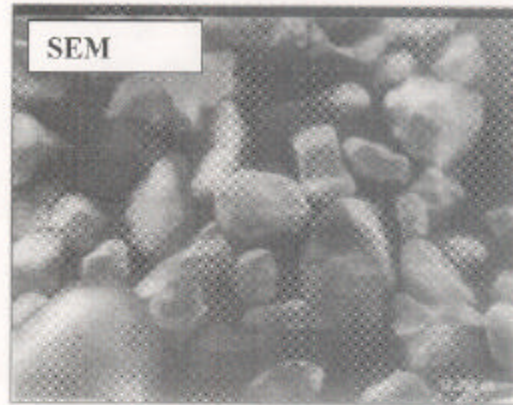
Above are SEM, Ca, and Si dot maps for a non-calcareous sand from Portland, OR. Chemical digestion indicates a trace of calcium carbonate (0.2%). The Ca dot map also indicates trace amounts, but this sand consists predominantly of silicate minerals (i.e., quartz and feldspars).



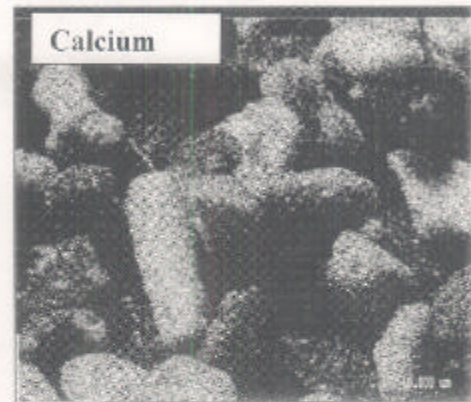
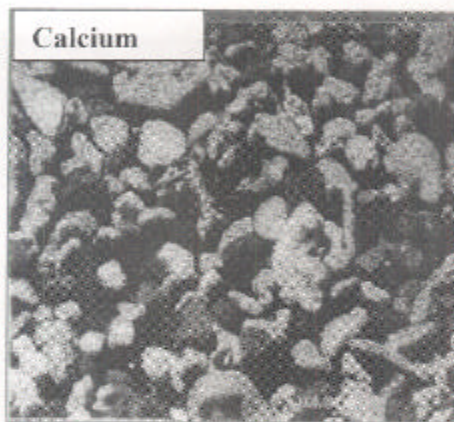
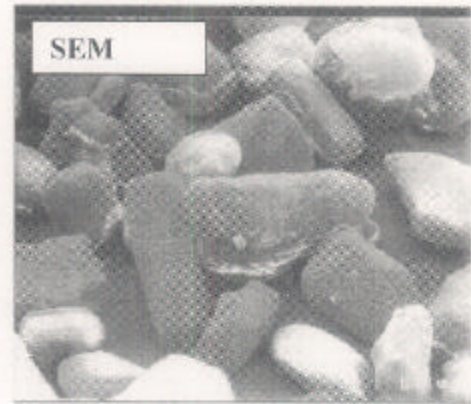
Sand of low calcite content (3%) from Spokane, WA. Careful comparison of the Ca and Si maps indicates that images appearing in the Ca map also appear in the Si map. This indicates that the Ca in this sample occurs most likely as a calcium carbonate layer on select silicate grains (i.e., quartz and feldspars).



This sample, obtained from a golf course in Las Vegas NV, is 10% calcite based on chemical digestion. (The sand reportedly came from central California, although we have been unable to identify the exact source.) The dot maps show two large discrete grains with Ca present, another large area (near bottom right) of predominantly Ca, and other smaller areas with both Ca and Si present. This suggests the presence of separate Ca mineral grains in a sand consisting mostly of silicate minerals (i.e., quartzite and feldspars). There may be a small amount of calcite coating on some grains.



This calcareous sand (35% calcite) is from Ontario, Canada. The areas illustrating high levels of Ca correspond with the darkest regions on the Si map. This sand is composed of a mixture of calcite and silicate grains. In comparing dot maps to the SEM image, calcite grains tend to be the smoother rounded grains, while the more angular grains are silicates.



This highly calcareous beach sand (70%) is from Maui, HI, and is predominantly derived from weathered coral. The images on the left indicate the high percentage of Ca present. The images on the right show again that calcite grains tend to be the smoother rounded grains, while the silicates are more angular. This sand is dominated by calcite.

The nature of the occurrence of calcite in various sands may be an important distinction. In previous experiments, we have shown that calcite can break down when subjected to acidification. Those experiments were not designed to distinguish between sands where calcite is present as discrete grains versus coatings. These different forms of calcite may have different solubilities, and may break down at different rates. This subject needs further investigation.

In addition to SEM analysis, we received samples of a sand that had been analyzed for carbonate mineral content using an optical microscope, designed to distinguish minerals based on visual characteristics. Samples from an Indiana golf course were previously analyzed in the laboratory of Darrell Schulze at Purdue University. We later received intact core samples from two putting greens from the same golf course. After conducting particle size analyses, Dr. Schulze examined two size fractions (0.25 – 0.5 mm and 0.5 – 1.0 mm) for mineral content by microscopic methods. We analyzed the same size fractions by chemical digestion.

Table 1. Percent carbonate content of two size fractions of a calcareous sand, analyzed by microscopic and chemical digestion methods.

<u>Size fraction (mm)</u>	<u>Optical microscope</u>	<u>Acid digestion</u>
0.25 – 0.5	18	25
0.5 – 1.0	23	36

There were large differences between the measured values from the different procedures. Although the samples analyzed by the two labs were collected at different times, they were from the same sites. The differences were probably due to the procedures as opposed to the samples. Differences between size fractions within each procedure were consistent. The large size fraction had about 50% more carbonate minerals than the smaller size fraction, as measured by both methods. The microscopic method also allows for a description of sand shape. This may help in describing relative amounts of calcareous and silicate particles. The microscopic method may be a useful tool in diagnosing the composition of sand. This is another technology that warrants further investigation.

#### Controlled Experiments

Previously, two “small column” experiments were conducted to evaluate the weathering potential of various sands (see previous reports). A third experiment was conducted in 2000 to assess the interaction of phosphorus with calcareous sands. The chemistry of P in the soil is complex. Some of the many reactions in which P is involved result in the precipitation of P with Ca to form a number of different calcium phosphate compounds, which are all highly insoluble. This may be significant because one of our hypotheses concerning the degradation of calcareous sands includes precipitation of Ca into insoluble mineral forms. These minerals could potentially be involved in changing the physical or hydraulic properties of the putting green profile. The previous two experiments had no P in the soil profile.

In experiment SC3, a highly calcareous sand (approximately 39%) was packed into PVC columns (1” diameter x 14” deep). The bottom 2” of the columns were first filled with gravel, resulting in a 12” sand column. The columns were first cut into 3” depth increments and taped together with waterproof tape. This simplified separation of the columns at the conclusion of the



experiment. There were three experimental treatments designed to evaluate the impact of phosphorus on calcite chemistry.

1. Unamended calcareous sand in sand column
2. 0 – 3” increment amended with fertilizer P to result in 100 ppm P in soil
3. 3 – 6” increment amended with fertilizer P to result in 100 ppm P in soil.

If Ca reacts with P, lower Ca concentrations in percolate may result, as well as accumulation of Ca-phosphates in the profile. The third treatment was designed to increase the potential for Ca-P precipitation; dissolved Ca from the 0 – 3” increment would be available to react, as well as Ca from the P amended 3 – 6” increment.

Once the columns were prepared, they were acidified as in the previous experiments. Every five days, hydrochloric acid was added to each column (0.2669M, pH = 0.60, EC = 10,700  $\mu\text{S/cm}$ , Ca = 27 mg/L). This resulted in acidifying the columns at a rate equivalent to adding 0.75 lb N (as  $\text{NH}_4^+$ ) per 1000 sq. ft. in each application (assuming complete nitrification of ammonium). This high rate of N was used to create an accelerated rate of weathering so that changes might be induced over the 30 day period of the experiment. In addition to acidification, distilled deionized water was added each day (excluding days of acid addition) at a rate equivalent to 0.15 in. (3.8 mm) of irrigation (pH = 6.96, EC = 17  $\mu\text{S/cm}$ , Ca = 2.6 mg/L). Percolate was collected continuously, and collection bottles were changed every ten days. Electrical conductivity (EC), pH, and Ca content of percolate samples were measured, and at the conclusion of the 30 day experiments columns were sectioned into 3 inch (7.5 cm) depth increments and analyzed for particle size distribution and calcium carbonate content. We have not yet analyzed for the presence of Ca-phosphate minerals. This will be done with the assistance of the soil chemistry laboratory at WSU-Puyallup.

At the conclusion of the study, there were no statistically significant differences in calcite content of the sand between treatments or profile depths (data not shown). Analysis of percolate indicated that EC, pH, and Ca content changed significantly over time (Table 2). Since there were no significant treatment x time interactions, means separation was performed only for averages of all three treatments.

Table 2. Electrical conductivity (EC), pH, and Ca content of percolate at 10 day intervals for Experiment SC3.

day	-----EC ( $\mu\text{S cm}^{-1}$ )-----				-----pH-----				-----Ca (ppm)-----			
	ck	Ptop	Pmid	mean	ck	Ptop	Pmid	mean	ck	Ptop	Pmid	mean
0	370	445	318	378	8.18	8.10	8.29	8.19	61	58	67	62
10	240	238	245	241	8.26	8.28	8.33	8.29				
20	2050	1925	1875	1950	7.97	7.94	8.01	7.97				
30	3378	3405	3450	3411	7.46	7.63	7.58	7.55	1367	1675	1583	1557
Lsd*				130				0.07				132

Ck = check; Ptop = 0 – 3” amended; Pmid = 3 – 6” amended

\*least significant difference at P = 0.05. Means separated by values equal or greater than the given lsd are significantly different.

Increases in EC and Ca with time indicate that Ca is dissolving and leaching through the profile as a result of acidification. The fact that there were no differences between treatments with respect to percolate Ca indicates that the effect of P may not be great enough to measure, or was not measurable with this system.

A larger long term column experiment has been initiated. PVC columns measuring 4" in diameter and 15" in length were constructed. These were cut into 3" depth increments and assembled with waterproof tape. Columns were filled with sand of three different calcite contents (0%, 3%, 37%). They are subject to two rates of acidification. The first rate is equivalent to the acidity produced by applying 0.75 lb N per 1000 sq ft per month. The second rate is three times the first. Irrigation is applied at a rate of 0.15 inches per day, using two different water sources: distilled water, and water with high bicarbonate levels. Free bicarbonate in the water may enhance the precipitation of calcite. Many of the reported problems with calcareous sand greens occur in areas where irrigation water may be of marginal quality, and bicarbonate is usually an important component of this. There are four replications of each treatment combination. Percolate is collected continuously and analyzed for pH, EC, and Ca monthly. After six months of acidification and irrigation, one half of the columns will be broken down into 3 inch depth increments. Selected increments will be analyzed for hydraulic conductivity and air-filled and capillary porosity. The remaining columns will be subjected to an additional six months of acidification and irrigation, and then will be similarly analyzed. The objectives of this experiment are:

1. to measure degradation of sands of varying calcite content
2. to measure physical changes in sand profiles due to calcareous sand degradation
3. to examine the impacts of irrigation water quality on sand profile degradation.

### **Future Research**

The column experiment described above will continue through 2001, with projected completion in the fall. Additional small column studies are planned to evaluate the importance of sand mineralogy (calcite grains versus calcite coating) and different components of irrigation water quality (bicarbonate levels, sodium, etc.). In addition, we plan to collect additional core samples from the Utah golf courses that were sampled in 1998. These two courses were built using the same calcareous sand source approximately four years apart (1989 and 1993). We intend to look at changes in the chemical nature of the sands in these profiles.