

NOTES

TECHNIQUE FOR THE SEPARATION OF CLINOPTILOLITE FROM SOILS

Key Words—Clinoptilolite, Separation, Soils, Specific gravity, Zeolite.

Clinoptilolite, $[\text{Ca}_x(\text{Na},\text{K})_{6-2x}](\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$, is the most abundant of the more than 40 naturally occurring zeolites (Ming and Mumpton, 1987). The clinoptilolite of particular interest in this study occurs in sediments of the Oligocene Catahoula Formation and in soils developed on the Catahoula Formation of southern Texas (Ming and Dixon, 1986). The sediments and soils contain calcite, quartz, feldspar, and smectite in addition to clinoptilolite, but the soils contain only 2–20% clinoptilolite (Ming and Dixon, 1986). Therefore, routine mineralogical and chemical analyses of clinoptilolite in soils are difficult because of dilution effects and interferences by other minerals.

By combining the low specific gravity and fine particle-size characteristics of clinoptilolite in soils, it is possible to separate the zeolite from complex mineral systems. Clinoptilolite has a specific gravity of about 2.16 (Breck, 1974), and most of the clinoptilolite in soils derived on the Catahoula sediments are concentrated in the 50–2- μm fraction (Ming and Dixon, 1986). The objectives of this study therefore were to: (1) separate clinoptilolite from soils, and (2) test for possible mineral alterations caused by the separation procedure.

MATERIALS AND METHODS

The clinoptilolite-bearing soil (Houla series, Aridic Calcicustoll) selected for this study was formed on the tuffaceous sediments of the Catahoula Formation in eastern Webb County, Texas. The A (0–25 cm), Bk1 (25–38 cm), and Bk2 (38–66 cm) horizons contain only 2–5 weight percent clinoptilolite; whereas, the BCk (66–89 cm), CBk1 (89–104 cm), and CBk2 (104–137) horizons contain 9, 15, and 20% clinoptilolite, respectively. Selected physical and chemical properties of the Houla soil were described by Ming and Dixon (1986), and a morphological description of the soil was presented by Ming (1985).

Air-dried soil samples were passed through a 2-mm mesh sieve. To enhance dispersion of the sample, cementing agents such as carbonates, organic matter, and free iron oxides were removed with separate treatments of 1 N NaOAc buffered to pH = 5, 30% H_2O_2 , and dithionite-citrate-bicarbonate, respectively (Jackson,

1974). After chemical dissolution treatments, the samples were dispersed by ultrasonification in pH 9.5 Na_2CO_3 , and the silt fraction (50–2 μm) was separated by conventional sieving and sedimentation methods. A Heat-Systems Ultrasonics Sonicator W-350 set at 105 volts in the continuous mode with a power output of 60 watts was used to sonicate samples. Chemical treatments were avoided for those soil samples requiring subsequent determinations of the cations on zeolitic exchange sites. These untreated samples were dispersed by ultrasonification in distilled deionized H_2O , and the silt fraction was separated by sieving and sedimentation methods. Both chemically treated and untreated silts were freeze-dried and then stored in a desiccator containing Drierite (anhydrous CaSO_4).

Clinoptilolite was separated from the silt fractions of the chemically treated and untreated samples using a heavy liquid. About 0.5-g samples were placed into 40-ml centrifuge tubes and dispersed by ultrasonification for 30 s in a heavy liquid mixture of s-tetrabromothane and bromobenzene, adjusted to a specific gravity of 2.28. Once dispersed, the samples were placed in a desiccator and evacuated to 30 torr with a roughing pump for 2–3 min to remove trapped air surrounding the soil particles in the heavy liquid mixture. The 40-ml tubes were centrifuged at about 2000 rpm for 5 min. Heavy separates were frozen with liquid nitrogen, and the unfrozen light fractions containing the clinoptilolite were then poured onto filter paper. Light separates were thoroughly washed with acetone applied with a squeeze bottle to remove the heavy liquids. The purity of the separation was checked by X-ray powder diffraction (XRD) using a Philips X-ray diffractometer with monochromatic $\text{CuK}\alpha$ radiation. XRD powder samples were prepared by compressing the light separate into a depression on a glass slide. The heavy liquid separation step was repeated on the light separate if XRD analysis did not indicate nearly monomineralic clinoptilolite. The complete separation procedure is summarized in Figure 1.

Types of exchangeable cations and the cation-exchange capacities (CEC) of the <2.28 sp. gr. separates were determined by a Cs-exchange method (Ming and

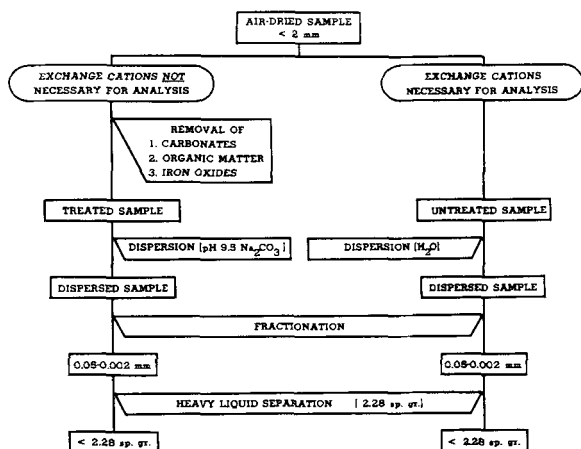


Figure 1. Flow chart illustrating separation procedure.

Dixon, 1986). Morphological characteristics of separated clinoptilolite were examined with a JEOL JSM-25II scanning electron microscope (SEM). For SEM analysis, samples were evenly dispersed over adhesive Cu tape cemented to 10-mm Al stubs, and grains were coated with about 200 Å of a Au-Pd mixture (60/40).

RESULTS AND DISCUSSION

Chemical pretreatments apparently caused no readily discernible modification of the clinoptilolite struc-

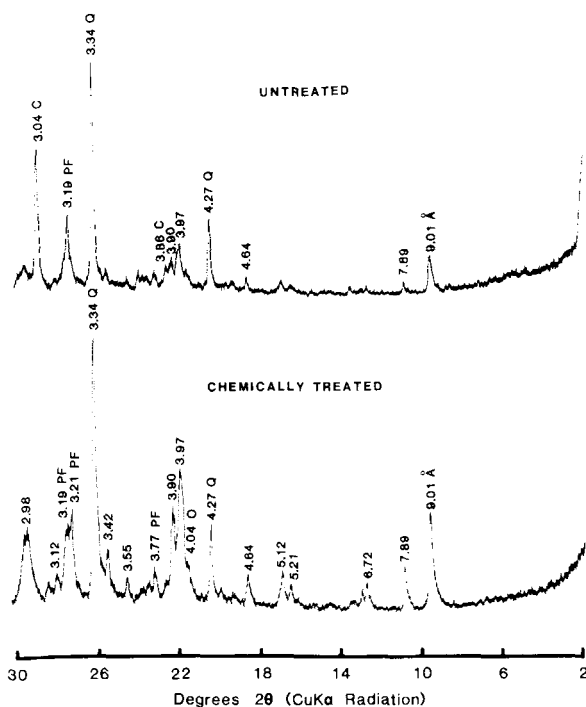


Figure 2. X-ray powder diffractograms of untreated and chemically treated silts (0.002–0.05 mm) prior to heavy liquid separation. All unlabelled peaks are clinoptilolite (Q = quartz, O = opal-CT, PF = plagioclase feldspar, C = calcite).

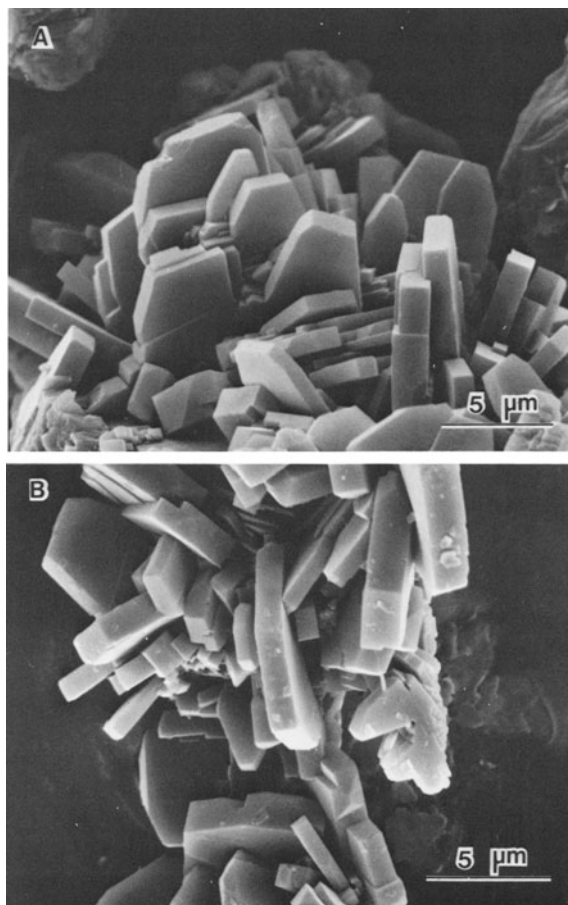


Figure 3. Scanning electron micrographs of clinoptilolite separated from the CBk2 soil horizon: A, no chemical treatments before separation; and B, chemical treatments before separation.

ture. No differences were observed for XRD patterns of clinoptilolite in the silt fraction made before and after chemical treatments (Figure 2). The only major mineralogical difference of the soils after chemical treatments was the dissolution of calcite. Removal of calcite and other cementing materials aids in the XRD identification of the zeolite as indicated by increases in peak intensities (Figure 2), probably due to concentrating clinoptilolite in the silt fraction. No evidence of dissolution, pitting, or other morphological changes on the crystal surfaces of the clinoptilolite were noted after the chemical treatments (Figure 3). Small fragments adhering to the surfaces of euhedral clinoptilolite crystals (Figure 3B) probably resulted from the mechanical breaking of clinoptilolite during the chemical dispersion phase of the separation procedure. Most of the clinoptilolite crystals in both the soil and underlying sediments displayed a morphology typical of sedimentary clinoptilolites (Mumpton and Ormsby, 1976).

For most soil samples, only one heavy liquid sepa-

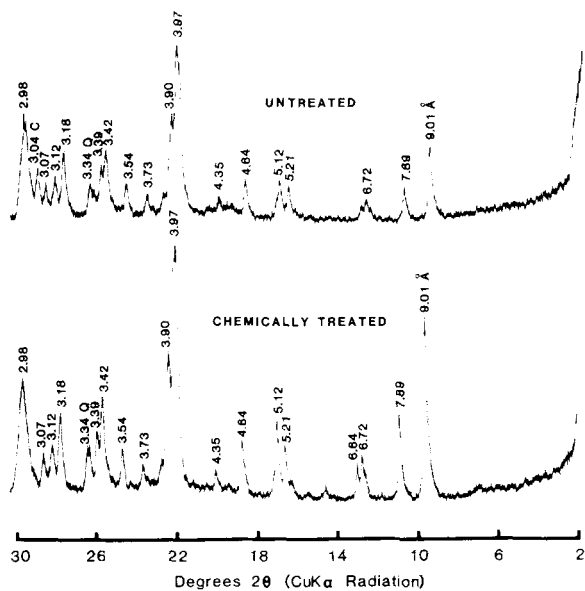


Figure 4. X-ray powder diffractograms of clinoptilolite separated in the <2.28 sp. gr. separate of silts for untreated and chemically treated samples. All unlabelled peaks are clinoptilolite (Q = quartz, C = calcite).

ration was required after chemical treatments and particle-size fractionation to separate nearly monomineralic clinoptilolite. The A (0–25 cm) and Bk1 (25–38 cm) soil horizons required an additional heavy liquid separation of the initial light fraction, primarily because of lower concentrations (i.e., 2–5%) of the zeolite in these horizons. Samples that were not chemically treated generally required two heavy liquid separations to separate clinoptilolite. Apparently, chemical treatments enhance the dispersion by removing cementing agents and, thus, unlocking the grains.

Comparisons of XRD patterns for chemically treated and untreated samples after the completion of the separation procedure are illustrated in Figure 4. The mineral contaminants in the untreated samples are calcite and quartz. Quartz is the only crystalline contaminant recognized in the treated samples. Opal-CT may be present in the silt fraction before separation by heavy liquids as suggested by a shoulder (4.04 Å) on the 331 peak (3.97 Å) of clinoptilolite (see Figure 2); however, the opal-CT seems to have been removed in the heavy

fraction after the heavy liquid separation setp (see Figure 4). This suggests that the opal-CT has a specific gravity above 2.28.

Cation-exchange capacities of sedimentary clinoptilolites vary from one deposit to another (Sheppard and Gude, 1982) depending on the amount of Al^{3+} substituting for Si^{4+} in the tetrahedral position; however, most sedimentary clinoptilolites have CECs of 175–200 meq/100 g (Semmens, 1984). The CECs of the chemically dispersed and untreated separates from the soil (66–137 cm) average 171 and 167 meq/100 g, respectively (Table 1), suggesting that the clinoptilolite concentrates are fairly clean. Clinoptilolite separated from the untreated silts is Ca-rich (see Table 1), unlike K- and Na-rich clinoptilolites found in most non-weathered, silicic, tuffaceous sedimentary deposits (Breck, 1974).

There is a disadvantage, however, in separating the zeolite using chemical dispersions. Undoubtedly, some of the exchangeable cations (e.g., Ca^{2+} , Mg^{2+} , and K^+) will be replaced by Na^+ , inasmuch as the treatment solutions contain predominantly Na^+ salts (see Table 1). The type of exchangeable cation affects qualitative and quantitative chemical analyses, thermal stability (Shepard and Starkey, 1964), and may slightly shift the XRD d-spacings upon heating (Bish, 1984). Various mineralogical measurements (e.g., measurement of structural Si and Al, distribution of Al and Si determined by solid state ^{27}Al and ^{29}Si magic angle spinning-nuclear magnetic resonance spectroscopy, and morphological features examined by SEM and TEM) may not be affected by the type of exchange cation, and for these analyses, the use of chemical cleansing and dispersion is justified.

This technique seems remarkably effective in concentrating clinoptilolite from the soils of this study and may be useful in separating clinoptilolite from other soils. Most occurrences of clinoptilolite in soils have similar mineralogical compositions as the soils used in our study (Ming and Mumpton, 1987; Ming and Dixon, 1987); however, if abundant light specific gravity (<2.28) components (e.g., volcanic glass) are in the silt fraction, this procedure may not cleanly separate clinoptilolite from these possible contaminants. A clean silt fraction (i.e., free from clay-sized materials) is necessary to prevent possible contamination from smec-

Table 1. Exchangeable cations and cation-exchange capacity (CEC) of clinoptilolite (<2.28 sp. gr. fraction) separated from untreated and chemically treated silts from selected soil horizons.

Horizon	Depth (cm)	Untreated					Chemically treated				
		Exchangeable cations (meq % of total)				Total CEC (meq/100 g)	Exchangeable cations (meq % of total)				Total CEC (meq/100 g)
		Na	Ca	K	Mg		Na	Ca	K	Mg	
BCK	66–89	18	76	2	4	162	94	3	2	1	170
CBK1	89–104	23	71	3	3	169	93	4	2	1	170
CBK2	104–137	23	71	3	3	171	93	4	2	1	172

tite and other clay minerals that may occur in the <2.28 sp. gr. fraction as aggregates of low bulk density. The presence of other zeolites having specific gravities and size characteristics similar to clinoptilolite will also complicate the procedure; however, clinoptilolite generally does not coexist with another zeolite in soils (Ming and Mumpton, 1987; Ming and Dixon, 1987). It was possible to separate clinoptilolite from the soils of this study having concentrations as low as 2 weight percent clinoptilolite, but it was time consuming to separate quantities of clinoptilolite sufficient for various chemical and mineralogical analyses. No problems were encountered in separating sufficient quantities of clinoptilolite from soils with higher concentrations of the zeolite (e.g., >5%). Inasmuch as the specific gravities of most zeolites are near that of clinoptilolite (e.g., 2.0–2.2), this procedure may be helpful in separating zeolites other than clinoptilolite from soils.

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