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**SORPTION AND HYDROLYSIS OF CARBARYL
IN CLAY-WATER SUSPENSIONS**

presented by

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SORPTION AND HYDROLYSIS OF CARBARYL IN CLAY-WATER SUSPENSIONS

By

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ABSTRACT

SORPTION AND HYDROLYSIS OF CARBARYL IN CLAY-WATER SUSPENSIONS

By

L. Jacqueline Arroyo Daul

We studied the influence of clay preparation methods on sorption and hydrolysis of carbaryl by reference clay K-SWy-2. Three different ways of preparation were used: (1) unfractionated (whole clay). (2) Fractionated by low-speed centrifugation (clay-cent). (3) Fractionated by sedimentation (clay-sed). All clay preparations were K^+ saturated. Each preparation manifested mineral fractions with significantly different abilities to hydrolyze carbaryl to 1-naphthol, decreasing in the order: whole clay > > clay-sed. > clay-cent. The extent of 1-naphthol disappearance from solution followed the order: whole clay >>> clay-sed. > clay-cent. X-ray diffraction of the heavy fraction revealed peaks corresponding to calcite and dolomite. Aqueous slurries of whole clay and clay-sed. were alkaline, whereas the pH of slurried clay-cent. was neutral. Dissolution of carbonates with sodium acetate buffer eliminated hydrolytic activity associated with SWy-2. We recommend for particle size separation the low speed centrifugation procedure followed by treatment with acetate buffer. Sorption of 1-naphthol, by reference clay K-SWy-2, at high and low pH, was studied. We used: (1) whole clay. (2) Carbonate-free clay. (3) Carbonate-free clay amended with calcite. For whole clay and carbonate-free clay amended with calcite, ~80% and 90% of the initial concentration of 1-naphthol disappeared from solution within 24 h, corresponding to 2.0 and 2.3 mg/g of clay, respectively. In carbonate-free

clay, ~35% of the initial concentration of 1-naphthol was sorbed by the clay within 24 h. Negligibly amounts (>1%) of 1-naphthol could be recovered from clay after methanol extractions. It is apparent that 1-naphthol is rendered unextractable by K-SWy-2. XRD patterns of sorbed 1-naphthol-K-smectite suggested that 1-naphthol was intercalated in whole and carbonate-free clay. The smectite basal spacings increased implying some intercalation of 1-naphthol and/or its transformation product(s) between smectite layers. FTIR spectra of sorbed 1-naphthol-K-smectite complexes demonstrated structural Fe^{3+} reduction. FTIR spectra also showed evidence of the transformation of 1-naphthol. It appears that reduction of structural iron may be coupled to oxidation of 1-naphthol. Unextractable oxidative products of 1-naphthol may be produced and caused the darkening of color in presence of clay and carbonates.

To my son Daniel R. Merino, the sunshine of my life.

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CHAPTER 1

HYDROLYSIS OF CARBARYL BY CARBONATE IMPURITIES IN REFERENCE CLAY SWY-2

ABSTRACT

The influence of clay preparation methods on the sorption and hydrolysis of carbaryl (1-naphthyl, *N*-methyl carbamate) by K^+-saturated reference smectite SWy-2 was studied. Four methods were utilized: (1) The reference (or specimen) clay used as received was K^+-saturated (hereafter referred to as whole clay). (2) High-speed centrifugation (3295 *g*) of whole clay resulted in a pellet with three discrete bands. The upper, light-colored low-density band was obtained by manual separation (light fraction). The higher density, dark-colored material comprising the lower band (heavy fraction) was also obtained manually. (3) SWy-2 was subjected to overnight gravity sedimentation to obtain the <2 μm particles (clay-sed.) and then K^+-saturated. (4) SWy-2 was subjected to low-speed centrifugation (58-60*g*) to separate the <2 μm particle size (clay-cent.) then K^+-saturated. Each preparation of mineral fractions manifested significantly different abilities to hydrolyze carbaryl to 1-naphthol, decreasing in the order whole clay > heavy fraction >> clay-sed. > light clay > clay-cent. The extent of 1-naphthol disappearance from solution, accompanied by a progressive darkening of the clay, followed the order whole clay > heavy fraction >>> light clay > clay-sed. > clay-cent. Using ring labeled [^{14}C]carbaryl, ~61 and 15% of the total ^{14}C activity added to the whole clay and light fraction, respectively, remained unextractable. X-ray diffraction of the heavy fraction revealed several peaks corresponding to minor impurities, including calcite and dolomite. Aqueous slurries of whole clay, light fraction, clay-sed., and heavy fraction were alkaline, whereas the pH of slurried clay-cent. was neutral. It was concluded that dissolution of inorganic carbonate impurities in SWy-2 caused alkaline conditions in the slurries leading to the hydrolysis of carbaryl. Dissolution of carbonates with sodium acetate buffer eliminated hydrolytic activity associated with SWy-2. None of the four preparation methods reliably removed inorganic carbonates. The use of commercial or reference smectites in surface chemistry studies should be accompanied by a treatment with acetate buffer to remove carbonate impurities.

INTRODUCTION

Currently, ~2.04 billion kilograms of chemicals are used as pesticides each year in the United States. Agricultural usage accounts for ~77% of the total, much of which is applied to soil (Aspelin, 1997). Surface and ground waters can be contaminated with pesticides because of the intensive use of pesticides in agriculture, leading to the potential for exposure of nontarget organisms (Zalkin et al., 1984; Barceló and Hennion, 1997; Yen et al., 1997). Sorption of soil-applied agrochemicals is a key determinant of environmental fate and impact of pesticides, including mobility, bioavailability, and persistence. Numerous studies of soil-applied pesticides have indicated the importance of soil organic matter (SOM) as a dominant sorptive phase (Chiou, 1990; 1998). Other studies have demonstrated the potential importance of clay minerals in the retention of certain classes of pesticides (Sheng et al., 2001; Laird et al., 1992; Laird and Fleming, 1999) and energetics (Weissmahr et al., 1997; 1999; Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Boyd et al., 2001; Johnston et al., 2001), and that they may contribute to the degradation of carbamate pesticides, for example, carbosulfan, carbofuran, aldicarb, pirimicarb (Wei et al., 2001) and other pesticides, for example, triasulfuron (Pusino et al., 2000).

Carbaryl is the common name for the carbamic acid derivative 1-naphthyl *N*-methyl carbamate. Carbaryl has been used for about 47 years as a contact and ingestion insecticide with slight systemic properties. The most common trade name for carbaryl is Sevin. It is widely used to control several species of insects that are pests in ornamentals, trees, and food crops. Carbaryl is also used on animals and livestock as an acaricide and molluscicide. The usual application rate for carbaryl is 0.25-2 kg/ha, but in fruit trees application increases to 10 kg/ha (WHO, 1993; 1994; Howard, 1991). Current carbaryl usages in the United States and the European Union are 50000-500000 kg/year (Barceló and Hennion, 1997; Larson et al., 1996; Barbash and Resek, 1996). In 1995 and 1996, exports of carbaryl from U.S. ports to developing countries were 1.04 and 1.42 million kilograms, respectively (FASE Research Report, 1998).

Technical grade carbaryl is a white crystalline solid with low volatility. Carbaryl is poorly soluble in water (104 mg/L at 25 °C), but is soluble in many organic solvents (log K_{OW} = 1.6–2.36) (Howard, 1991; Montgomery, 1993; Roberts, 1999). Carbaryl is readily hydrolyzed in alkaline media, but resistant to hydrolysis at neutral and acidic pH (Kuhr and Dorough, 1976; Matsumura, 1985; Howard, 1991; WHO, 1993; 1994; Montgomery, 1993; Roberts, 1999). The primary hydrolysis product of carbaryl in soil is 1-naphthol (Kuhr and Dorough, 1976; Mount and Oehme, 1981; Rajagopal et al., 1983; Matsumura, 1985; Howard, 1991; WHO, 1993, 1994; Montgomery, 1993; Roberts, 1999), which can be metabolized by soil microorganisms (Mount and Oehme, 1981; Rajagopal et al., 1984; Racke and Coats, 1988; WHO, 1993, 1994), Figure 1.1. The reported persistence of carbaryl in soils is considered to be short (e.g., 2 weeks) to moderate (e.g., 16 weeks) (Rajagopal et al., 1984), depending on environmental factors such as pH and temperature, as well as the rate of application, chemical formulation, and frequency of application (Rajagopal et al., 1984). The half-life of carbaryl in soils was reported as 8-15 days, depending substantially on the aeration status (flooded *vs.* unflooded) of the soil (Howard, 1991; Rajagopal et al., 1983, 1984). Small amounts of carbaryl present in soil solution may be absorbed by plant roots but are not expected to persist in the dissolved state (Howard, 1991; Rajagopal et al., 1984; Jana and Das, 1997).

Although carbaryl is not generally considered to be recalcitrant in the environment (WHO, 1993, 1994), its transformation products (e.g., 1-naphthol) have been found in California ground-water at concentrations up to 610 µg/L (Barceló and Hennion, 1997; Barbash and Resek, 1996). Howard (1991) reported that carbaryl persisted in the environment (soil and water) from a few weeks up to 3 months. Carbaryl persisted for 3 weeks in mud, but 1-naphthol did not (Rajagopal et al., 1984). Rajagopal et al. (1984) reported that > 50% of the soil-applied carbaryl accumulated as 1-naphthol, which was more toxic to molluscs and three species of marine fish than the parent compound in 24 and 48 hours laboratory experiments (Mount and Oehme, 1981; Day, 1991).

Retention of carbaryl in soils may result from sorption by clay minerals. Carbaryl sorption by bentonite clay (composed of a large amount of smectite) was greater than by kaolinite (Rajagopal et al., 1984). The ability of smectite to adsorb organic contaminants and pesticides from aqueous solution is influenced by the exchangeable cation, as well as the extent of structural charge and its origin (Haderlein et al., 1996; Boyd et al., 2001). Aly et al. (1980) studied sorption isotherms of carbaryl and found that Ca^{2+}-bentonite exhibited the highest affinity for carbaryl, followed by an alluvial soil, a calcareous soil, and calcite. Although carbaryl is subject to alkaline hydrolysis, its degradation by calcite was not noted (Aly et al., 1980). Sheng et al., (2001) evaluated the potential contribution of smectite and organic matter to pesticide retention in soils, and concluded that homoionic K^+-smectite was a more effective sorbent than muck soil for carbaryl.

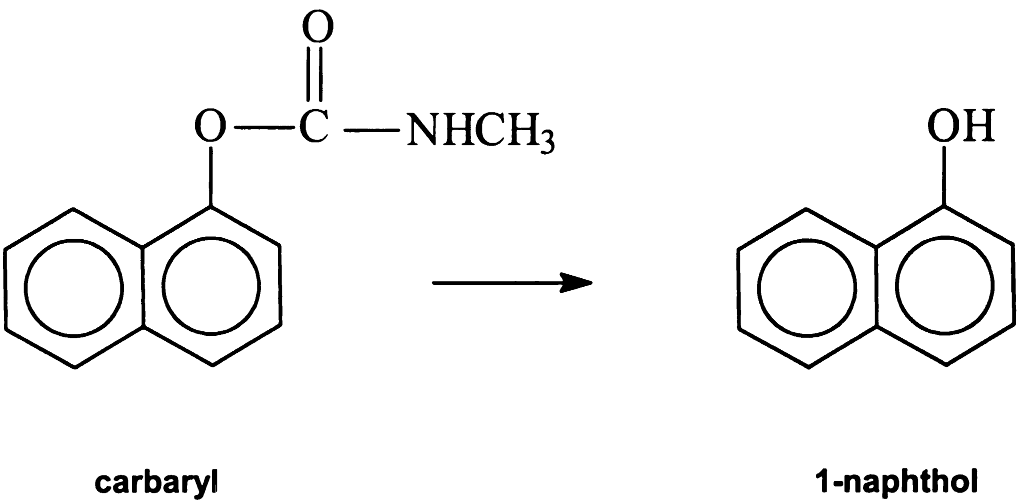

Figure 1.1. Hydrolysis of carbaryl.

The Source Clays Program of the Clay Minerals Society (CMS) was initiated in 1972 to provide a common set of reference clays to researchers (Costanzo, 2001). The initial descriptions of these materials were presented in the *Data Handbook for Clay Materials and Other Non-Metallic Minerals* (Van Olphen and Fripiat, 1979). An updated version of this book provides descriptions of materials added to the original reference set and additional data obtained with new analytical techniques (Costanzo and Guggenheim, 2001). Chipera and Bish (2001) established that most of the Source Clays, which are naturally occurring materials, contain discernible amounts of other materials, which are considered to be impurities. The nature of clay impurities may vary considerably among reference clays. Although the availability of reference clays has greatly improved our ability to compare results from different studies and laboratories, different sample preparation methods may undercut these efforts to ensure the use of common standard materials in studies utilizing clay minerals. A cursory examination of recent literature established that Source Clays are treated in different fashions prior to use, for example to prepare different homoionic forms of the clays or to remove impurities. Preparations reported in the literature include a simple wet sedimentation, that is, gravity settling overnight, to obtain the <2 µm fraction (Sheng et al., 2001; Laird et al., 1992; Boyd et al., 2001; Wei et al., 2001; Pusino et al., 2000; Liu et al., 2002; Hofstetter et al., 2003; Boyd et al., 1988; Li et al., 2003; Sheng et al., 2002; Aguer et al., 2000; García-Junco et al., 2003), and Na^+-saturation followed by low speed centrifugation to separate larger particles from the < 2 µm fraction (Johnston et al., 2001, 2002; Stucki et al., 1991). Often, reference clays are used without previous Na^+-saturation, wet sedimentation, or centrifugation (Haderlein et al., 1996). They are sometimes subject to atypical pretreatments such as the removal of organic matter and metal oxides by 0.1 M KOH solution and 0.1 M HNO_3 solution, respectively (Schmitt et al., 2002) prior to cation saturation, or do not have defined pretreatment procedures at all (Aly et al., 1980, Mogyorósi et al., 2002; Kutsuna et al., 2002; Celis et al., 1997). Experimental details such as dispersal method, sedimentation time, centrifugation forces, and type of membranes used for dialysis are often not given. Potentially these different methodological approaches may differentially include/exclude impurities and particles of different sizes, which may influence sorption and degradation processes.

OBJECTIVE

The objective of this study was to determine the influence of clay preparation/purification methods on the sorption and hydrolysis of carbaryl by reference clay SWy-2 in the K^+-saturated form. The reference clay used without purification was compared to clays subjected to centrifugation or gravity sedimentation as essential purification steps. Each of the clay preparations manifested significantly different degrees of carbaryl sorption and hydrolysis.

MATERIALS AND METHODS

The reference smectite clay, SWy-2, was used in the study. The clay was obtained from the Source Clays Repository of the CMS (Columbia, MO) and has been characterized previously (Grim and Guven, 1978; Van Olphen and Fripiat, 1979; Mermut and Cano, 2001; Vogt et al., 2002). Four separate procedures, detailed below, were used to prepare homoionic K-SWy-2.

Whole Clay

In this case, no preparation/purification step was utilized prior to making the homoionic K-SWy-2. The reference clay used as received, was saturated with K^+ by mixing 5.0 g of clay with 200 mL of 0.1 M aqueous KCl in 250 mL polypropylene screw-cap bottles and shaking on a reciprocating shaker for 24 hours. The mixture was centrifuged for 20 minutes at 3295*g* (4500 rpm) using a Sorvall GSA rotor and centrifuge (DuPont Co., Wilmington, DE). The pellet was collected and the supernatant discarded. The pellet was re-suspended in 150 mL of 0.1 M KCl and then shaken and centrifuged as above. This K^+-saturation process was repeated four times. The clay was then mixed with 150 mL of Milli-Q (deionized, d.i.) water (Millipore Corp.), shaken overnight, and centrifuged as above, and the supernatant was discarded. Another 150 mL portion of d.i. water was added to the clay pellet, and the whole was placed in porous membrane tubing (four 30 cm x 50 mm of molecular weight cutoff 6000–8000) obtained from VWR Scientific-Spectrum Medical Industries, Inc.

(Laguna Hills, CA) and dialyzed against d.i. water until free of chloride as indicated by $AgNO_3$. The sample was quick-frozen, freeze-dried, and stored.

Light Fraction

A fraction of the whole clay was collected after the formation of three distinctly colored bands was noted in the centrifuge pellet obtained after the fourth K^+-saturation step (from above). The light fraction was collected by scraping the upper part (band) of the pellet, which presented a distinguishing light-yellow color, with a metal spatula. The clay pellet was then washed with d.i. water and dialyzed as above. The sample was quick-frozen, freeze-dried, and stored.

Heavy Fraction

The pellet remaining after isolation of the light fraction was composed of two distinctly colored bands. The upper dark-yellow band was manually removed using a metal spatula. The remaining dark-brown material (heavy fraction) was redispersed in d.i. water and centrifuged at 60*g* for 6 minutes and the supernatant discarded. The sample was quick-frozen, freeze-dried, and stored.

Clay-cent.

To obtain the clay-sized particles (<2 µm), 25 g of SWy-2 was placed in a 1 L beaker with 500 mL of d.i. water and stirred for 24 hours using a magnetic stir-bar and plate to hydrate the clay and to form a stable suspension. The suspension was then poured into four 250 mL polyethylene centrifuge bottles and centrifuged for 6 minutes at 58–60*g* (~600 rpm) using a Sorvall GSA rotor and centrifuge. The supernatant suspension containing the <2 μm clay-sized particles was then collected in six polyethylene centrifuge bottles and centrifuged again for 30 minutes at 3295*g* (4500 rpm). The supernatant was discarded. The clay pellet was K^+ saturated (4x) with 0.1 M KCl, washed with d.i. water, and dialyzed as above. The sample was then quick-frozen, freeze-dried, and stored.

Clay-sed.

To obtain the clay-sized particles (<2 μm), 25 g of SWy-2 was placed in a 2 L beaker with 1.8 L of distilled water and stirred for 8 hours using a magnetic stir bar and plate to hydrate the clay and to form a stable suspension. After overnight (~18 hours) settling, the supernatant suspension containing the <2 μm clay-sized particles was poured into 12 polyethylene centrifuge bottles and then centrifuged for 30 minutes at 3295*g* (4500 rpm). The supernatant was discarded. The clay pellet was K^+ saturated (4x) with 0.1 M KCl. After K^+-saturation, the clay was washed with d.i. water until free of chloride as indicated by $AgNO_3$. The sample was then quick-frozen, freeze-dried, and stored.

X-ray Diffraction (XRD)

X-ray diffractograms of K-SWy-2 clays were determined by XRD analysis. Suspensions of K-SWy-2 were dropped onto glass slides and allowed to air-dry at ambient conditions to obtain oriented clay films. XRD patterns of oriented films were analyzed before and after 24 hours of ethylene glycol saturation at 40 °C. The XRD patterns were recorded using Cu-Kα radiation and an XRD system consisting of a Philips 3100 X-ray generator (Philips Electronic Instrument, Inc., Mahwah, NJ), a Philips 3425 wide-range goniometer fitted with a θ-compensating slit, a 0.2 mm receiving slit, a diffracted-beam graphite monochromator, and PW1877 automated powder diffraction (Philips Electronics) control software. Diffraction patterns were measured from 4 to 60° 2θ, in steps of 0.02° 2θ, at 2 s/step.

Chemicals

Carbaryl (>99% purity) was obtained from ChemService (West Chester, PA), and 1-naphthol (>99% purity) was obtained from Sigma-Aldrich (St. Louis, MO). Carbaryl and 1-naphthol solutions were prepared in 0.01 M KCl at pH 3.0 (adjusted with HCl) and used as standards for analysis by high pressure liquid chromatography (HPLC). Carbaryl-naphthalene-1-^{14}C with a specific activity of 8.4 mCi/mmol and a radiochemical purity of 97% was obtained from Sigma-Aldrich. Solutions of 40 µg/mL of carbaryl in 0.01 M KCl solution at pH 6.5, protected from light, were prepared and used immediately for the sorption/degradation experiments. In some instances, the 40 µg/mL carbaryl solution was amended with the ^{14}C-ring-labeled carbaryl. The labeled [^{14}C]carbaryl solution was prepared as follows: 100 µCi of [^{14}C]carbaryl (~2.4 mg of [^{14}C]carbaryl) was dissolved in 1 mL of methanol, and then 100 mL of 40 µg/mL unlabeled carbaryl solution was amended with 10 µL (~1 µCi) of labeled carbaryl stock solution. The final carbaryl solution contained ~0.01 µCi/mL.

Kinetics

Kinetics data concerning carbaryl disappearance and 1-naphthol appearance were determined directly in aqueous samples taken from slurries of K-SWy-2 clays using a batch method. A certain amount (5.0 mL) of a 40 µg/mL carbaryl solution (in 0.01 M KCl, pH 6.5) was pipetted into 7.4 mL borosilicate amber glass vials from Supelco (Bellefonte, PA) containing 60 mg of clay. The pH values of the clay slurries were not adjusted. Vials, in replicates of three, were mixed briefly using a Fisher Vortex mixer from Fisher Scientific (Bohemia, NY) and then mechanically rotated continuously at room temperature (23 ± 1 °C). Vials were then centrifuged at ~3500*g* for 20 minutes (whole clay and heavy fraction) or for 40 minutes (light fraction and clay-cent.) to separate solid and liquid phases. Centrifugation occurred after 2, 4, 8, 12, 16, 24, 48, 72, and 96 hours reaction times. Methanol extractions of the centrifuged clay pellets were conducted to determine (by HPLC) the amounts of adsorbed carbaryl. Amounts of carbaryl extracted from the clay pellets were obtained by subtracting the mass of carbaryl present in residual water associated with the clay after centrifugation from the mass of carbaryl extracted by methanol. To assess mass balance, experiments were run utilizing (otherwise identical) solutions containing ^{14}C-ring-labeled carbaryl, for the whole clay and the light-fraction. Concentrations of carbaryl and ^{14}C activity in the liquid phase were determined by HPLC and liquid scintillation counting (LSC), respectively.

Water and methanol were used sequentially to extract the adsorbed ^{14}C activity from the clay, which was determined by LSC. To determine residual ^{14}C activities, the extracted clays were air-dried and combusted at 900 °C in an OX-300 Harvey biological oxidizer. The $^{14}CO_2$ produced by combustion was trapped and quantified by LSC.

In another set of experiments, the pH values of clay slurries used in the kinetic experiments were measured. After it was determined that whole clay, light fraction, clay-sed., and the heavy fraction slurries were alkaline, but the pH of clay-cent. was neutral, two additional kinetic experiments were performed. First, carbaryl hydrolysis was evaluated in a suspension of calcium carbonate using the batch equilibration method. A certain amount (5.0 mL) of a 40 µg/mL carbaryl solution (in 0.01 M KCl, pH 6.5) were pipetted into 7.4 mL borosilicate amber glass vials containing 1.3 mg of calcium carbonate, which corresponded to the amount of calcium carbonate present in 60 mg of whole clay (see above), according to recent analysis of K-SWy-2 (Mermut and Cano, 2001). Vials, in replicates of three, were mixed briefly using a Fisher Vortex mixer from Fischer Scientific (Bohemia, NY) and then mechanically rotated continuously at room temperature. Aqueous concentrations of carbaryl and 1-naphthol were sampled and determined by HPLC as above. Second, inorganic carbonates in the whole clay were removed by incremental additions of a 0.5 M sodium acetate buffer at pH 5.0 (Kunze and Dixon, 1986) until the clay suspension reached pH 6.8. The Na^+-saturated clay (whole clay, but now without solid-phase carbonates) was then exchanged with K^+ ions, which was prepared using the method described above for the whole clay. Kinetics of carbaryl sorption/hydrolysis in slurries of the whole K-SWy-2 (without carbonates, at pH 6.8) were obtained using the batch method as above. The percentage of carbonate carbon present in clay samples used in our experiments was determined titrimetrically by Huffman Laboratories, Inc. (Golden, CO) by collecting the CO_2 evolved from inorganic carbonates.

Aqueous carbaryl and 1-naphthol concentrations were determined by a Perkin-Elmer HPLC (Shelton, CT) consisting of a binary LC 250 pump, a UV-vis detector set at 230 nm, and a series 200 autosampler. Chromatographic data were acquired using Turbochrom software 6.1. Chromatography was carried out using a 150x4.6 mm Supelcosil-C_{18} column, of 5 µm particle size and 120 Å pore size. The mobile phase was a mixture of 71% methanol and 29% 0.025 M KH_2PO_4 solution at pH 3.2. The injection volume was 25 µL, and the flow rate was 1.0 mL/min. This chromatographic condition allowed baseline resolution and well defined carbaryl and 1-naphthol peaks for identification and quantification.

Half-Life Analysis

The rate law for dissipation of pesticides is often described as a pseudo-first-order reaction:

$$\ln(M_t/M_0) = -k_{obs}\, t \qquad (1)$$

where M_0 and M_t are the masses of carbaryl in the whole system at time zero (applied) and time t, respectively, and k_{obs} is the observed first order rate constant (Schwarzenbach et al., 1993). A plot of the natural logarithm of the mass of carbaryl in the system versus time yielded a straight line, with its slope equal to the first order rate constant (k). The half-live ($t_{1/2}$) for the dissipation of carbaryl from solution in these clays were estimated by assuming first order dissipation processes (Lee et al., 2003) using k_{obs} from the equation 1.

$$t_{1/2} = \frac{\ln 2}{k_{obs}} = \frac{0.693}{k_{obs}} \qquad (2)$$

RESULTS

Clay samples obtained from commercial sources are often assumed to be pure; hence, they are used without further purification. The attachment of labels such as “reference clay”, “specimen clay”, or “clay mineral standard” to the samples obtained from sources such as the CMS Repository may further give the mistaken impression that these samples are free of impurities. We prepared a homoionic K-smectite under the “assumption” of sample purity. This involved mixing the reference smectite clay SWy-2 (as received from the CMS Repository) with aqueous KCl (whole clay). Centrifugation of K-SWy-2 at high speed immediately after saturation of the whole clay with K^+ showed a clear separation of particle sizes, as indicated by three distinctly colored bands in the centrifuged pellet. The upper part of the pellet (referred to as the light fraction), was a pale yellow color with a gel-like consistency. It comprised ~20% (w/w) of the whole clay. The second band in the pellet was darker yellow, and a third (bottom) one was dark brown in color. The dark-brown material comprised ~14% of the total weight of clay, and is referred to as the heavy fraction. The ionic strength of the 0.1 M KCl solution used in the K^+-saturation process inhibited clay particle dispersion, resulting in a distinct separation of particle sizes after centrifugation (at 3295*g*). This facilitated physical separation of the light and heavy fractions.

Clay-sized particles (<2 μm) were obtained from SWy-2 (prior to K^+-saturation) by gravity sedimentation are referred to as clay-sed. According to

Stokes equation, the >2 μm particles should settle 23.5 cm in 18 hours, which forms the basis of the gravity sedimentation procedure (Moore and Reynolds, 1989). The fine clay-sed. was then K^+ saturated with 0.1 M solution of KCl solution. Some of very fine particles were lost in the subsequent washing process. Removing excess salts by washing with d.i. water caused re-suspension (dispersion) of some clay that could not be effectively separated even after high speed centrifugation. The amount of this material discarded in the washing water was minimized as much as possible. The clay-sed. obtained corresponded to 60–70% (w/w) of the original SWy-2 and consisted almost entirely of dark-yellow material plus a small amount of brown material.

Clay-sized particles were also obtained by low speed centrifugation to separate coarser particles (Moore and Reynolds, 1989). The clay-cent., obtained from the resultant aqueous suspension corresponded to ~70% (w/w) of the original SWy-2. When this suspension was centrifuged at high speed (3295*g*) the pellet consisted almost entirely of an intermediate yellow material plus a very small amount of brown material.

XRD patterns of both the whole clay and light fraction (Figure 1.2) show the distinguishing smectite peaks in the air-dried and ethylene glycol-solvated states. Basal spacings of 11.2 and 11.5 Å in the air-dried state for whole clay and light fraction, respectively, correspond to the d_{001} XRD peak of smectite. The 11.2 and 11.5 Å peaks in the XRD patterns of the whole clay and the light fraction shifted to 16.2 and 17.0 Å, respectively, after ethylene glycol saturation, which expands the smectite interlayers. The light-fraction and clay-cent. appeared to be without crystalline impurities based on XRD analysis.

Additional peaks not assignable to smectite occurred in the XRD patterns obtained for the whole clay and clay-sed., indicating the presence of crystalline impurities. The 3.34 Å peak indicates the presence of quartz, and the 3.24 Å peak may be due to feldspar. The XRD pattern for the heavy fraction is also shown in Figure 1.2. Peaks corresponding to quartz, orthoclase and plagioclase feldspar, calcite, dolomite, and rutile are apparent. Chipera and Bish (2001) and Vogt et al. (2002) reported similar impurities in their investigations of reference clays.

Batch equilibrium sorption experiments were conducted in an attempt to measure the distribution of carbaryl between K-SWy-2 and water. During preliminary kinetic studies of carbaryl sorption by the whole-clay, a color change in the clay from pale yellow to gray was noted. It was clearly observable within minutes after the whole clay had been mixed with aqueous solutions of carbaryl, and the color intensified over time. Interestingly, the light fraction did not manifest a similar change of color under otherwise identical conditions. Slight color formation was observed with the clay-cent. but did not change over time. Similar color formation was observed with the clay-sed., and the color intensified slightly over time. When mixed with aqueous carbaryl, the heavy fraction immediately developed the gray color, which intensified over time as observed with the whole clay.

Analysis by HPLC of the aqueous phase from K-SWy-2 slurries clearly demonstrated that carbaryl was hydrolyzed to 1-naphthol (Figure 1.3). Hydrolysis of carbaryl in blanks not containing clay was minimal after 48 hours, and the amount hydrolyzed remained constant at ~8% (of initial carbaryl concentration) between 48 and 96 hours. Disappearance of carbaryl and the formation of 1-naphthol in solution were evident in slurries of each clay preparation, but to different extents. During the initial 24 hours reaction time, the rate and extent of carbaryl degradation followed the order whole clay > heavy fraction >> clay-sed. > light clay > clay-cent. Accumulation of 1-naphthol in solution maximized at ~24 hours for the heavy fraction and the whole clay and then declined steadily during the remainder of the experiment. The decline in aqueous phase 1-naphthol was more gradual in the heavy fraction than in the whole clay. Overall, it appeared that carbaryl hydrolysis and disappearance of 1-naphthol (produced via carbaryl hydrolysis) were most rapid in slurries that contained smectite and the heavy fraction together (i.e., the whole clay). Carbaryl hydrolysis, as evidenced by 1-naphthol accumulation in solution, was much slower in slurries of the light fraction than clay-sed. and negligible in the clay-cent (Figure 1.3c–e).

In experiments utilizing the whole clay, ~80% of carbaryl plus 1-naphthol (on a molar basis) had disappeared from the aqueous solution within 48 hours (Figure 1.3a). If sorbed, this would correspond to ~3.0 mg of carbaryl/g of clay. This is in contrast to the light fraction and fine clay-cent., where ~80% of carbaryl plus 1-naphthol (on a molar basis) was present in the aqueous solution after 48 hours of reaction time. In these slurries, disappearance of carbaryl from solution occurred only during the first 2 hours, after which its concentration remained almost constant. The calculated half-lives of carbaryl were 9 and 10 hours in the presence of the whole clay and the heavy fraction, respectively. Due to the slow hydrolysis of carbaryl in light fraction and clay-cent. slurries, its half-life in these systems was estimated at 204 and 770 hours, respectively. Although carbaryl disappeared completely, and 1-naphthol disappeared substantially from solution in slurries of the whole clay, quantities of these compounds that could be extracted from the whole clay (or the heavy fraction) by methanol were small (<10% of amount presumed sorbed based on disappearance from solution). Recoveries from extraction of the light fraction or the clay-cent. with methanol were much higher, ca. 30 and 65%, respectively (Figure 1.4). These extracts contained primarily carbaryl with very little 1-naphthol present.

To achieve mass balance for carbaryl in the slurries of the whole clay and light fraction, ^{14}C-ring-labeled carbaryl was used. Total recoveries were 100 ± 6% (Tables 1.1 and 1.2). For the whole clay slurries after 48 hours, ^{14}C activity in the aqueous phase was ~16% of the total ^{14}C activity added (Table 1.1). Water and methanol extracted 25% of the total ^{14}C activity added (or ~29% of the activity adsorbed by the clay). Approximately 61% of the total ^{14}C activity added was sorbed by the whole clay but not extractable after 48 hours of reaction time (Table 1.1). For the whole clay slurries in general, the amount of solution phase activity decreased steadily over time (up to 48 hours), and the amount of sorbed but not extractable activity increased. For the light fraction slurries after 48 hours, ^{14}C activity in the aqueous phase was ~50% of the total ^{14}C activity (Table 1.2). Water and methanol extracted 31% of the total ^{14}C activity added (or ~67% of the activity sorbed by the clay). Approximately 15%

of the total carbaryl/naphthol activity was sorbed by the light fraction but not extractable after 48 hours of reaction time.

The pH values of the various clay slurries increased in the order clay-cent. (pH 6.7) < light fraction (pH 8.2) < clay-sed. (pH 8.5) < whole clay (pH 8.8) < heavy fraction (pH 9.1). Note that this order correlates very well with rates of carbaryl hydrolysis in these slurries (Figure 1.3). In an aqueous suspension of calcium carbonate, the pH was 9.5, and hydrolysis of carbaryl proceeded rapidly, similar to that observed in slurries of the whole clay and heavy fraction (Figure 1.3a,b,f). Although hydrolysis of carbaryl was rapid and complete, 1-naphthol accumulated in a nearly stoichiometric quantity in the calcium carbonate suspension.

Sodium acetate buffer (pH 5) was used to remove carbonate impurities from SWy-2 (Kunze and Dixon, 1986) by titrating the clay suspension until the pH was 6.8. The Na^+-saturated clay was subsequently exchanged with K^+ and then amended with carbaryl. After 48 h, ~30% of carbaryl had disappeared from the aqueous solution. This corresponds to an amount sorbed of ~1.0 mg/g of clay (Figure 1.3g). There was negligible formation of 1-naphthol in this clay slurry.

DISCUSSION

The availability of specimen (or reference) clays from the Clay Minerals Source Repository and their extensive characterization (van Olphen and Fripiat, 1979; Chipera and Bish, 2001; Grim and Guven, 1978; Mermut and Cano, 2001; Vogt et al., 2002) are important in providing standardized materials for research in clay, soil, and environmental sciences. Although there are published methods for the separation and purification of clays from soils and sediments (Kunze and Dixon, 1986; Gee and Bauder,1986), and for purifying clay samples (Moore and Reynolds, 1989), there is still no general recognition of the need to purify reference (or commercial) clays prior to use (Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996). It is probably most common in the fields of clay and soil science to purify clay mineral samples by fractionation based on particle size, although this is not performed consistently or by any uniform method. Clay-sized particles are generally defined as those <2 μm in effective spherical diameter. These are usually obtained by gravity sedimentation or by low-speed centrifugation to remove the >2 μm particles. The clay-sized particles remain suspended and are physically isolated by separating the non-clay-sized sediment from the aqueous suspension containing clay-sized particles. Frequently, however, no attempt is made to purify or fractionate clay minerals obtained from commercial sources, encouraged perhaps by monikers such as "reference" or "specimen" clays and, perhaps, by the lack of a standard purification procedure.

There are a number of minor impurities in reference SWy-2 that could reasonably lead to the hydrolysis of carbaryl, including mineral forms of Ti, Mn, and Fe (Mermut and Cano, 2001; Vogt et al., 2002). However, in searching for the causative hydrolytic agent, we noted a direct relationship between the pH of the clay suspension and its hydrolytic activity. Only the clay-cent. had a pH of <7 in aqueous suspension, and it was the only clay sample devoid of apparent hydrolytic activity (i.e., no 1-naphthol formation). We hypothesized that dissolution of some carbonate mineral in the aqueous clay suspensions may raise the pH sufficiently to cause alkaline hydrolysis of carbaryl. Calcite and/or dolomite were likely candidates because small peaks corresponding to these minerals were resolved in the XRD pattern of the heavy fraction (Figure 1.2). Direct measurement of inorganic carbonate showed it to be present in the whole clay (0.12%), and heavy fraction (0.12%), but it was not detectable in the light clay or fine clays (<0.02%). Previous authors have reported CaO contents between 1.68 and 0.05% (Mermut and Cano, 2001; Vogt et al., 2002); the CaO content in the bulk CMS sample of SWy-2 was higher than in the corresponding clay-sized fraction (Chipera and Bish, 2001).

Adding carbaryl to an aqueous calcite suspension resulted in the rapid and stoichiometric hydrolysis of carbaryl to 1-naphthol (Figure 1.3f). Furthermore, the hydrolysis of carbaryl by whole clay suspensions was eliminated when SWy-2 was subjected to carbonate dissolution by sodium acetate buffer (Kunze and Dixon, 1986) prior to use (Figure 1.3g). These results seem to confirm our suspicion that inorganic carbonate impurities present in SWy-2 were responsible for causing the alkaline pH, leading to alkaline hydrolysis of carbaryl to 1-naphthol.

In slurries where the hydrolytic activity was high (e.g., whole clay), recovery of sorbed substrate by extraction with methanol was low (Figure 1.4 and Tables 1.1 and 1.2), indicating some irreversible process. In contrast, recoveries of sorbed substrate from slurries with low hydrolytic activity (e.g., light fraction or clay-cent.) were much higher and consisted almost entirely of carbaryl. These results suggest some reaction of 1-naphthol after its adsorption to smectite clay. This is consistent with our observation of a color change (to dark gray) of the clay in the most hydrolytically active clay slurries.

This study provides a case-in-point that small amounts of impurities present in reference clay mineral samples may substantially alter their apparent sorptive properties or reactivities. These impurities may not be completely removed using common purification procedures based on particle size separation (Pusino, et al., 2000; Sheng et al., 2001; Wei et al., 2001). In this study, even miniscule quantities of inorganic carbonates, carried through the sedimentation procedure, were sufficient to cause substantial alkaline hydrolysis of carbaryl. Such reactivity, present in the reference clay, as well in the purified or fractionated reference clays, may mistakenly be attributed to the clay mineral itself, rather than to the actual causative agent. It is advised that reference or specimen clays should not be used in surface chemistry studies without such prior treatment. We suggest adoption of some standard fractionation/purification procedure for commercially available reference clays prior to their use in studies on sorption and reactivity. The essential steps of such a procedure would include (1) Hydration of the clay, (2) separation of the <2 μm clay-sized particles by low-speed centrifugation or gravity sedimentation, (3) dissolution of carbonates and soluble salts with sodium acetate buffer, (4) washing with water to remove residual salts and decrease ionic strength, and (5) metal homoionic saturation.

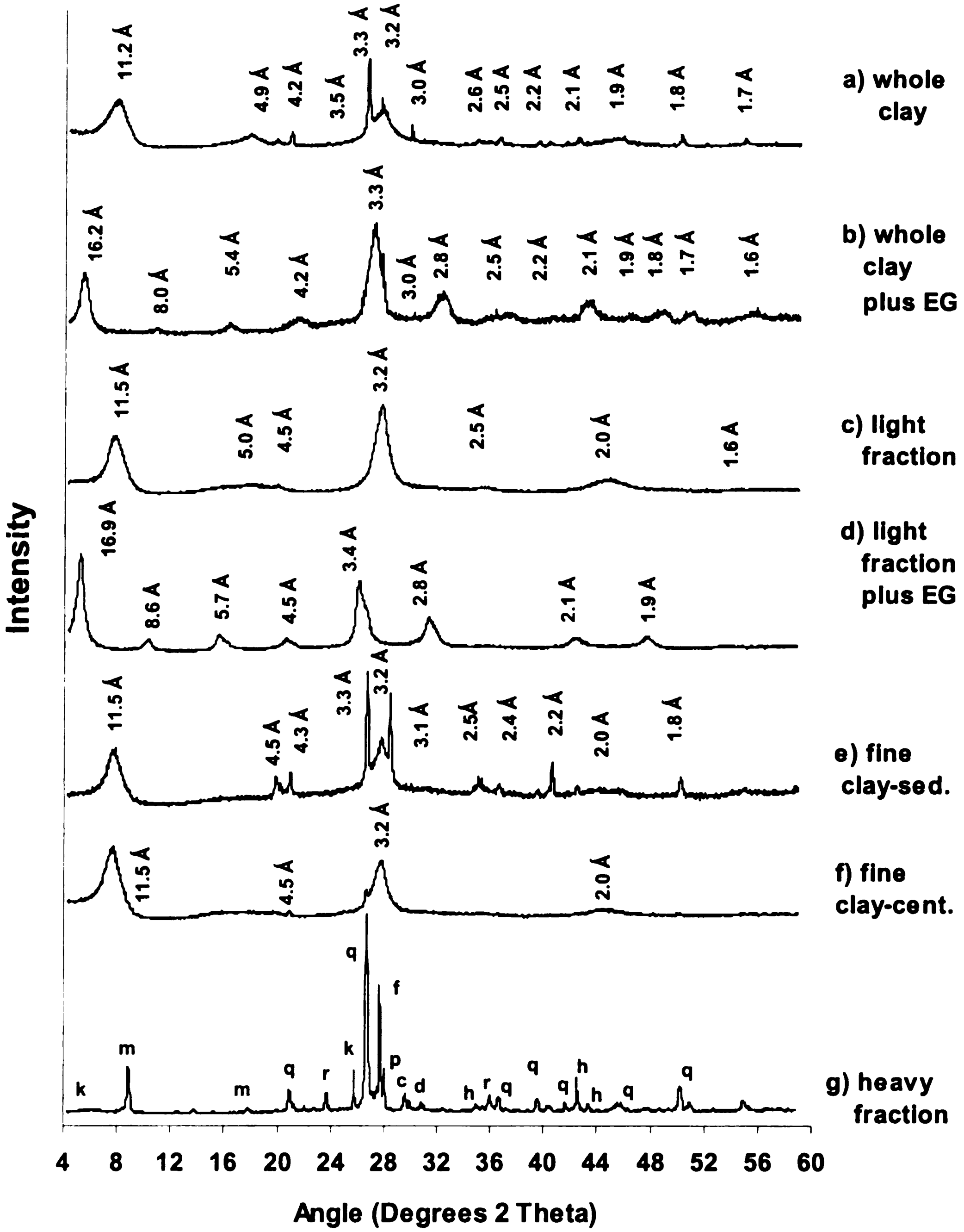

Figure 1. 2. XRD patterns of K-SWy-2: (a) whole clay, oriented air-dried and (b) after ethylene glycol salvation; (c) light fraction, oriented air-dried and (d) after ethylene glycol salvation; (e) clay-sed., oriented air-dried; (f) clay-cent., oriented air-dried; (g) heavy fraction, oriented air-dried. Lower case letters show the probable mineral present in the heavy fraction, k = chlorite (?), r = rutile, q = quartz, h = iron oxide, c = calcite, d = dolomite, m = mica and/or illite, f = orthoclase feldspar, and p = plagioclase feldspar.

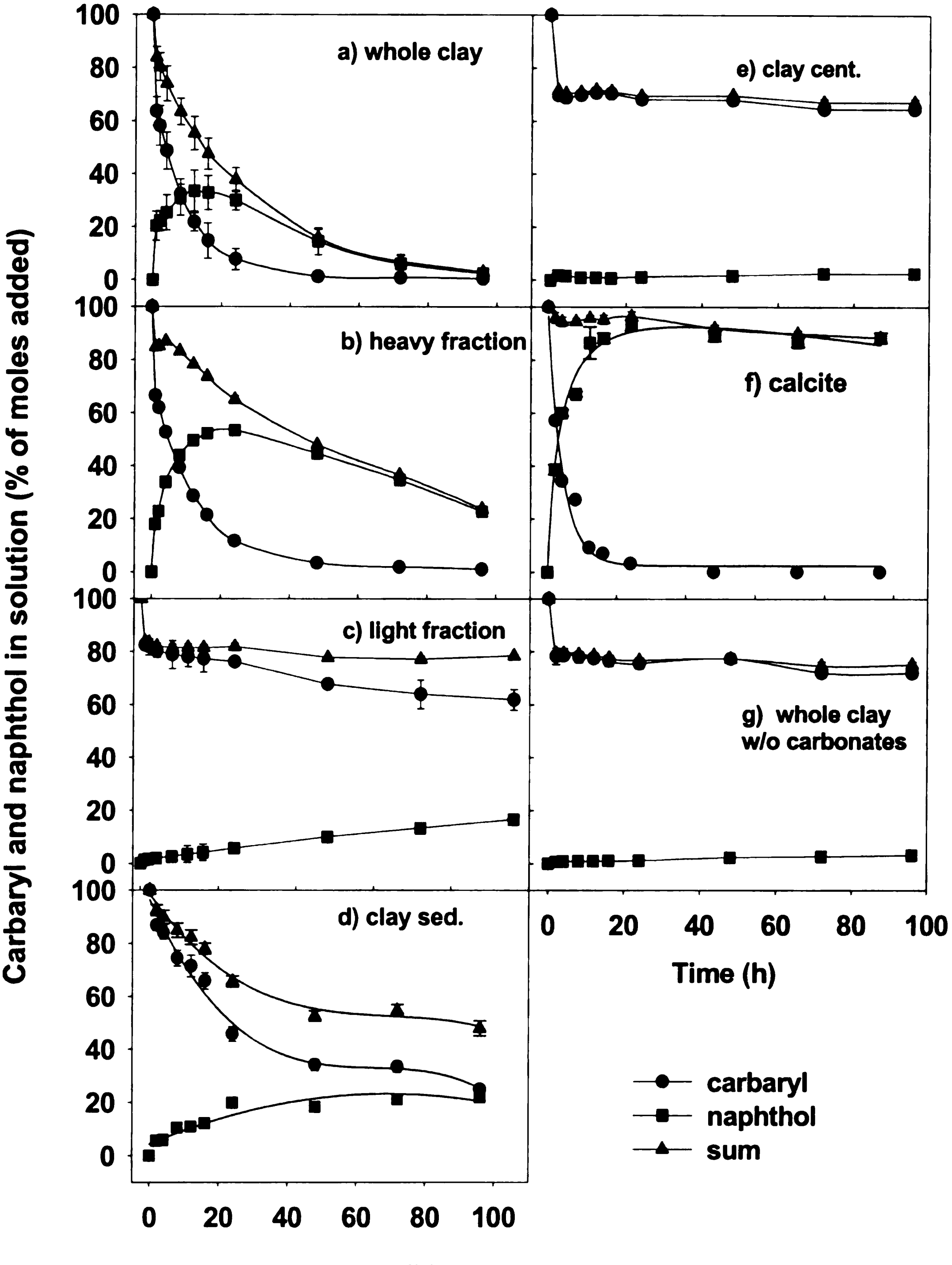

Figure 1.3. Hydrolysis of carbaryl by smectite clay K-SWy-2: (a) whole clay; (b) light fraction; (c) heavy fraction; (d) clay-cent.; (e) clay-sed.; (f) whole clay (now without carbonates); (g) hydrolysis of carbaryl by calcite.

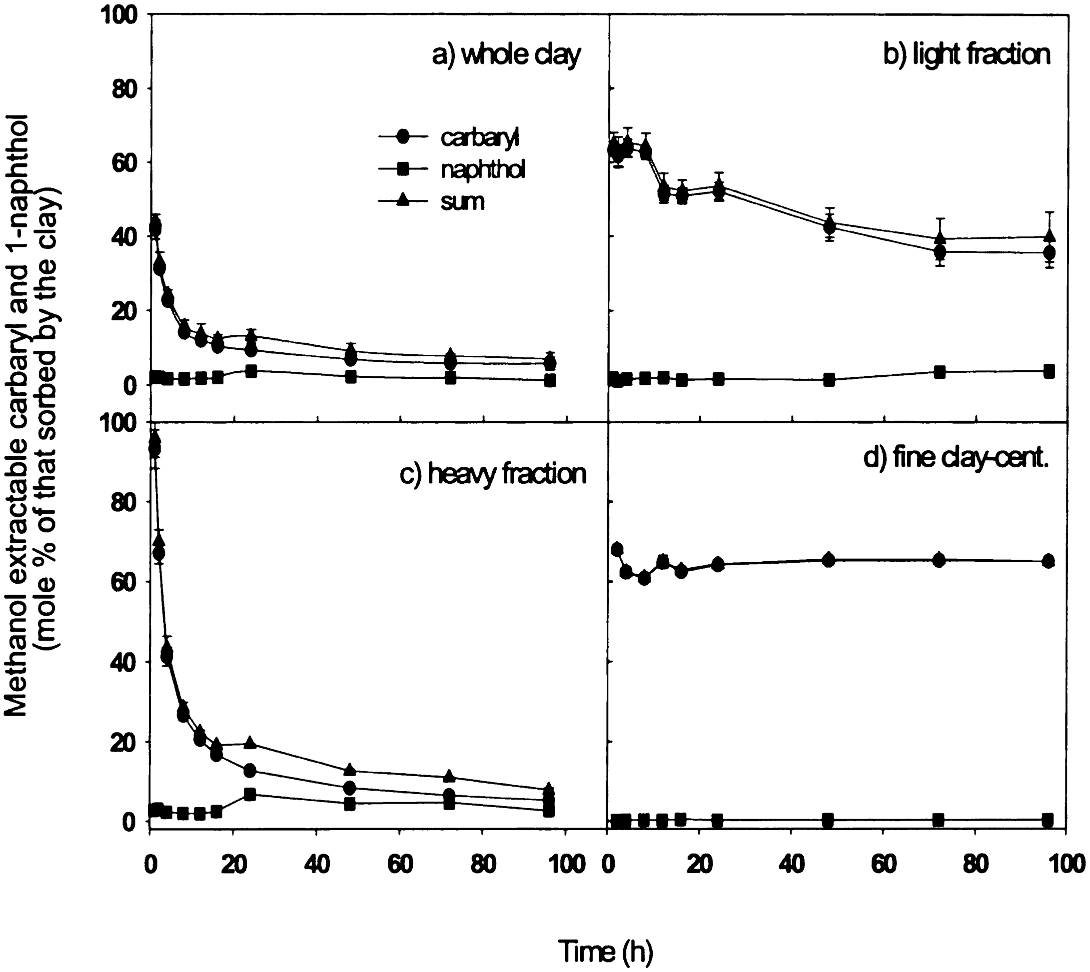

Figure 1.4. Amounts of methanol extractable carbaryl and 1-naphthol from K-SWy-2: (a) whole clay; (b) light fraction; (c) heavy fraction; (d) clay-cent.

Table 1.1. Time-Dependant Distribution of ^{14}C Activity in Whole K-Smectite (SWy-2) Slurries Amended with [^{14}C]Carbaryl

					^{14}C activity[a]						
time	in solution		sorbed by K-SWy-2		sorbed but water extractable		sorbed but MeOH extractable		sorbed and nonextractable		total recovery
(h)	(%)	SD	(%)	SD	(%)	SD	(%)	SD	(%)	SD	(%)
2	80	1	25.9	0.1	4.0	0.3	4.6	0.2	17.3	0.2	106
8	59	1	43	2	2.0	0.1	11.3	0.4	30	2	101
12	53	4	49	2	2.1	0.3	13.4	0.3	34	2	102
16	49	10	53	3	3.0	0.4	12	4	38	2	102
24	41	2	62	2	3.1	0.3	14.0	0.2	45	2	103
48	16	1	85.7	0.1	6.6	0.2	18.0	0.4	61.1	0.3	102

[a] Expressed as a percentage of the initial added ^{14}C activity.

Table 1.2. Time-Dependent Distribution of ^{14}C Activity in Light Fraction K-Smectite (SWy-2) Slurries Amended with [^{14}C]Carbaryl

	^{14}C-carbaryl[a]										
time	in solution		sorbed by K-SWy-2		sorbed but water extractable		sorbed but MeOH extractable		sorbed and nonextractable		total recovery
(h)	%	SD	%	SD	%	SD	%	SD	%	SD	%
2	75	3	19	2	2.0	0.4	8.1	0.1	9	1	94
8	73	2	24	3	1.8	0.3	12.2	0.3	10	2	97
12	70	1	29	3	1.4	0.2	18	1	10	3	99
24	63	2	35	2	2.5	0.4	19	1	13	3	98
48	52	1	46	2	3.2	0.5	28	2	15	1	99
72	47	2	54	4	3.7	0.2	35.4	0.4	15	4	101

[a] Expressed as a percentage of the initial added ^{14}C activity.

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CHAPTER 2

A SIMPLE METHOD FOR PARTIAL PURIFICATION OF REFERENCE CLAYS

ABSTRACT

The influence of clay preparation procedure on sorption and hydrolysis of carbaryl (1-naphthyl, *N*-methyl carbamate) by the reference smectite clay SWy-2 was examined. For research purposes, reference clays are sometimes used without purification, or more commonly, the <2 μm size fraction is obtained by gravity sedimentation or low-speed centrifugation. We determined that these common methods were unreliable in removing inorganic carbonate impurities present in SWy-2, and that these impurities caused alkaline conditions in aqueous clay suspensions leading to the alkaline hydrolysis of carbaryl to 1-naphthol. The hydrolytic activity of K-SWy-2 disappeared once carbonates were eliminated. Two methods were evaluated for preparing K-SWy-2 devoid of inorganic carbonates. In Method A inorganic carbonates were first removed by incremental additions of a 0.5 M sodium acetate buffer (pH 5.0) until the clay suspension reached pH 6.8, followed by low-speed centrifugation to obtain the <2 μm size fraction; in Method B the order of these steps was reversed. Carbaryl hydrolysis was used as a probe to determine the effectiveness of the two clay purification methods. Homoionic K-SWy-2 obtained by Methods A and B produced near neutral pH when suspended in water and hydrolysis of carbaryl in these suspensions was not evident. In this regard, both clay preparation

methods were acceptable. However, there were procedural advantages with Method B, which is therefore recommended for the partial purification of reference clays, as detailed in this paper.

INTRODUCTION

Our previous study showed that carbaryl (1-naphthyl, *N*-methyl carbamate) hydrolysis in slurries of the reference clay SWy-2 was due to the presence of inorganic carbonates impurities (e.g., calcite and dolomite) (Arroyo et al., 2004). Dissolution of these carbonates created alkaline conditions leading to the alkaline hydrolysis of carbaryl to 1-naphthol. Other organophosphorus and carbamate pesticides are also unstable under alkaline conditions (Fukuto, 1987). Carbonates are often present in reference clays as sparingly soluble clay-sized minerals (Grim and Guven, 1978; Mermut and Cano, 2001; van Olphen and Fripiat, 1979; Vogt et al., 2002). Although such carbonates are not reliably removed by common purification procedures based on particle size separation (Arroyo et al., 2004), they are subject to selective dissolution (Kunze and Dixon, 1986; Gee and Bauder, 1986; Moore and Reynolds, 1989). Treatment of clays with strong acids (e.g., HCl) to remove carbonates can cause destruction of the crystalline lattice of clay minerals (Gee and Bauder, 1986; Loeppert and Suarez, 1996). Therefore, weak acid treatment with 0.5 M sodium acetate buffer at pH 5 is recommended for removal of carbonates from clay mineral samples (Kunze and Dixon, 1986).

Although several methods have been published for separation and purification of clays from soils and sediments (Jackson, 1979; Kunze and Dixon, 1986; Gee and Bauder, 1986; Moore and Reynolds, 1989), and for purifying clay samples (Moore and Reynolds, 1989), it appears that there is no general recognition of the need to purify commercially available clay minerals prior to use in surface chemistry studies, and certainly no uniform experimentally validated method in use for doing so. Many previous studies of the complexation polymerization, sorption and degradation of organic contaminants and pesticides by clays have reported some type of clay purification method based on wet sedimentation (Haderlein and Schwarzenbach, 1993; Aguer et al., 2000; Pusino et al., 1988,1995, 2000, 2003; Mortland and Halloran, 1976; Sawhney et al., 1984, Soma et al., 1986; Sheng, et al., 2001; Mingelgrim et al., 1977; Fusi et al., 1983; Wei et al., 2001), whereas other studies used clay samples without prior purification (e.g.,Forteza et al., 1989; Haderlein et al., 1993, 1996; Li et al., 2003). Experimental details regarding purification such as dispersal methods, sedimentation times, centrifugation forces and times, and type of membranes used for dialysis, etc, are often different or unspecified. This situation may have been exacerbated by the commercial availability of "standard", "reference" or "specimen" clays, and the inference by some that such samples are free of impurities. Certainly failure to purify clay minerals and/or utilization of nonuniform purification procedures diminish our ability to compare and reproduce results from different studies and laboratories even when standard clay mineral samples are used. Consequently, there is a need to operationally standardize purification procedures for reference clays.

OBJECTIVE

The objective of this study is to develop a convenient and reliable procedure for the partial purification of reference clays, avoiding any harsh chemical treatments that may cause alteration or destruction of the clay structures. All relevant experimental details and observations regarding such a method are described herein. The recommended method should advance the use of standard materials in surface chemistry studies utilizing clay minerals.

MATERIAL AND METHODS

The reference smectite clay (SWy-2) used in this study was obtained from the Source Clays Repository of the Clay Minerals Society (Columbia, MO). Milli-Q (deionized, d.i.) water (Millipore Corp., Bedford, MA), was used for all sample preparations.

Method A. Removal of carbonates prior to particle size fractionation

Sample dispersion

The reference clay, as received, was suspended in d.i. water for 24 hours while stirring using a magnetic stir-bar and plate to hydrate the clay. The suspension was obtained by mixing 5.0 g of clay with 100 mL of d.i. water in a 1 L beaker.

Chemical Removal of Carbonates.

After suspending the clay, the pH was measured (>7) and then the clay suspension was titrated with 0.5 M sodium acetate buffer, pH 5.0 (Kunze and Dixon, 1986), until the pH of the clay suspension reached 6.8. During the titration, water was added to decrease the viscosity of the clay suspension, which increased over time with the incremental addition of the sodium acetate buffer. The total amount of water added to the clay was 800 mL (700 mL d.i. water added + 100 mL d.i. water added initially). After a pH of 6.8 was reached initially, the sample was stirred for one hour, and the pH increased to 8. Titration with 0.5 M sodium acetate was then continued until pH 6.8 was again reached. This step was repeated three times until pH remained constant at 6.8 for 30 minutes. The total volume of 0.5 M Na-acetate buffer added was 39.5 mL.

Removal of Soluble Salts.

The neutral clay suspension was poured into four 250 mL polyethylene centrifuge bottles, closed with screw-on caps, and then centrifuged for 30 minutes at 3295*g* (4500 rpm) using a Sorvall GSA rotor and centrifuge (DuPont Co., Wilmington, DE). The supernatant containing soluble salts was discarded. The clay pellets from the four bottles were combined into two bottles, and then washed by resuspending the clay in 200 mL of d.i. water. The two bottles were laid on a rotary Innova 2300 Platform Shaker (New Brunswick Scientific Co., Edison, NJ) and shaken at 120 rpm for 8 h or until well resuspended. The two bottles were then centrifuged as above and the clear supernatant discarded.

Particle size fractionation.

The clay, now presumably free of carbonates and other soluble salts, was resuspended in 200 mL d.i water by laying the bottles on a rotary shaker and shaken at 120 rpm for 8 hours. The <2 µm clay-sized particles were obtained by separating the >2 µm particles using low speed centrifugation (58-60*g* (~600 rpm) for 6 minutes (Costanzo, 2001). The supernatants, containing clay suspensions of <2 µm particles, were siphoned into separate 250 mL centrifuge bottles. The >2 µm particles (sediment) were collected, quick-frozen, freeze-dried and stored. The clay suspension was subject again to high speed centrifugation (3295*g* for 30 minutes) and the clear supernatant discarded. Clay-size particles were combined in one 250 mL centrifuge bottle and then subjected to K-saturation (see below).

Method B. Particle size fractionation and partial physical removal of carbonates

Sample dispersion

The reference clay, as received, was suspended in d.i. water for 24 hours while stirring using a magnetic stir-bar and plate to hydrate the clay. The suspension was obtained by mixing 5.0 g of clay with 100 mL of d.i. water in a 250 mL polyethylene centrifuge bottle.

Particle size fractionation

To obtain the <2 μm clay-sized particles, the clay suspension was centrifuged for 6 minutes at 58–60*g* (~ 600 rpm) using a Sorvall GSA rotor and centrifuge (Costanzo, 2001). The supernatant suspension containing the <2 μm clay-sized particles was then siphoned and collected into a 250 mL polyethylene centrifuge bottle. The pellet containing the >2 μm particles was re-suspended with 100 mL of d.i. water by mixing briefly using a Vortex mixer, and then subjected to low speed centrifugation as before to recover additional clay-sized particles. The supernatant suspension was siphoned and added to the previously collected suspension of clay sized materials. The >2 μm particles (sediment) were collected, quick-frozen, freeze-dried and stored for scanning electron microscopy (SEM) analysis.

Chemical Removal of Carbonates.

The clay suspension from above was then titrated with 0.5 M sodium acetate buffer at pH 5.0 (Kunze and Dixon, 1986) to pH of 6.8. After the desired pH was reached, the sample was stirred for one hour during which the pH remained stable. The total volume of sodium-acetate buffer added was 6.5 mL. Compared to Method A this process yielded a stable pH more quickly and did not require numerous increments of water to reduce viscosity of the suspension. The volume of acetate buffer used to remove carbonates was considerably less in Method B than in Method A.

Removal of Soluble Salts

To promote flocculation of the clay, ~1.5 g NaCl was added to the single bottle containing the clay suspension and stirred for approximately 5 minutes until the salt was dissolved, then the suspension was centrifuged for 20 minutes at 3295*g* (4500 rpm). The supernatant containing soluble salts was discarded. The clay pellet was resuspended in 200 mL of d.i water. The centrifuge bottle was laid on a rotary shaker and shaken at 120 rpm for 8 hours to wash out the excess NaCl. The clay suspension was subject again to centrifugation at 3295*g*

(4500 rpm) for 30 minutes and the supernatant containing soluble salts was discarded. The clay-size particles were then subjected to K-saturation.

Preparation of homoionic clays for Methods A and B

The clay pellets contained in the 250 mL centrifuge bottles from Methods A and B were each resuspended in 200 mL of 0.1 M KCl; the bottles were laid on a rotary shaker and shaken at 120 rpm for 8 hours, then the clay suspension was centrifuged for 20 minutes at 3295*g* (4500 rpm) and the supernatant containing excess KCl discarded. This step was repeated four times. Then, the clay was resuspended in 200 mL of d.i. water and shaken at 120 rpm on the rotary shaker for 8 hours, then centrifuged at 3295*g* (4500 rpm) for 30 minutes. The supernatant containing excess KCL was discarded. A 50 mL portion of d.i. water was added to each clay pellet to resuspend the clay, and the whole was placed in porous membrane tubing (two 30 cm x 50 mm sections of molecular weight cut-off 6000-8000, obtained from VWR Scientific-Spectrum Medical Industries, Inc., Laguna Hills, CA) and dialyzed against distilled water until free of chloride as indicated by $AgNO_3$. Both samples were quick-frozen, freeze-dried and stored in polyethylene bottles.

A description of materials and methods used to prepare other clay samples referred to in this paper, i.e., whole clay (no purification at all is used), clay-sed. (obtained by gravity sedimentation without carbonate dissolution), clay-cent. (obtained by low speed centrifugation without carbonate dissolution), and light fraction (a sub-fraction of SWy-2, comprised of the lightest colored material, obtained manually), as well as characterization of mineral phases by x-ray diffraction (XRD) were previously reported (Arroyo et al., 2004). Each of those samples was K-saturated by the same procedure reported above.

Scanning electron microscopy (SEM)

The K-SWy-2 samples were studied by scanning electron microscopy (SEM); the SEM analysis included qualitative analytical x-ray energy-dispersive spectra (EDS) and imaging of gold/carbon-coated clay films using a JSM-6400V Scanning Microscope equipped with a Noran Detector unit. The EDS spectra were obtained using electron-beam spot sizes of ~2–10 μm, and a lifetime of 120 seconds. Analyses were standardless.

Chemicals

Carbaryl (>99% purity) was obtained from ChemService (W. Chesnut, PA) and 1-naphthol (>99% purity) was obtained from Sigma-Aldrich (St. Louis, MO). Carbaryl and 1-naphthol solutions were prepared in 0.1 M KCl at pH 3.0 (adjusted with HCl) and used as standards for analysis by high pressure liquid chromatography (HPLC) (see below). Sodium acetate trihydrate was A.C.S. reagent and obtained from J.T. Baker (Phillisburg, NJ) and glacial acetic acid was obtained from Mallinckrodt-Baker, Inc. (Paris, KY).

Sorption kinetics

Kinetics of carbaryl adsorption were measured in slurries of K-SWy-2 clays using a batch method. Solutions of 40 µg/mL of carbaryl in 0.1 M KCl at ambient pH 6.5, protected from light, were prepared and used immediately for the sorption/degradation experiments. Five mL volumes of a 40 µg/mL carbaryl solution (in 0.1 M KCl, pH 6.5) were pipetted into 7.4 mL borosilicate amber glass vials (Supelco, Bellefonte, PA,) containing 60 mg of clay. Contents of the vials, in replicates of three, were mixed briefly using a vortex mixer, then continuously rotated for various time intervals at room temperature (23 ± 1 °C), then centrifuged at ~3500*g* for 20 minutes to separate solid and liquid phases. Centrifugation occurred after 2, 4, 24, 48, 72, and 96 hours reaction times. Aqueous concentrations of carbaryl and 1-naphthol were determined by HPLC using a Perkin Elmer (Shelton, CT) instrument consisting of a binary LC 250 pump, a UV-vis detector set at 230 nm, and a series 200 autosampler/injector. Chromatographic data was acquired using Turbochrom software 6.1. Reverse-phase chromatography was carried out using a 150 x 4.6 mm Supelcosil-C_{18} column, of 5µm particle size and 120Å pore size (Supelco). The mobile phase was an isocratic mixture of 71% methanol and 29% water at pH 3.2 (adjusted with HCl). The injection volume was 25 µL and the flow rate was 1.0 mL/min. Identification and quantification of carbaryl and 1-naphthol were achieved using analytic standards of known concentrations.

Methanol extractions of the centrifuged clay pellets were conducted to determine (by HPLC) the amounts of adsorbed carbaryl. After determining carbaryl concentrations in aqueous phase from kinetics experiments, amounts of aqueous solutions from weighted vials were taken out with a Pasteur pipette. Vials containing clay pellets and residual water were weighted. Five mL of methanol minus the volume of residual water remaining in clays were added to vials containing clays and residual water. Vials were well mixed using a Vortex mixer and then rotated continuously at room temperature. Vials were centrifuged at 24 hours to separate clay from methanol phase. Methanol carbaryl concentrations were determined by HPLC as above. Amounts of carbaryl extracted from clay were obtained by subtracting the mass of carbaryl present in residual water (determined gravimetrically) associated with the clay after centrifugation from the mass of carbaryl extracted by methanol.

RESULTS

Two methods were used to isolate carbonate-free clay-sized particles from the reference smectite SWy-2. In Method A, carbonates were removed prior to separating the <2 µm particles and in Method B after separating the <2 µm particles (Method B), by low-speed centrifugation. Clay samples prepared by these methods were compared to the reference clay (SWy-2) as received (whole clay) and to clays where the <2 µm particles were obtained, without removal of carbonates, utilizing either gravity sedimentation (clay-sed.) or low speed centrifugation (clay-cent.); details in preparation of the latter three clays can be found in Arroyo et al. (2004).

Method A

In Method A, clay-sized particles (<2 µm) were obtained from SWy-2 after removal of carbonates. To briefly re-cap, SWy-2, as received from the CMS Repository, was mixed with d.i. water (1:20) to form a suspension. Carbonates were removed by slow addition of sodium acetate solution (pH 5) to lower the clay suspension pH to 6.8. During this operation the viscosity of the clay suspension increased making it difficult to stir with a magnetic bar. Since the clay suspension became too thick for effective mixing, addition of water was necessary to allow effective stirring, causing substantial increase in total volume of the suspension. By the end of the titration (pH 6.8) the volume of clay suspension was four times greater than that in Method B. High speed centrifugation was used to separate the clay from the aqueous phase containing soluble salts. The clay-sized particles were then obtained by washing the clay to remove soluble salts, resuspending the clay in d.i. water, and low-speed centrifugation. The yield of clay-sized particles was ~74% (w/w) of the original SWy-2. Visually, it consisted mostly of yellow colored material plus a small amount of brown colored material. The dark-brown sediment (obtained during low speed centrifugation) comprised about 10% of the original weight of the SWy-2 clay, free of carbonates. In Method A, the total mass removed during isolation of carbonate-free clay-sized particles (obtained by subtracting the mass of the neutralized-clay and neutralized-sediment from the initial amount of clay) was ~16% (w/w) of the whole clay.

Method B

In Method B, the reference clay was initially suspended in d.i. water as above, and then clay-sized particles (<2 μm) were obtained by low speed centrifugation *prior* to removal of carbonates by titration with Na-acetate buffer. The volume of acetate buffer needed to remove inorganic carbonates from the <2 μm fraction (i.e., obtain stable pH = 6.8) was only one sixth that used in Method A where the whole clay was titrated. After titration with Na-acetate buffer, the <2 μm fraction was isolated by high speed centrifugation, but washing the clay pellet with deionized water caused dispersion of some clay particles. Incomplete flocculation of the clay was apparent from the presence of turbidity and the yellow color of the supernatant. The method was therefore modified by increasing the ionic strength of the original <2 μm clay suspension (acetate buffer titrated) to 0.1 M by adding NaCl prior to high-speed centrifugation. The previously suspended fine particles appeared to flocculate and be effectively removed from suspension by centrifugation as indicated by loss of turbidity and color in the supernatant. The material obtained in this fashion, after K^+ saturation, corresponded to 77% (w/w) of the original SWy-2 and consisted mostly of yellow colored material plus a very small amount of brown material. The dark-brown sediment (obtained from the original low-speed centrifugation) comprised about 18% of the total weight of clay, and is referred to as the >2 μm fraction, and contains carbonates and other impurities. In Method B, the mass removed by titration of the fractionated clay (obtained by difference from the initial amount of clay minus the sum of neutralized-clay and sediment) comprised about 5% (w/w) of the whole clay.

The time required to achieve a stable pH of 6.8 while titrating with the Na-acetate buffer was ~3 times greater in Method A than in Method B. Additionally, ~6-fold greater volume of sodium acetate buffer was used to remove carbonates in Method A as compared to Method B. These both represent procedural disadvantages to Method A. The yields of clay-sized particles recovered from Methods A and B were similar.

Carbaryl sorption

Batch equilibrium experiments were conducted to measure the distribution of carbaryl between K-SWy-2 and water and to evaluate hydrolysis of carbaryl to 1-naphthol. Hydrolysis of carbaryl was used as an ultra-sensitive probe to detect the presence of carbonates impurities in the various clay preparations. In our previous study (Arroyo, et al., 2004) we observed a color change in SWy-2 from pale-yellow to gray when carbaryl was added to suspensions of the unfractionated (whole) clay or to clays fractionated based on conventional <2 μm particle size separations, but where carbonates were not removed using acetate buffer. In this study, the carbonate-free clays obtained by Methods A and B did not manifest a change of color when mixed with aqueous carbaryl solutions.

Two kinetic experiments of carbaryl sorption and hydrolysis were performed utilizing the carbonate-free clay slurries prepared by Methods A and B, and the results compared to our previous data (Arroyo, et al., 2004). The previous study utilized whole unfractionated clay, whole clay subjected to gravity sedimentation overnight (clay-sed.), and whole clay subjected to low-speed centrifugation (clay-cent.); the latter two methods are commonly used to obtain the <2 μm particle size fraction (Figure 2.1). Sorption in the carbonate-free clay slurries appeared to reach equilibrium within 4 hours, ~30% of carbaryl was removed from aqueous solution in these slurries during the 96 hours equilibration. This corresponds to an amount sorbed of ca. 1.0 mg/g clay. No appreciable production of 1-naphthol was noted in these slurries. This is in contrast to the fate of carbaryl in suspensions of the whole clay and clay-sed. (Arroyo et al., 2004), where disappearance of carbaryl from aqueous solution was continuous; 80% and 40% of carbaryl had disappeared within 48 hours, respectively. In slurries of the whole clay, 1-naphthol concentration maximized at about 24 hours, then declined to nearly zero between 24 and 96 hours, whereas with clay-sed., 1-naphthol concentrations were nearly constant between 24 and 96 hours (Figures 2.1.a,b). There was negligible formation of 1-naphthol in slurries of the clay-cent., similar to the carbonate-free Methods A and B clay slurries (Figures 2.1.c–e).

Recovery of sorbed carbaryl by methanol extraction of the carbonate-free clays was ~100% (Figures 2.2.a,b). This is in stark contrast to the very small quantities of carbaryl and 1-naphthol that could be extracted with methanol from whole clay (Arroyo, et al., 2004).

Scanning electron microscopy (SEM)

The >2 µm particles (sediment without carbonates removed and named "heavy fraction" in our previous study, Arroyo et al., 2004) from Method B were examined to determine particle morphologies and semi-quantitative elemental compositions. Figure 2.3 shows x-ray maps of the >2 µm fraction for O, Fe, Na, Mg, Al, Si, K, Ca, and Ti. Note the presence of a Ca-rich but Si-poor particle in the lower left that is probably a carbonate mineral. Figure 2.4 shows a photomicrograph of the light fraction (Arroyo et al., 2004), a sample much like clay-cent. but containing only the pale yellow-colored material. As described in Arroyo et al. (2004), this version of purified smectite yields a suspension pH of 8.2 and causes carbaryl to hydrolyze to 1-naphthol. The SEM image (Figure 2.4) looks like a pure smectite due to its closed fine texture and honeycombed arrangement of particles, presenting no visual evidence of solid phase carbonates. Also EDS spectra for whole clay show the presence of Ca and Ti (Figure 2.5.a), but neither were detected in EDS spectra of the light fraction (Figure 2.5.b). Thus, solid-phase carbonates can be present and chemically active, despite not being apparent in SEM images (Figure 2.4), and undetected by x-ray diffraction (Arroyo et al., 2004) or by EDS analysis (Figure 2.5.b).

DISCUSSION

Since 1972 the Clay Minerals Society (CMS) has provided a common set of well characterized reference clays for research purposes through the Source Clays Project (Costanzo, 2001). The reference clays facilitate comparisons of data obtained from different studies and laboratories. However, different sample purification/preparation methods may undercut efforts to ensure the use of common standard materials in studies utilizing clay minerals, and in allowing comparison of results from different studies. It is probably most common in the fields of clay and soil science to purify clay mineral samples by fractionation based on particle size, although this is not performed by any uniform method. In some instances, commercially available clays, including the CMS reference clays, are used as received without purification. The variety of clay preparation methods utilized in the past demonstrates the necessity of developing a standard method for purifying reference clays prior to their use in surface chemistry studies. Such a method would be useful to clay scientists and those in related fields such as soil and environmental sciences that commonly use commercially available clay mineral samples.

It has been demonstrated that smectite clays may potentially contribute to the degradation of certain carbamate pesticides (Wei, et al., 2001) and other pesticides (Pusino, et al., 2000). In our previous study (Arroyo et al., 2004) we observed both the apparent sorption and hydrolysis of carbaryl in slurries of the reference smectite K-SWy-2. The extent of carbaryl disappearance from solution and appearance of its hydrolytic product 1-naphthol in solution varied depending on the clay preparation and purification method. We reported that several different methodological approaches used would not reliably removed carbonate impurities, and that such carbonate impurities may influence or even control sorption and degradation processes. We concluded that even trace quantities of carbonates in K-SWy-2 could, through dissolution, cause alkaline pH manifesting the alkaline hydrolysis of carbaryl. Such hydrolytic activity, present even in partially purified clays (e.g. after overnight gravity sedimentation), could be mistakenly attributed to the clay mineral itself or to some other reactive mineral component. Other reference clays obtained from natural deposits may contain even greater amounts of carbonate impurities (e.g., Hectorite SHCa-1), where commonly used purification approaches based on sedimentation or low-speed centrifugation would be even less proficient at removing carbonates. In fact, when we collected the <2 µm particle size of the hectorite SHCa-1 clay by gravity sedimentation and low-speed centrifugation methods, both caused alkaline pH after stirring the clay in water for a few minutes. It therefore seems apparent that particulate carbonate impurities as well as carbonate cementing materials should be removed by selective acid dissolution, along with other soluble salts (e.g., gypsum and metal oxides present as coatings), which potentially may be reactive or cause chemically reactive conditions.

Particle size separations are commonly recommended prior to mineralogical analyses of mineral components present in soils and other geosolids. Other methods are used to remove carbonates, organic matter and free iron oxides from soil samples (Jackson, 1979; Kunze and Dixon, 1986; Gee, and Bauder, 1986; Moore and Reynolds, 1989). The need for use of such treatments when dealing with soil samples is widely recognized. Specimen clays or reference clays, like soils, are natural materials that may require pretreatment to remove impurities. In a previous study (Arroyo et al., 2004) the use of the carbamate pesticide carbaryl, which is subject to alkaline hydrolysis, provided an excellent case-in-point that reference clays should be chemically treated to remove carbonates, which might otherwise dissolve and cause alkaline conditions leading to unexpected chemical reactivity. To achieve this, the method of Kunze and Dixon (1986) was modified to avoid subjecting the clay to high temperatures or to large volumes of buffer at low pH, yet to ensure that reference clays be free of carbonates and other soluble impurities. Dissolution of carbonates in clay suspensions, and removal of CO_2 (g), was reliable achieved by constant stirring in an open beaker accompanied by the slow addition of Na-acetate acid buffer (pH 5). The clay suspensions titrated to stable pH of 6.8 in this manner minimized the potential for silicate dissolution.

In developing and evaluating methods for preparing carbonate-free clay sized materials, it was noted that a clay-water mixing period of 24 hours was required to ensure the hydration and dispersion of clay particles. Although, Na^+-saturation provides a high degree of hydration and gives effective dispersion of the clay, we did not add Na^+ during the initial clay-water mixing period in order to prevent flocculation of the clay during the acetate buffer titration (Moore and

Reynolds, 1989). The initial clay-water ratio of 1:20 suggested by (Costanzo, 2001) was appropriate.

The fractionation process to obtain the <2 μm particles and the purification of SWy-2 clay by Na-acetate buffer by Method B was simpler and easier than by Method A. Using Method A to remove carbonate impurities from the SWy-2 clay suspension by titration with Na-acetate buffer, prior to particle size separation was laborious and required a considerable amount of time (one working day). Carbonates dissolved by the Na^+-acetate buffer caused an increase in suspension viscosity. The addition of water to decrease the ionic strength caused a large increase in volume of clay suspension and consequently an increase in the time spent for centrifuging. It was also more difficult to obtain a stable pH of 6.8 when titration of the clay with Na-acetate buffer was the initial purification step, i.e., in Method A. In Method B, after the initial clay-water mixing period, the clay-sized particles are separated by low-speed centrifugation (~600*g*). During this step, some clay-sized particles were removed along with the coarser particles. Therefore, the centrifuge pellet was redispersed in water to resuspend and capture more clay-sized particles. Carbonate impurities present in the resultant fractionated SWy-2 clay suspension were easy to eliminate by titration with Na-acetate buffer, i.e., much less buffer was required and pH in the titrated sample was more stable. When preparing larger amounts of clays, the practical advantages of Method B (more stable pH and much less volume enhancement) are particularly attractive. The washing process to eliminate soluble salts and the homoionic cation saturation is similar in complexity in both methods A and B. Likewise, similar yields of carbonate-free clay sized materials are afforded by Methods A and B. Both methods achieved removal of carbonates and eliminated the hydrolytic activity associated with the smectite SWy-2. Method B is recommended due to its convenience.

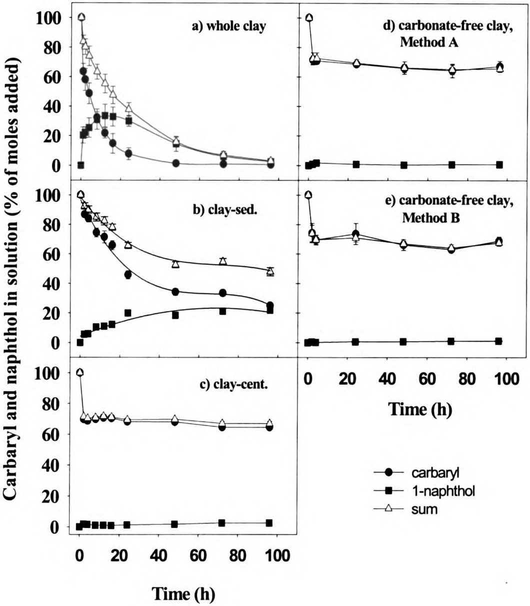

Figure 2.1. Sorption and hydrolysis of carbaryl by clay K-SWy-2: (a) whole clay; (b) clay-sed.; (c) clay-cent.; (d) carbonate-free clay, Method A; (e) carbonate-free clay, Method B.

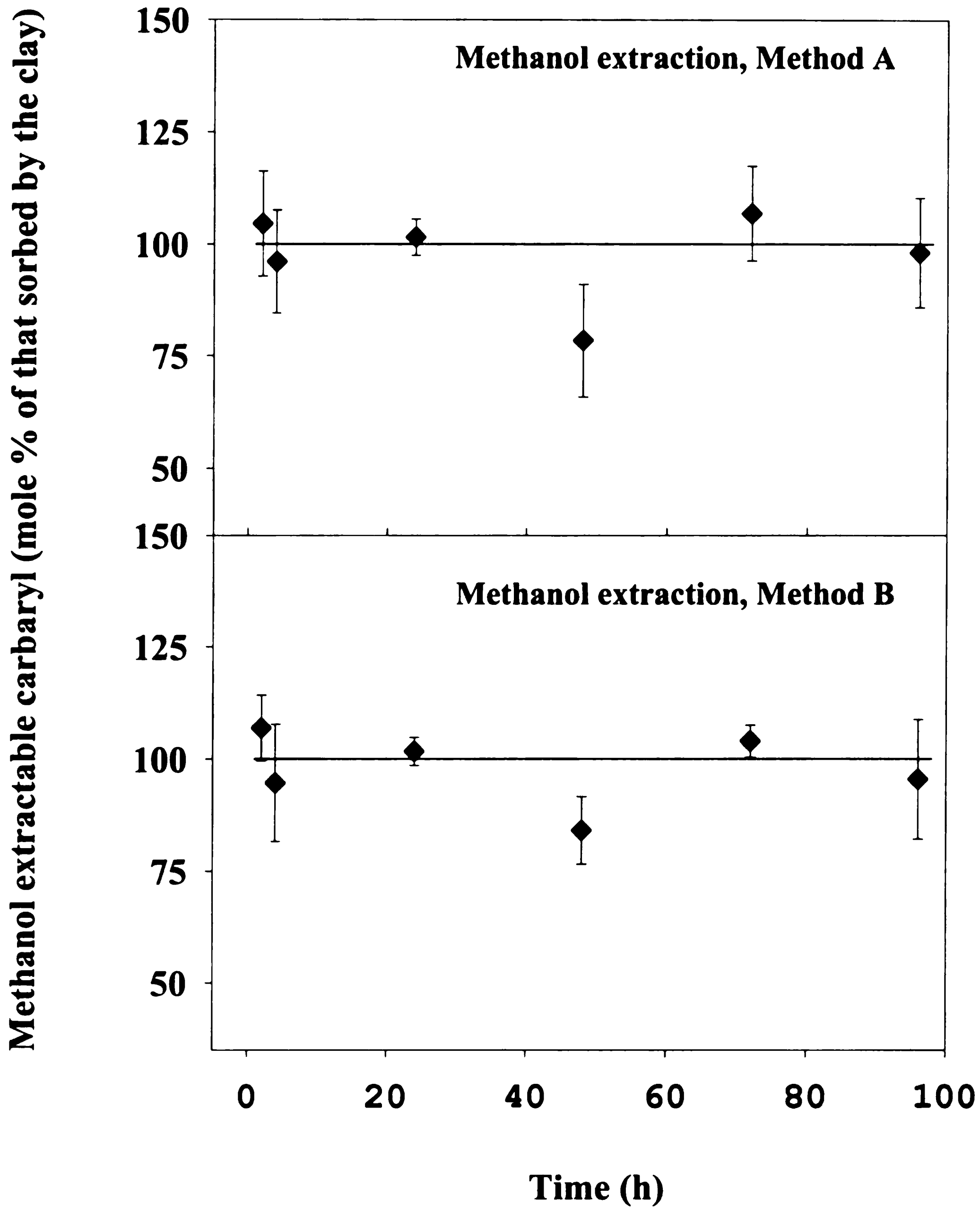

Figure 2.2. Amounts of methanol extractable carbaryl from carbonate-free K-SWy-2: (a) Method A and (b) Method B.

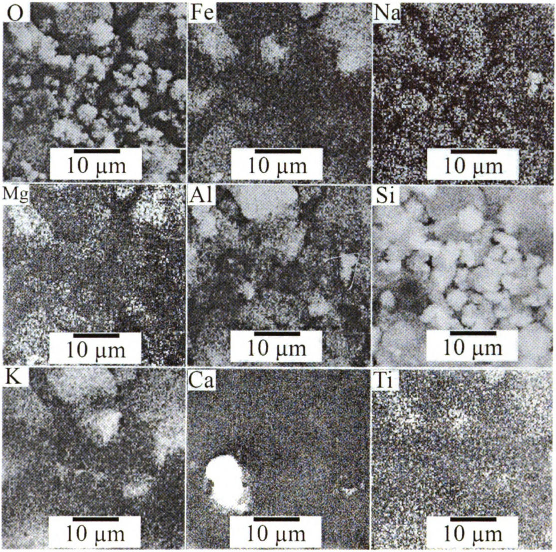

Figure 2.3. X-ray map of the heavy fraction. Elements as O, Fe, Na, Mg, Al, Si, K, Ca, and Ti, were identified. The brightness of pixel in x-ray map is directly proportional to the quantity of element present.

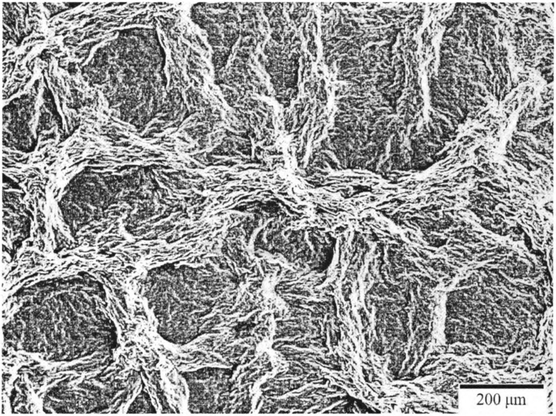

Figure 2.4. SEM photomicrographs of the SWy-2 “light fraction” (Arroyo et al., 2004), which occurs in a closed fine texture showing a honeycombed arrangement of particles.

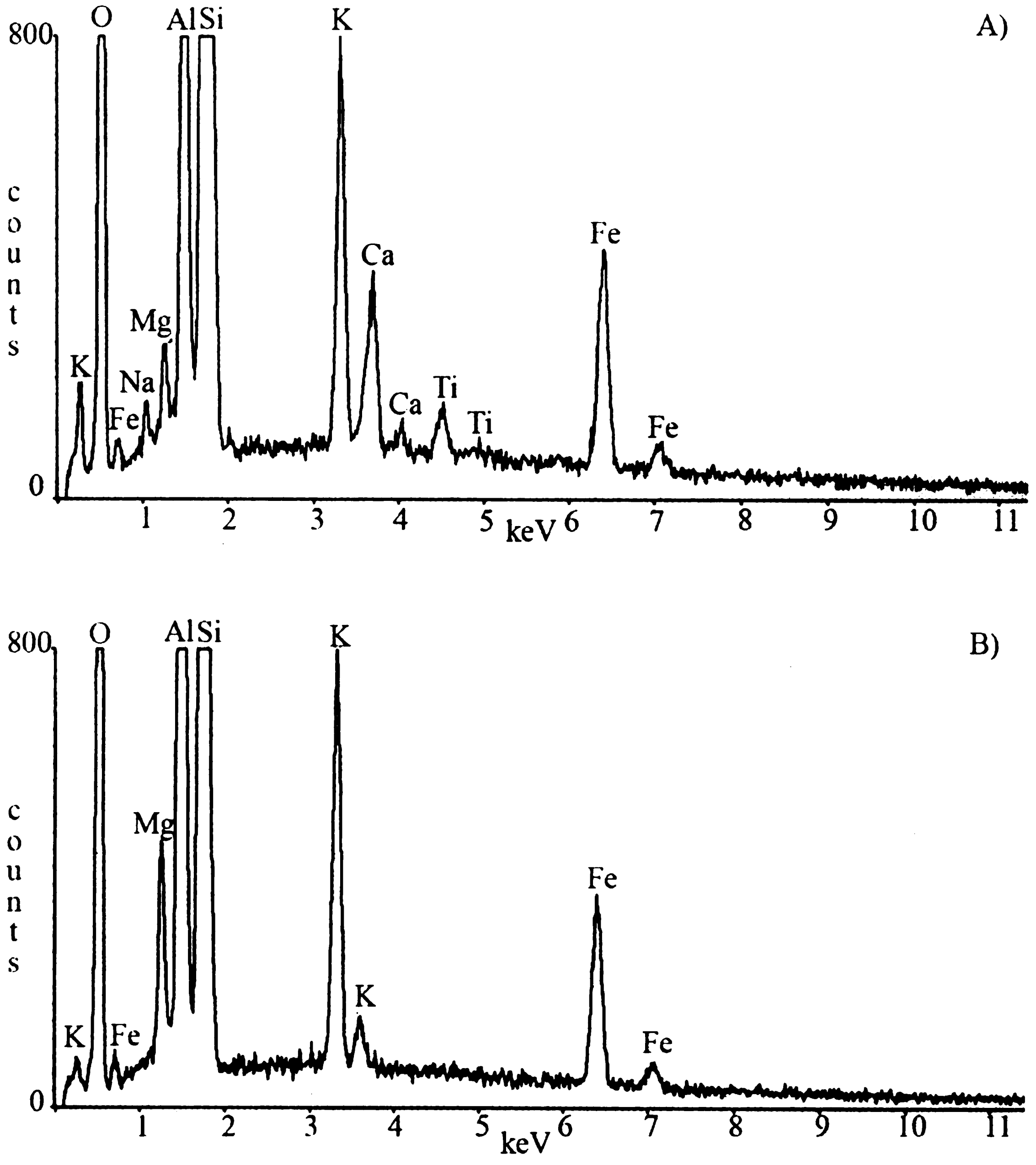

Figure 2.5. EDS spectra of K-SWy-2: (a) whole clay, with elemental composition of O (50.1%), Mg (0.6%), Al (4.9%), Si (35.6%), K (2.7%), Fe (3.6%), Na (0.7%), Ca (1.2%), and Ti (0.5%), and (b) "light fraction" with elemental composition of O (51.5%), Mg (1.7%), Al (11.5%), Si (28.3%), K (3.5%), Fe (3.4%). While qualitative, this analysis would result in a unit cell formula of $K_{0.34}(Si_{3.88}Al_{0.12})(Al_{1.51}Fe^{3+}_{0.23}Mg_{0.26})O_{10}$ H_2O.

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CHAPTER 3

REDUCTION OF STRUCTURAL FE^{+3} IN SMECTITE COUPLED TO OXIDATION OF 1-NAPHTHOL

ABSTRACT

Sorption, oxidation and transformation of 1-naphthol by K-smectite (K-SWy-2) were studied using batch sorption isotherms, Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). Three preparations of the reference smectite clay (SWy-2) were evaluated: (a) whole clay (with naturally occurring carbonate impurities), (b) the <2 μm fraction of SWy-2, extracted to remove carbonate impurities, and (c) the carbonate-free <2 μm fraction of SWy-2 amended with calcite. For the whole clay and carbonate-free clay amended with calcite, >80% of added 1-naphthol disappeared from aqueous solution within 24 h, corresponding to a sorbed concentration of ≥2 mg/g of clay. In the carbonate-free clay only 35% of the added 1-naphthol disappeared from solution after 24 h. For all clay preparations studied only small amounts of sorbed 1-naphthol (<1%) could be recovered by methanol extraction of the clay. XRD patterns suggested that 1-naphthol was intercalated in the smectite, but were not conclusive because 1-naphthol sorption of 1.5–2.8 mg/g of clay had relatively minor effects on XRD patterns. FTIR spectra of sorbed 1-naphthol-clay complexes demonstrated structural Fe^{3+} reduction. FTIR spectra also showed evidence of the transformation of 1-naphthol. It appears that reduction of structural iron may be coupled to oxidation of 1-naphthol. Further

transformation of oxidized 1-naphthol, e.g. by coupling reactions, is indicated by a darkening of color of the clay and the inability to extract sorbed 1-naphthol.

INTRODUCTION

Carbaryl (1-naphthyl *N*-methylcarbamate) is one of the most commonly used carbamate insecticides (EPA, 1987; USDA, 1994–2001). In 1997, estimated carbaryl usage in the United States was 50000 kilograms (Barceló and Hennion, 1997) which increased in to 1.4 million kilograms in 2001 (USDA, 1994–2001). The Mississippi River Basin Study (May to September, 1991) conducted by Larson et al. (1996) found carbaryl in surface water at ~0.010 µg/L (detection limit of 0.002 µg/L) at seven of eight sampling sites. Carbaryl is subject to alkaline hydrolysis in aqueous media resulting in the formation of 1-naphthol. Rajagopal et al. (1984) reported that more than 50% of the soil-applied carbaryl accumulated as 1-naphthol. 1-Naphthol has been detected in California groundwater at concentrations up to 610 µg/L (Barbash and Resek, 1996; Barceló and Hennion, 1997). It was reported that 1-naphthol was more toxic to soil bacteria, mollusks, invertebrate insects, and three species of marine fish compared with carbaryl (Bollag and Liu, 1971; Mount and Oehme, 1981; Day, 1990).

Recent studies demonstrated that under environmentally relevant conditions clay minerals provide binding sites for certain aqueous phase pesticides and organic contaminants including triazines, nitroaromatics, ureas and carbamates (Laird et al., 1992; Hinedi, et al., 1993; Haderlein et al., 1996; Boyd et al., 2001; Sheng et al., 2001; Li et al., 2003; Li et al., 2004a, Arroyo, et al., 2004a). It has been demonstrated that phenol and phenolic compounds react with clay minerals and form high molecular-weight products (Mortland and Halloran, 1976, Larson and Hufnal, 1980, Stone and Morgan, 1984; Soma et al., 1986; Ukrainczyk and McBride, 1992). Final products of these redox reactions depended on pH, exchangeable cations on the clay and availability of *ortho* and *para* positions of the phenolic compounds (Ukrainczyk and McBride, 1992; del Castillo et al., 1996; Mortland and Halloran, 1976; Larson and Hufnal, 1980; Sawhney et al., 1984; Kung and McBride, 1988. Wang et al. (1978) and Wang and Huang (1989) showed that humic and fulvic acid-like products were formed by oxidative polymerization of naturally occurring phenolic compounds (e.g., gallic acid, protocatechuic acid, and pyrogallol) by clays.

Recent studies have implicated clay minerals in the degradation of several pesticides including carbosulfan, carbofuran, aldicarb, pirimicarb, chlorprofan and triasulfuron (Wei et al., 2001; Pusino et al., 2000). Arroyo et al. (2004a) studied sorption and hydrolysis of carbaryl by reference smectite clay SWy-2 and demonstrated that carbaryl was hydrolyzed to 1-naphthol in aqueous slurries of K-SWy-2. Hydrolysis of carbaryl was attributed to alkaline conditions caused by dissolution of carbonate impurities present in the reference smectite. Darkening of the clay was also observed, suggesting some chemical transformation of sorbed carbaryl or 1-naphthol. When ^{14}C-labeled carbaryl was added to slurries of SWy-2 most of the carbaryl removed from solution was unextractable from the clay by methanol. In contrast, when carbaryl was added to slurries of SWy-2 which had been treated to remove carbonates, no hydrolysis to 1-naphthol was observed and 100% of the clay-sorbed pesticide was methanol extractable (Arroyo et al., 2004b).

OBJECTIVE

The objective of this study was to evaluate the reactions of 1-naphthol in aqueous slurries of the reference smectite clay SWy-2. Sorption and transformation of 1-naphthol by SWy-2 was studied using two different clay preparations, i.e., unfractionated clay and the clay-sized (<2 μm) fraction of SWy-2 which was treated to remove carbonate impurities. Sorption and transformations of 1-naphthol in slurries of homoionic K-SWy-2 was evaluated using batch sorption isotherms, Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

MATERIALS AND METHODS

The reference clay, SWy-2, used in the study was obtained from the Source Clays Repository of the Clay Minerals Society (Columbia, MO). Milli-Q deionized (d.i.) water (Millipore Corp.) was used for all sample preparations. Two separate procedures were used to prepare homoionic K-SWy-2 (whole clay and carbonate-free clay). First, the reference clay, as received, was suspended in water, then K^+ saturated using 0.1 M KCl solutions; this material is referred to as whole clay. Second, SWy-2 was suspended in water, subjected to low-speed centrifugation to isolate the <2 μm particles, titrated to pH 6.8 with sodium acetate buffer (pH 5.0) to remove carbonate impurities, and subjected to K^+-saturation (as above). This clay sample is referred to as carbonate-free clay. After K^+-saturation, clays were washed with d.i. water until free of chloride as indicated by $AgNO_3$. Samples were quick-frozen, freeze-dried and stored. Additional details regarding clay preparation procedures can be found in Arroyo et al. (2004b).

1-Naphthol (>99% purity), obtained from Sigma-Aldrich (St. Louis, MO), was used to prepare standard solutions (0.1 M KCl at pH 3.0 adjusted with HCl, protected from light) for subsequent HPLC analysis of experimental samples. Solutions of 30 μg/mL of 1-naphthol (in 0.1 M KCl solution at pH 6.5, protected from light) were prepared and used immediately for sorption/transformations experiments.

A batch equilibration method was used to evaluate sorption of 1-naphthol by K-SWy-2 clay. Five mL of the 30 µg/mL 1-naphthol solution (described above) were pipetted into 7.4 mL borosilicate amber glass vials containing 60 mg of clay which were sealed with Teflon-lined caps. Vials, in replicates of three, were mixed briefly using a vortex mixer, then mechanically rotated continuously at room temperature (23 ± 1 °C) for intervals of 2, 4, 8, 12, 16, 24, 48, 72, and 96 hours. Vials were centrifuged at ~3500*g* for 20 minutes to separate solid and liquid phases and the latter analyzed for 1-naphthol by HPLC. The centrifuged clay pellets were extracted with methanol, and the extracts analyzed by HPLC for 1-naphthol. Amounts of 1-naphthol extracted from the clay pellets were obtained by subtracting the mass of 1-naphthol present in residual water from the mass of 1-naphthol extracted by methanol. Two kinetics experiments were performed to evaluate the effect of alkalinity produced by the dissolution of carbonate impurities present in SWy-2. First, 1-naphthol was added to a calcite suspension, and second, to a carbonate-free clay suspension amended with calcite. In these experiments 5.0 mL of the 30 µg/mL 1-naphthol solution were pipetted into 7.4 mL borosilicate amber glass vials containing 1.3 mg of calcium carbonate (with and without clay). Vials, in replicates of three, were mixed briefly using a vortex mixer and then mechanically rotated continuously at room temperature (23 ± 1 °C). The 1-naphthol concentration was determined after equilibration times of 2, 4, 8, 12, 24, 48, 72, 96 hours. Sampling and analyses of 1-naphthol were as described above.

The HPLC system consisted of a Perkin-Elmer 250 pump connected to a UV–vis detector (230 nm) and a 150 x 4.6 mm Supelcosil-C_{18} column (5 µm particle size and 120 Å pore size, Supelco). Chromatographic data were acquired using Turbochrom software 6.1. The mobile phase was an isocratic mixture of 71% methanol and 29% water adjusted to pH 3.2 with HCl. The injection volume was 25 µL and the flow rate was 1.0 mL/minute.

Basal spacings of K-SWy-2 clays with and without sorbed 1-naphthol were determined by XRD analysis. Suspensions of K-SWy-2 were dropped onto glass slides and allowed to air-dry at ambient conditions to obtain oriented clay films. XRD patterns of oriented films were also analyzed after exposure for 48 hours to 1% relative humidity (RH) and after 48 h exposure to 100% RH at 25 °C. The XRD patterns were recorded using Cu-K-α radiation and an XRD system consisting of a Philips 3100 X-ray generator (Philips Electronic Instrument, Inc., Mahwah, NJ), Philips 3425 wide range goniometer fitted with a θ-compensating slit, a 0.2 mm receiving slit, a diffracted-beam graphite monochromator, and PW1877 automated powder diffraction (Philips Electronics) control software. Diffraction patterns were measured from 4 to 11° 2θ, in steps of 0.02° 2θ, at 2 s/step.

FTIR experiments were performed to evaluate the potential transformations of 1-naphthol sorbed by K-SWy-2. Batch equilibrations of 1-naphthol in aqueous suspension of the whole clay and carbonate-free clay were set up as described above. Experiments were stopped after 48 and 144 hours, and the whole clay- and carbonate-free clay-1-naphthol suspensions were used to prepare self-supporting films for FTIR analysis. Films were prepared in triplicate by passing a volume of clay-1-naphthol suspension containing 20 mg of clay through a 0.45 μm Supor-450 hydrophilic polyethersulfone membrane (47 mm diameter) on a Millipore filtration system. The resulting clay deposit on the filter was protected from light, allowed to air-dry overnight, and then removed from the filter by using a metal spatula (Johnston et al., 2002). Infrared spectra were obtained on a Perkin-Elmer GX2000 FTIR spectrometer equipped with deuterated triglycine (DTGS) and mercury-cadmium-telluride (MCT) detectors, an internal wire grid IR polarizer, a KBr beam splitter, and a sample compartment purged with dry air. The unapodized resolution for the FTIR spectra was 2.0 cm^{-1}, and a total of 64 scans were collected for each spectrum. GRAMS/32 (Galactic Software) program was used to analyze and plot spectra. Post processing of the FTIR spectra was restricted to baseline correction.

RESULTS

Transformation of 1-naphthol in aqueous suspension containing the whole clay was indicated by a color change of the clay from off-white to gray, similar to the observations reported in our previous study with carbaryl (Arroyo et al., 2004a) and by Wang et al. (1978). 1-Naphthol added to the carbonate-free clay slurry amended with calcite also developed a gray color, which intensified over time. In contrast, color change was not observed when 1-naphthol was added to the carbonate-free clay suspension or to the aqueous suspension containing only calcite. Thus, it was apparent that that combination of smectite and calcite was necessary to produce the 1-naphthol transformations indicated by the color change of the clay.

Analysis by HPLC of the aqueous phase from slurries of whole K-SWy-2 and carbonate-free clay amended with calcite clearly demonstrated the disappearance of 1-naphthol from solution (Figure 3.1). In whole clay slurries, ~ 80% of 1-naphthol initially added had disappeared from solution after 24 hours, corresponding to ~2.0 mg/g of clay. In slurries of carbonate-free clay amended with calcite, ~95% of 1-naphthol had disappeared from solution after 24 hours, corresponding to ~2.4 mg/g of clay. After 96 hours, 1-naphthol had completely disappeared from solution in both clay slurries. Disappearance of 1-naphthol from solution in carbonate-free clay slurries (not amended with calcite) occurred to a much lesser extent. Approximately 35% of the initially added 1-naphthol had disappeared from solution within 24 hours, and ~45% after 96 hours.

Disappearance of 1-naphthol in the calcite suspension was ~2% after 24 hours, and ~20% at 48 hours. The disappearance of 1-naphthol was very similar in slurries of whole SWy-2 that naturally contain carbonate impurities (e.g. calcite, dolomite) and the SWy-2 that had been extracted to remove these naturally occurring carbonates then amended with calcite. It appeared that disappearance of 1-naphthol from solution was strongly favored by alkaline pH (produced by the dissolution of carbonates) and the presence of SWy-2.

Concentrations of sorbed 1-naphthol that could be methanol extracted from any K-SWy-2 samples were minimal (<1%). Arroyo et al. (2004a) demonstrated that ~61% of ^{14}C activity, added as ^{14}C-ring labeled carbaryl to whole SWy-2, was nonextractable by methanol. In that study, recovery of sorbed carbaryl by methanol extraction of carbonate-free clays was ~100%.

The XRD patterns for air-dried films of whole clay, carbonate-free clay, and these two clays after treatment with 1-naphthol for 120 h are shown in Figure 3.2. In both cases the clay basal spacings increased (to ~11.2 Å, Table 3.1) implying some intercalation of 1-naphthol and/or its transformation products between smectite layers. Similar expansions of the interlayer distances were noted for these same clay films that were equilibrated at 1% relative humidity (RH) (Table 3.1). The shapes and widths of the XRD patterns for both untreated clays (Figure 3.2) imply an interstratified mixture of clay layers with ~10 and 12.5 Å d_{001}-spacings, which are both quite reasonable for K-saturated smectites at low humidity (MacEwan et al., 1980). When 1-naphthol was added to the carbonate-free clay, there was a modest increase in the number of ~12.5 Å layers in this mix, shifting the overall XRD peak to a slightly larger d_{001}-spacing (Figure 3.2b). This is consistent with our previous observations of intercalated aromatic compounds (Li et al., 2004b), in which the d_{001}-spacings of air-dried K-smectite clay films increase slowly toward ~12.5 Å as the aromatic compound (i.e. 1,3-dinitrobenzene) loading increases from 0–34 mg/g of clay. Here, the 1-naphthol loading rate is only 1.4 mg/g of clay (Figure 3.1b), so the XRD data are consistent with our hypothesis of weak interlayer sorption of 1-naphthol in the carbonate-free system.

Interactions between 1-naphthol and the whole clay seem to produce transformation products, as described below, and the XRD data (Figure 3.2a) also indicate differences in the interlayer distances induced by sorption of 1-naphthol. The maximum intensity of the XRD pattern for the 1-naphthol-whole-clay systems (air-dried, or air-dried then equilibrated at ambient condition or at 1% RH) still occurs near 11.2 Å, indicating again that most d_{001}-spacings are either ~10 or 12.5 Å (Figure 3.2a). However, the peak is much broader than that for the carbonate-free clay (Figure 3.2b), implying that many ~15 Å up to even ~18 Å d_{001}-spacings are present in the K-smectite film of the whole clay after exposure to 1-naphthol. These larger d_{001}-spacings may indicate that some transformation products of 1-naphthol in the whole clay are nonplanar and serve to prop the layers open. Alternatively, Ca^{2+} ions from dissolved carbonates occupy some interlayer cation-exchange sites and cause those interlayers to remain more swollen upon air-drying.

To investigate the effect of 1-naphthol sorption on interlayer expansion by water, the air-dried clay films were exposed to 100% RH. Under these conditions the clay control not treated with 1-naphthol expanded to 15.55 Å, and the clay treated with 1-naphthol to 15.39 Å (Table 1). Note that other studies (Sheng et al., 2002; Li et al., 2004b) have shown that intercalated aromatic compounds inhibit K-smectite swelling at 100% humidity. In those studies, organic solute (e.g. 1,3-dinitrobenzene) sorption >8.4 mg/g of clay was sufficient to retain ~12.5 Å d_{001}-spacings even after exposure to 100% RH, with d_{001}-spacings steadily increasing toward 15.5 Å as organic solute loading rates decreased (Li et al., 2004b). Thus, swelling of our clay-1-naphthol complex at 1-naphthol loading of 1.4 mg/g to a slightly lower d_{001}-spacing (compared to the K^+-saturated clay alone) upon exposure to 100% RH is again consistent with our hypothesis that 1-naphthol is intercalated in K-smectite.

FTIR absorbance spectra of 1-naphthol sorbed to the carbonate-containing SWy-2 and to carbonate-free SWy-2 clay are compared in Figure 3.3 in the 4000 to 400 cm^{-1} region. An expanded region of these spectra in the 2200 to 1350 cm^{-1} region are shown (baseline corrected) in Figure 3.4. This spectral region contains the most prominent bands from the sorbed 1-naphthol and its transformation products. As shown in Figure 3.4, the relative intensity of the FTIR bands from the sorbed organic species are low compared to the strong clay bands. This is consistent with the fact that a relatively small amount of 1-naphthol was added initially (<4 mg/g of clay). The spectra of the whole clay K-SWy-2 (carbonate-containing clay, represented by the dotted lines) has additional band intensity present as a broad spectral component under the 1701, 1636, and 1531 cm^{-1} bands. This 'new' spectral features present in the carbonate-containing clay is attributed to the transformation product(s) of 1-naphthol. The FTIR spectra are consistent with our macroscopic evidence (e.g. unextractability of sorbed 1-naphthol, color change of clay) showing that a new spectral component is present in the whole clay. Unfortunately, the spectral fingerprint of the sorbed species is characterized by broad, overlapping bands that do not provide detailed clues as to the identification of the sorbed species. Similar broad, featureless bands have been observed in other chemisorption studies of other aromatic compounds on smectites. In a FTIR study of benzene chemisorption on Cu-smectite, for example, FTIR spectra of the benzene polymerized on the clay surface showed similar broad features in this spectral region (Hinedi et al., 1993).

FTIR spectra of the OH bending and stretching regions of the carbonate-containing and carbonate-free K-SWy-2 smectite samples are shown in Figures 3.5 and 3.6, respectively. SWy-2 has three bands at 920, 885, and 845 cm^{-1} which are assigned to the structural OH-bending vibrations of AlAlOH, $AlFe^{3+}OH$, and AlMgOH groups, respectively (Farmer, 1974). The spectra were run in triplicate and there are a total of six spectra overlaid in Figure 3.5. There is a consistent reduction in intensity of the $AlFe^{3+}OH$ bending mode of the carbonate-containing K-SWy-2 smectite relative to the intensity of this band in the carbonate-free clay. There has been renewed interest in this spectral region of smectites, and quantitative analyses of these three bands have been used to predict the extent and isomorphic substitution in smectites (Vantelon et al., 2001). As shown, there was virtually no change in the intensities of the AlAlOH and AlMgOH bands (Figure 3.6). This result provides surprisingly clear evidence that structural Fe^{3+} is being reduced during the 1-naphthol transformation. Reduction of structural Fe^{3+} may be coupled via electron transfer to oxidation of sorbed 1-naphthol.

Further support of this proposed electron transfer mechanism is observed in the ν(OH) region of the structural OH group (Figure 3.6). The band at 3624 cm^{-1} corresponds to the ν(OH) mode of the structural OH group of K-SWy-2 smectite. Because of the isomorphous substitution, there are several types of structural OH groups, similar to the OH bending region, corresponding to AlAlOH, $AlFe^{3+}OH$, AlMgOH groups. What is observed in the 1-naphthol FTIR spectra is a composite band that reflects the overall contribution of each band. In a recent study of dioctahedral smectites, the ν(OH) band of the structural OH groups of different dioctahedral smectites was decomposed into individual components of AlOHAl (3630), AlMgOH (3601), $AlFe^{3+}OH$ (3595), FeOHFe (3572) (Zviagina et al., 2004). Of particular interest to this study is that the Fe^{3+} containing components have the lowest position, relative to the AlAlOH and AlMgOH bands. Consequently, reduction of structural Fe^{3+} would cause a decrease in the lower energy portion of this band and the 3595 and 3572 cm^{-1} components were lost due to reduction. The FTIR spectra are consistent with this hypothesis. The ν(OH) band of the whole clay (carbonate-containing clay) has lower intensity in the lower energy portion of this spectrum precisely in the area where the $AlFe^{3+}OH$ and FeOHFe components occur. Furthermore, these spectral results are strongly correlated and supportive of the changes observed in the OH bending region. The FTIR spectra provided direct evidence that structural Fe^{3+} was involved in the transformation of 1-naphthol on the whole clay (carbonate-containing clay).

DISCUSSION

Batch sorption experiments, XRD and FTIR in spectral analysis have produced insights into the reactions of 1-naphthol with smectite clay. It is clear that upon treatment with 1-naphthol octahedral Fe^{3+} in K-SWy-2 was reduced to Fe^{2+} (Figures 3.5 and 3.6). Furthermore, reduction of structural Fe^{3+} appears to be accompanied by oxidation of 1-naphthol and the formation of dark-colored products. Alkaline pH conditions emanating form the dissolution of carbonate impurities in SWy-2 are likely to promote proton extraction from the hydroxyl groups of 1-naphthol, followed by electron transfer to structural Fe^{3+} in SWy-2. It is plausible that reactive aryloxy radicals produced from 1-naphthol in this fashion underwent coupling reactions on the clay surface. The presence of bound residues in the whole clay, which resist extraction by water and methanol, is consistent with the formation of higher molecular weight products. This type of oxidative-coupling reaction is thought to be involved in humic substance formation from polyphenols in soils (Stevenson, 1981). Our results suggest a role for smectite clays in these processes.

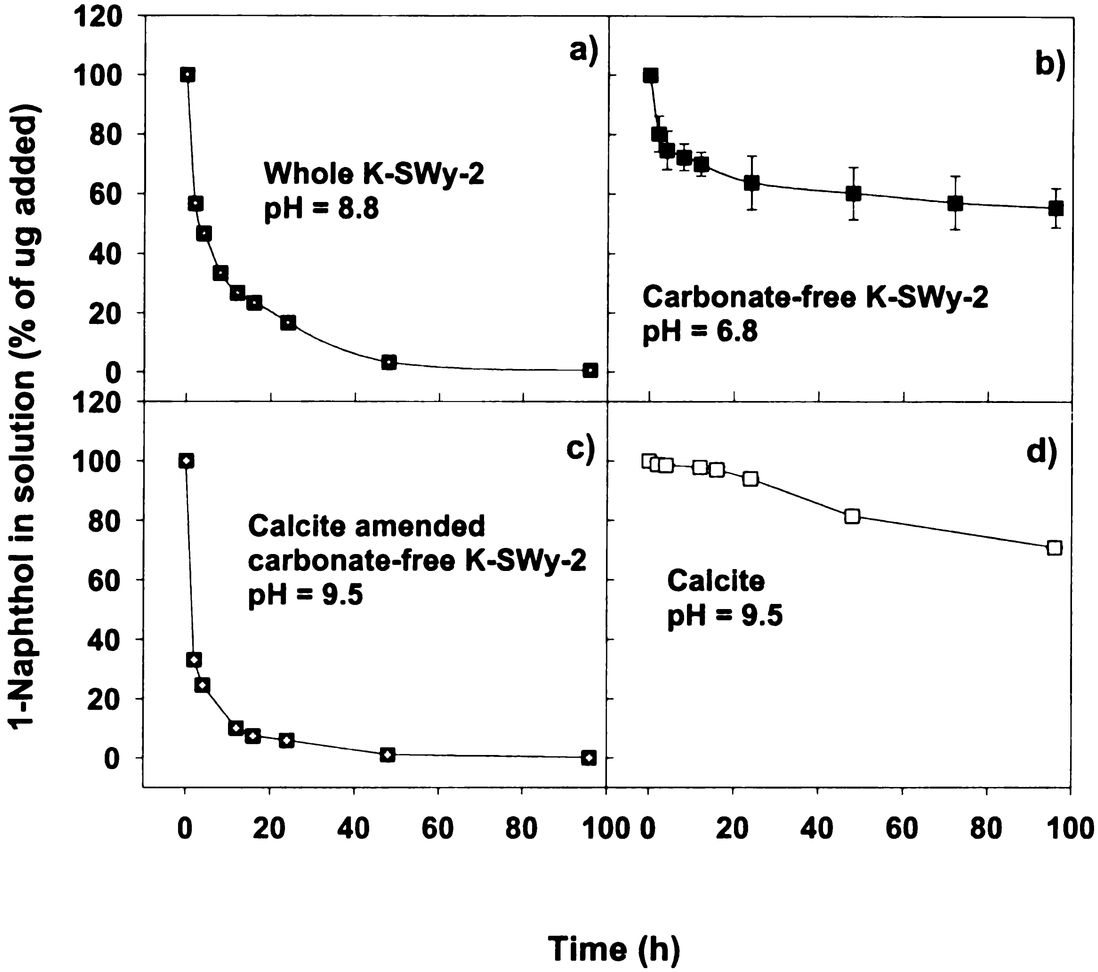

Figure 3.1. Disappearance of 1-naphthol from aqueous solution by: (a) whole clay (carbonates-containing); (b) carbonate-free clay; (c) carbonate-free clay, amended with calcite; (d) disappearance of 1-naphthol in a 0.01% calcite solution.

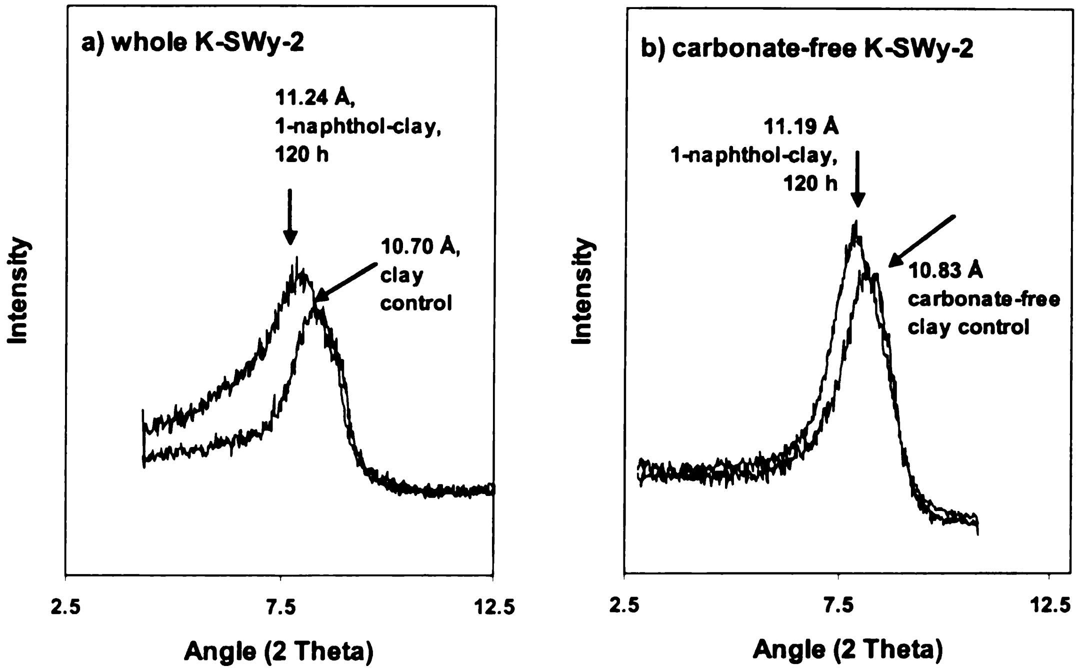

Figure 3.2. X-ray diffraction patterns of oriented air-dried films of 1-naphthol and clay K-SWy-2: (a) whole clay (control) and 1-naphthol--whole-clay complex at 120h; (b) carbonate-free clay (control) and 1-naphthol-carbonate-free-clay complex at 120h.

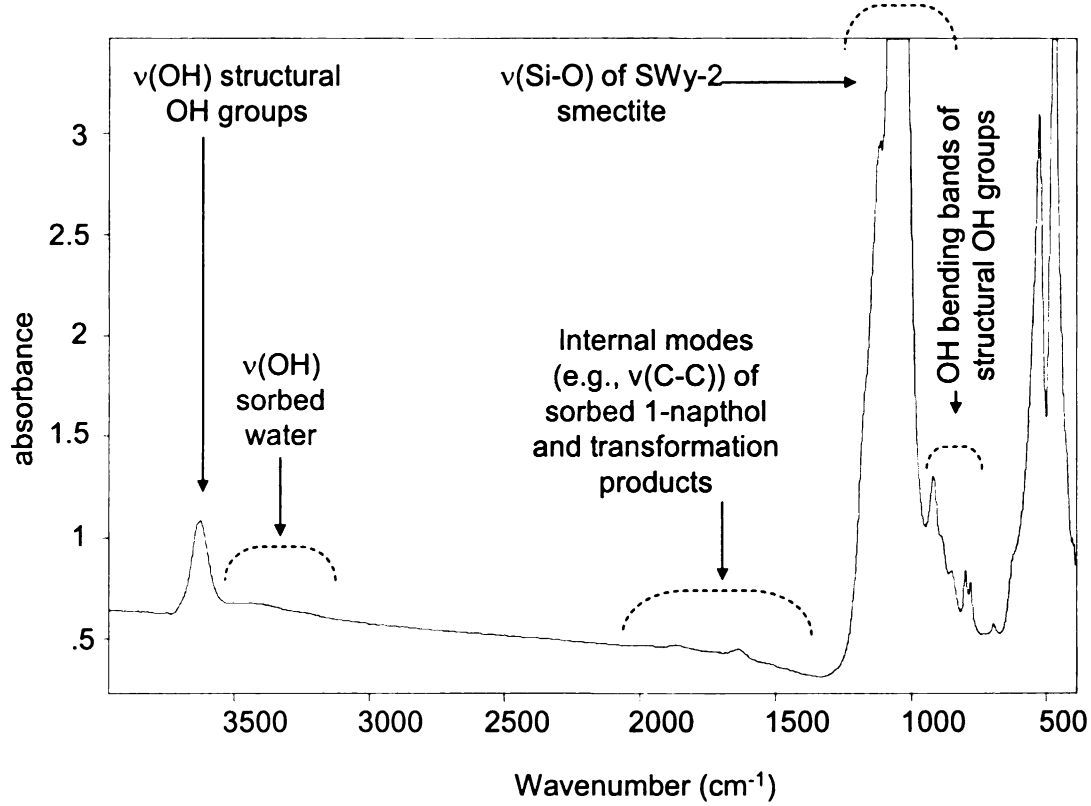

Figure 3.3. FTIR spectra of 1-naphthol sorbed to the carbonate-containing SWy-2 and to carbonate-free SWy-2 clay in the 4000 to 400 cm^{-1} region, containing the most prominent bands from the sorbed 1-naphthol and its transformation products.

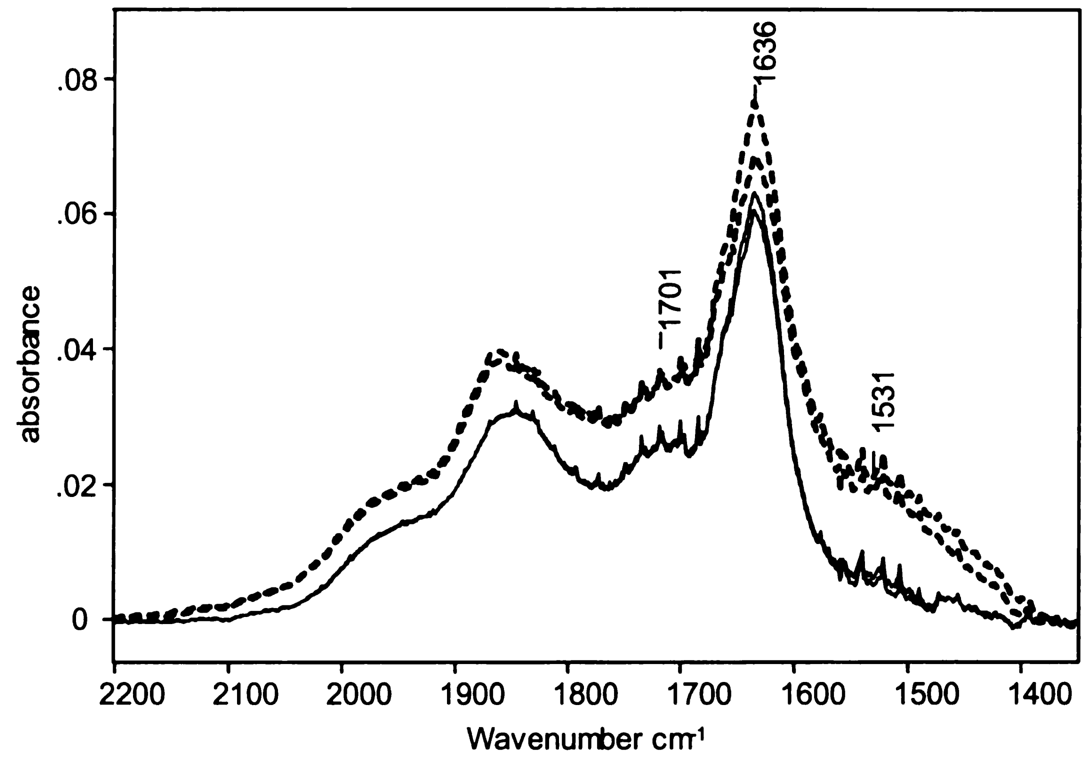

Figure 3.4. An expanded region in the 2200 to 1350 cm^{-1} of the FTIR spectra of whole K-SWy-2 (carbonate-containing clay, represented by the dotted lines) shows additional band intensity present as a broad spectral component under the 1701, 1636 and 1531 cm^{-1} bands, which is attributed to the transformation product(s) of 1-naphthol.

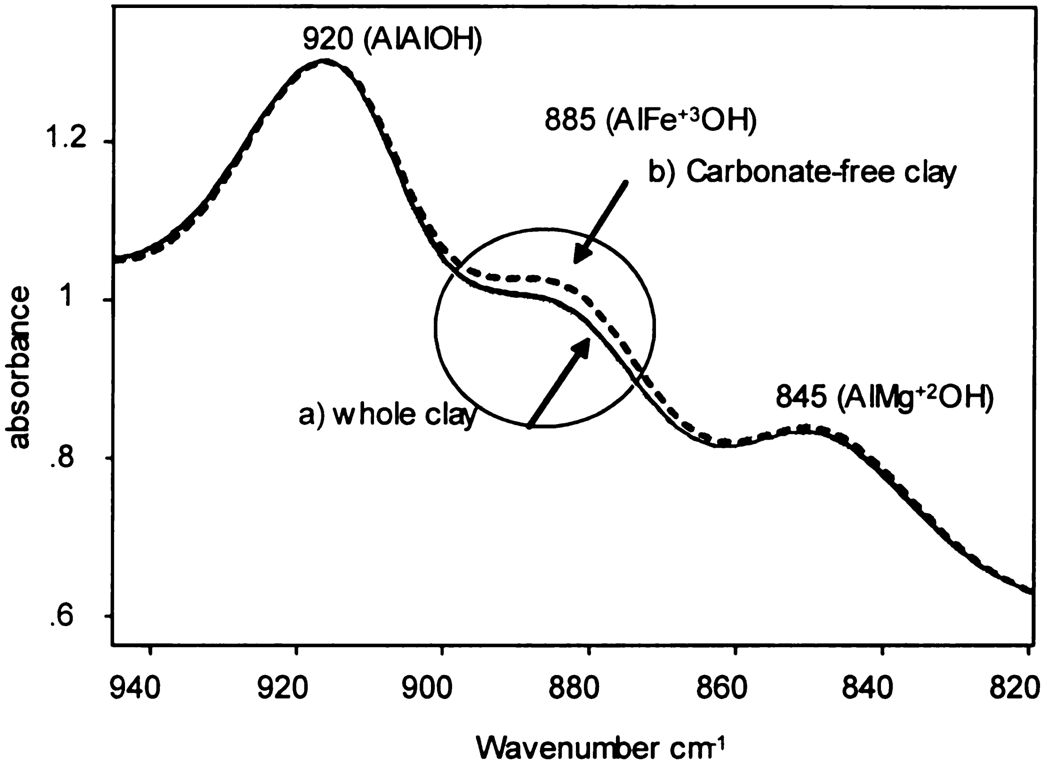

Figure 3.5. FTIR spectra of the structural OH bending region of the (a) carbonate-containing clay and (b) carbonate-free K-SWy-2 smectite show a reduction in intensity of the AlFe^{+3}OH bending mode of the carbonate-containing K-SWy-2 smectite relative to the intensity of this band in carbonate-free clay and no change in the intensities of the AlAlOH and AlMgOH bands.

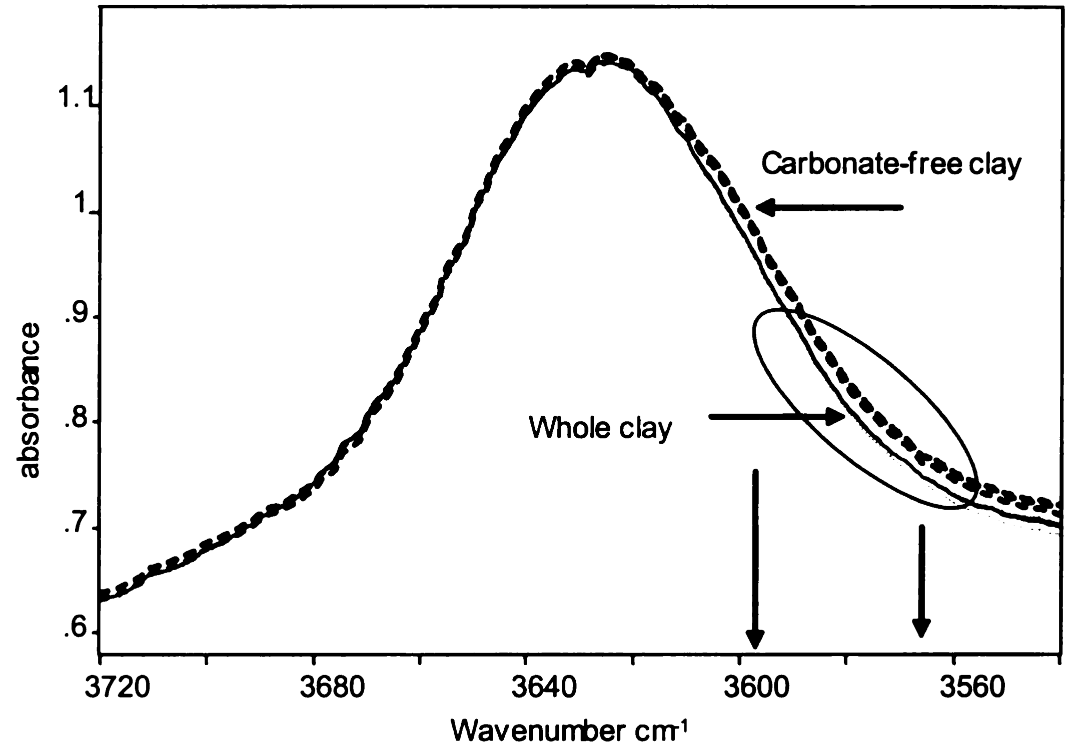

Figure 3.6. FTIR spectra of the structural OH stretching region of the carbonate-containing and carbonate-free K-SWy-2 smectite show a composite band that reflects the overall contribution of AlAlOH, $AlFe^{+3}OH$, AlMgOH bands. The v(OH) band of the whole clay (carbonate-containing clay) shows a lower intensity in the lower energy portion (3595 to 3572 cm^{-1}) of this spectrum, which is the area where $AlFe^{+3}OH$ and FeOHFe components occur.

Table 3.1. d_{001}**-Spacings (Å) for K-SWy-2, and K-SWy-2 Extracted to Remove Carbonate Impurities. The clay films with and without 1-naphthol sorption were analyzed by XRD after air-dried, then exposed the air-dried clay films to 1 and 100% relative humidity (RH).**

Treatment	K-SWy-2		Carbonate-free K-SWy-2	
	With 1-naphthol	Without 1-naphthol	With 1-naphthol	Without 1-naphthol
Air-dried	11.24	10.7	11.19	10.83
Exposure to 1% RH	11.16	9.99	nd	nd
Exposure to 100% RH	15.39	15.55	nd	nd

nd = not determined

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CHAPTER 4

SUMMARY AND CONCLUSION

This dissertation provides a case-in-point that small amounts of impurities present in reference clay mineral samples may substantially alter their apparent sorptive properties or reactivities. The study of the influence of clay preparation methods on sorption and hydrolysis of carbaryl by reference clay K-SWy-2 demonstrated that common methods used to fractionated and purified reference clays were not enough to eliminate carbonate impurities. In this study, small quantities of inorganic carbonates were sufficient to cause substantial alkaline hydrolysis of carbaryl. Carbaryl was hydrolyzed to 1-naphthol in different degrees depending on the method used. Methods to purified available commercial reference clay minerals includes the use of fractionation based on particle size separation, e.g., the sedimentation and low-speed centrifugation procedures (Kunze and Dixon, 1986; Gee and Bauder, 1986; Moore and Reynolds, 1989), but they are not uniformly performed consistently.

This dissertation covers a critical description of the development of a standard fractionation and partial purification procedure for commercial available reference clays prior to their use in studies on sorption and reactivity. This study proved the need to purify reference clays prior to use them in any study of surface chemistry. The essential steps of such a procedure would include: (1) separation of the <2 μm clay-sized particles by low speed centrifugation or gravity sedimentation. (2) Dissolution of carbonates and soluble salts with sodium acetate buffer. (3) Washing with water to remove residual soluble salts and decrease ionic strength. (4) Re-suspension of the (now predominantly Na-) clay in water. (5) Homocation saturation of the clay. In this dissertation, we suggest adoption of method B because of its convenience.

The study using [^{14}C]carbaryl provided valuable information on the fate of the pesticide carbaryl. The use of the radiolabeled compound verified results of the hydrolysis of carbaryl, obtained by the HPLC/UV and the resistance for extraction of the sorbed compound.

Analysis of the FTIR spectra about the interaction between the hydrolytic product 1-naphthol and the reference clay K-SWy-2 confirmed the formation of new product(s) that may explain its nonextractability. There is also evidence that structural iron of the reference K-SWy-2 was reduced to Fe^{2+} and 1-naphthol was oxidized to dark-colored products, which are weakly intercalated in the clay, as shown by XRD patterns of clay-1-naphthol complexes. This type of oxidative-coupling reaction is thought to be involved in humic formation from polyphenols in soils (Stevenson, 1981).

More research is needed on exploring new experiments using carbaryl, other carbamates and their degradation products with clay homoionized with higher polarizing and/or transitional cations. The use of better methods for extraction of clay bound residues and techniques such as GC/MS and HPLC/MS could give more information about the formation of new products. Studies on bioavailability of these bound residues could also be of interest.

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