

CHEMICAL DISAGGREGATION OF KAOLINITIC CLAYSTONES (TONSTEINS AND FLINT CLAYS)

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Abstract—The coarse, non-clay fraction of many flint-like kaolinitic claystones often contains mineral grains diagnostic of the claystone's origin and, in the case of tonsteins (altered volcanic ashes), may also provide minerals suitable for radiometric dating. Separation of the non-clay mineral fraction is often difficult because flint clays and flint-like clays resist slaking in water and thus are difficult to disaggregate. Chemical disaggregation of resistant kaolinitic claystones may be achieved by immersion in either hydrazine monohydrate or DMSO for periods ranging from one day to several weeks. Generally, hydrazine monohydrate works more quickly and efficiently than DMSO to disaggregate most kaolinitic claystones and flint clays.

Key Words—Disaggregation, DMSO, Flint Clay, Hydrazine Monohydrate, Kaolinitic Claystone, Tonstein.

INTRODUCTION

The purpose of this report is two-fold; firstly, to describe a relatively simple and effective technique for chemical disaggregation of otherwise slake-resistant kaolinitic claystones, such as flint clays and many flint-like tonsteins, and secondly, to discuss why such techniques are useful for determining the composition and origin of these claystones.

Many hard, fine-grained, kaolinitic claystones are difficult to disaggregate in water. This resistance to 'slaking' in water is an essential part of the concept of flint clay, defined as "A very hard, smooth, flint-like fireclay that breaks with a conchoidal fracture and that develops no plasticity when ground up" (Gary *et al.*, 1974). The composition of these flint-like fireclays (flint clays) is dominantly kaolinitic; thus, they should not be confused with the rock term 'flint', which is a form of microcrystalline silica. Both flint clays and true siliceous flint seem to have developed through crystallization from a gel phase, resulting in their distinctive, tightly interlocking, microcrystalline texture. 'Flint-like' claystones bear some of the properties of true flint clays, such as conchoidal fracture and resistance to slaking, but generally are not quite as hard and have not developed from a gel phase.

Since the 1960s, efforts to distinguish kaolinite from chlorite (and later from halloysite) included intercalation of kaolinite by a variety of reagents that expanded the kaolinite, resulting in distinctive X-ray powder diffraction (XRD) patterns with increased *d*-values. Dimethylsulfoxide (DMSO) and hydrazine monohydrate were among the more effective reagents (Weiss *et al.*, 1963; Weiss and Range, 1970; Wada and Yamada, 1968;

Jackson and Abdel-Kader, 1978; Lim *et al.*, 1981; Calvert, 1984). Although the purpose of these intercalation studies was solely to aid in clay mineral identification, we adapted these treatments for the disaggregation of kaolinitic claystones. Intercalation of these polar molecules swells the kaolinite structure perpendicular to the *c* axis, thereby mechanically prying the kaolinite layers apart and facilitating disaggregation of kaolinitic claystones previously resistant to slaking.

Short-term (one day or less) applications of hydrazine monohydrate produced good results for kaolinitic tonsteins, but a flint clay took somewhat longer; disaggregation in DMSO was slower for all samples. However, we will show that extended reaction times in either reagent resulted in nearly complete disaggregation of both types of claystones, and how dilution of the reagents with water affected the rates of disaggregation.

COARSE SIZE-FRACTIONS OF TONSTEINS AND FLINT CLAYS

Separation and concentration of the coarse non-clay fraction of claystones is important for several reasons. Although the non-clay fraction is often present in only minor or trace amounts, it may provide critical evidence of origin or be useful for correlation and provenance studies (Weaver, 1963). For example, evidence of volcanic origin in tonsteins is often only evident by examination of their coarse (non-clay) fractions. This includes a mineral suite comprising volcanic phenocrysts with characteristic grain morphology (*e.g.* beta-quartz paramorphs, euhedral biotites and zircons, and replaced glass-shard forms). Non-volcanic components in the coarse fraction may include diatoms, sponge spicules, and resin rodlets, as well as a variety of forms of pyrite and other diagenetic minerals. Some volcanic

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phenocrysts, such as biotite, feldspars, zircon and amphiboles, may be used for radiometric dating (for detailed discussion of coarse fractions of tonsteins see Triplehorn and Bohor, 1986; Bohor and Triplehorn, 1993).

The composition, grain-size, and grain morphology of the coarse fraction of claystones cannot be determined satisfactorily from thin-sections due to dispersion of the grains, and rare components may be missed entirely. Instead, the clay matrix must be removed, usually by mechanical dispersion in water followed by decantation of clay. Concentrates of coarse grains may then be studied under the optical microscope in grain mounts. Chemical and mineral composition, as well as morphology and surface textures of individual grains, can be determined by XRD, scanning electron microscopy (SEM) or electron microprobe.

LABORATORY METHODS

Description of samples

A flint clay and three flint-like tonsteins were selected for a series of controlled disaggregation tests: all contain well-crystallized kaolinite as the major clay mineral and do not slake in water to any appreciable degree.

(1) A Pennsylvanian flint clay from Savage Mountain, near Grantsville, Maryland (Waage, 1950). This is a true commercial flint clay used for making fire brick; it breaks conchoidally, and will not slake in water. It will be referred to here as the Savage Mtn. flint clay.

(2) A Pennsylvanian tonstein from the Fire Clay (Hazard #4) coal of eastern Kentucky (Bohor and Triplehorn, 1981). This 10 cm thick, hard, flint-like claystone (probably recrystallized) breaks conchoidally and resists slaking in water; thus, it closely resembles a true flint clay. It will be called the Fire Clay tonstein here.

(3) A Cretaceous tonstein from the Ferron 'A' coal near Emery, Utah (Triplehorn and Bohor, 1981). This thin, dark tonstein is quite hard and tends to break semi-conchoidally, but is less flint-like than the Fire Clay tonstein. We will refer to this sample as the Ferron tonstein.

(4) A Cretaceous tonstein from the Dakota Group near Denver, Colorado: Unit 19 of Waage (1961). This cream-colored claystone is dense, compact and hard, but is the least flint-like of the three tonsteins. We will call this sample the Dakota tonstein.

Reagents used

DMSO – the chemical name of this organic reagent is dimethylsulfoxide; it is a product of paper manufacturing. The oily liquid has a strong, garlicky smell and is relatively safe to handle, although it should not be allowed to contact the skin. It is also relatively inexpensive in the technical grade. Triplehorn (2002)

published pertinent data on obtaining and handling DMSO, as well as some general laboratory techniques.

Hydrazine monohydrate – this is a N-rich organic compound, not to be confused with anhydrous hydrazine or asymmetric hydrazine which are unstable liquids sometimes used as rocket fuel. Even the much more benign hydrazine monohydrate form must be handled carefully, as it is fairly caustic and will react strongly with oxidizers, and certain metal filings or powders (especially of Fe and Mo); it is also relatively expensive.

Because of the potential danger associated with DMSO and hydrazine monohydrate (the latter much more so) researchers considering using these chemicals are cautioned to read carefully the Material Safety Data Sheets (MSDS) and follow instructions therein for their handling and disposal.

Procedure

For each test, samples were split into four 14 g aliquots of 1–2 mm (10–18 mesh) double-sieved claystone fragments and put into 125 mL bottles, to which 50 mL of reagent were added. At the end of selected time intervals, samples were transferred to 1000 mL beakers, diluted with water, stirred, and the suspended clays decanted after 15 min. This was repeated several times to remove all traces of reagents. Strong ultrasonic treatment for five minutes was followed by repeated decantation of suspended clay until the supernatant liquid remained clear. Residues were dried and weighed. The effectiveness of disaggregation is expressed in terms of the weight percent not disaggregated (dried residue). Dilutions of reagents with water were made prior to adding these to dry sample aliquots of claystone.

An initial series of experiments (Figure 1a) was designed to test the relative effectiveness of several different treatments on a single sample (Bohor *et al.*, 1993). Weighed amounts of Fire Clay tonstein were soaked for periods of 7, 14, 21 and 28 days in undiluted DMSO and in DMSO diluted with ~15% water by volume, and for 1, 3, 7 and 14 days in undiluted hydrazine monohydrate. Another set of weighed samples of this tonstein was soaked in dilutions of this latter reagent with 8, 15 and 30% water. Use of water with DMSO was based on experience which indicated that water enhanced its effectiveness, and is consistent with results obtained by Olejnik *et al.* (1968).

A second series of experiments (Figure 1b) was designed to test the relative effectiveness of hydrazine monohydrate on several different claystones. Separate weighed aliquots of each sample were soaked in undiluted hydrazine monohydrate for 1, 3, 7 and 14 days; a separate aliquot of each sample was prepared and run for each of the time periods. After the first day, the relative percentage of residue from the three tonsteins remained relatively constant over the two-week period of treatment. The residue is attributed mostly to the

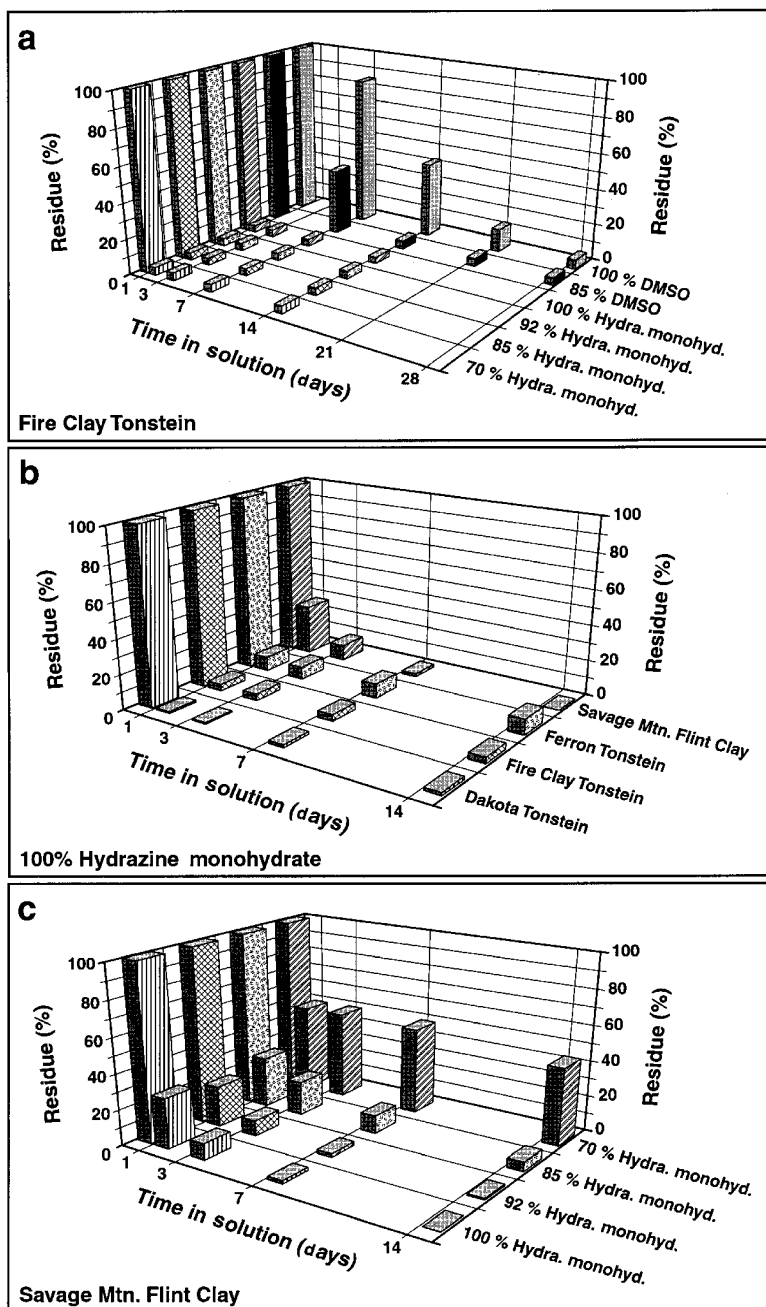


Figure 1. (a) Rate of disaggregation of Fire Clay tonstein in 100% DMSO, and DMSO diluted with 15% water, 100% hydrazine monohydrate, and 8, 15 and 30% dilutions of this reagent with water. (b) Rates of disaggregation of a flint clay and three flint-like kaolinitic claystones (tonsteins) in 100% hydrazine monohydrate. (c) Rate of disaggregation of the Savage Mtn. flint clay in 100% hydrazine monohydrate and dilutions of this reagent with 8, 15 and 30% water.

unexpandable vermicule content of these altered volcanic ashes. In contrast, the residue from the Savage Mtn. flint clay continued to decrease over the two-week period of treatment.

A third series of experiments (Figure 1c) was run on Savage Mtn. flint clay to evaluate the effects of various dilutions of hydrazine monohydrate on disaggregation rates of a true flint clay.

RESULTS AND DISCUSSION

Figure 1a shows that hydrazine monohydrate is clearly the most effective disaggregation treatment for the flint-like Fire Clay tonstein. After 1 day, no solid claystone aggregates remained. The 4% residual fraction is mainly small kaolinite vermicules, sand- and silt-sized quartz and other volcanic mineral grains, and traces of other minerals. For the DMSO diluted with 15% water,

essentially complete disaggregation was obtained in two weeks. Undiluted DMSO was notably slower, with the greatest effect occurring during the second and third weeks, and disaggregation was still incomplete at the end of four weeks.

Figure 1b shows the effect of undiluted hydrazine monohydrate on 4 different claystones. The three tonsteins were completely disaggregated within 1 day, with a residue of ~8% or less composed of small kaolinite vermicules, sand- and silt-sized quartz, and traces of other minerals. Any apparent increases of residue % with increasing time (as exemplified by the Ferron tonstein results in Figure 1b), are due either to decantation errors or sample heterogeneity. The Savage Mtn. flint clay proved to be the most resistant (Figure 1c); only about half disaggregated the first day and complete disaggregation required nearly two weeks. There appeared to be two different phases in this sample — a light-colored and a dark-colored claystone. The dark-colored phase was more resistant to disaggregation, possibly because of an organic cementing agent that accounts for its color.

The results of these experiments support our earlier uncontrolled tests, in which a larger group of tonsteins, not flint-like, were completely disaggregated by DMSO (with or without a small amount of water) over periods of between 6 weeks and 4 months. During these same time periods, two flint clays were largely, but not completely, disaggregated in this reagent.

Figures 1a and 1b show that hydrazine monohydrate often produces immediate disaggregation of most kaolinitic claystones and is usually effective in <1 day. However, if fragments of claystone >1–2 cm are used, disaggregation is slower and repeated treatments may be necessary. Sand- and silt-sized single crystals and vermicules of kaolinite may resist disaggregation even with much longer treatments in either reagent. Figure 1b shows that extended treatment in hydrazine monohydrate beyond 1 day does not substantially reduce the residual portion of the tonstein samples; this residue is composed primarily of tiny vermicules (~1 mm) of kaolinite. If all traces of kaolinite need to be removed, treatment with hydrofluoric acid will destroy even these resistant vermicules, but caution is needed to prevent solution of feldspars and other minerals that are attacked by this acid. Sieving to remove these vermicules is probably the most effective way to separate them from the crystal residue.

Generally, hydrazine monohydrate, either full strength or diluted with up to 8% water, can disaggregate even flint-like tonsteins in <1 day (Figure 1a) but some true flint clays may take about a week to completely break down (Figure 1c). DMSO can disaggregate most claystones, including tonsteins and some flint-like types, over a period of a few weeks to a few months, but is less effective on other true flint clays. Addition of a small amount of water (up to 15%) to DMSO can substantially

improve its effectiveness, probably because the smaller polar water molecules promote an initial penetration between kaolinite layers and allow the larger DMSO molecules to fill in behind them.

The experiments reported here explore only a limited number of variables that might be involved. For example, we did not test the effect of temperature or grain-size of crushed samples. Nor have we tested some of the procedures used by previous workers, such as thermal pre-treatment and reaction with carbamide (Blumenthal *et al.*, 1990), grinding with K acetate (Wada, 1961; Miller and Keller, 1981), heating the reagents in a sealed chamber (Calvert, 1984), washing with K acetate and methanol (Lim *et al.*, 1981), or adding metal salts to DMSO to increase its intercalation (penetration) efficiency (Koshevar and Lukavykh, 1992).

Our samples were relatively free of organic material, so the effectiveness of these treatments on organic-rich claystones is untested. An obvious inclination would be to pretreat for organics with oxidizing agents. Any residual oxidizing agents should be carefully removed prior to treatment with hydrazine monohydrate to avoid possible dangerous reactions with this chemical. The DMSO is used industrially as an organic solvent, so it will readily dissolve organic compounds from claystones, becoming darkened (almost to black) in the process. This darkening from dissolved organics does not seem to affect the effectiveness of DMSO for disaggregation.

The intercalation effects (swelling) of kaolinite with these reagents (especially DMSO) can be useful in applications other than disaggregating claystones. Triplehorn (2000) and Triplehorn and Severin (2002) have shown that kaolinite-cemented sandstones may also be disaggregated by treatment with DMSO. In a related area, Mason and Triplehorn (2000) discuss the use of DMSO for freeing fossils from their sandstone/mudstone matrices.

CONCLUSIONS

(1) Hydrazine monohydrate (diluted with up to 8% water) effectively disaggregates most kaolinitic claystones (including flint-like types) within a few hours to a day or so; true flint clays may require a slightly longer treatment time.

(2) DMSO (diluted with up to 15% water) adequately disaggregates most kaolinitic claystones over a period of weeks to months, but is not completely effective for some flint clays.

(3) Although hydrazine monohydrate produces faster and more complete disaggregation than DMSO, it is more expensive and more hazardous than the latter. The choice of reagent will probably depend on the relative resistance of the claystones involved, time available for treatment, and cost of the reagents.

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