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Hydrolysis of Carbaryl by Carbonate Impurities in Reference Clay SWy-2

L. JACQUELINE ARROYO,[†] HUI LI,[†] BRIAN J. TEPPEN,[†] CLIFF T. JOHNSTON,[‡] AND
STEPHEN A. BOYD^{*,†}

Department of Crop and Soil Sciences, and Environmental Science and Policy Program,
Michigan State University, East Lansing, Michigan 48824, and Crop, Soil and Environmental
Sciences, Lilly Hall of Life Sciences, Purdue University,
West Lafayette, Indiana 47907

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 (3295g) 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 high-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 μ m particles (clay-sed.) and then K⁺-saturated. (4) SWy-2 was subjected to low-speed centrifugation (58–60g) to separate the <2 μ m particle size (clay-cent.) and 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 [¹⁴C]carbaryl, ~61 and 15% of the total ¹⁴C 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.

KEYWORDS: Adsorption; carbonate; carbaryl; hydrolysis; smectite

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 (1). Surface and ground waters can be contaminated with pesticides because of the intensive use of pesticides in agriculture, leading to the potential for exposure to nontarget organisms (2–4). 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 (5, 6). Other studies have demonstrated the importance of clay minerals in the retention of certain classes of pesticides (7–9) and energetics (10–15) and that they may contribute to the degradation of carbamate pesticides, for example, carbosulfan, carbofuran, aldicarb, and pirimicarb (16), and other pesticides, for example, triasulfuron (17).

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

* Corresponding author [telephone (517) 355-0271, ext. 252; fax (517) 355-0270; e-mail boyds@msu.edu].

[†] Michigan State University.

[‡] Purdue University.

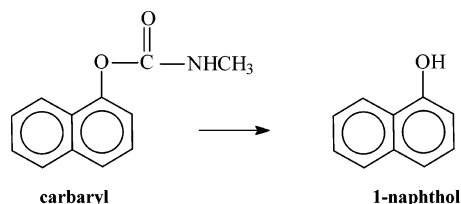


Figure 1. Hydrolysis of carbaryl.

kg/ha, but in fruit trees application increases to 10 kg/ha (18, 19). Current carbaryl usages in the United States and the European Union are 50000–500000 kg/year (3, 20, 21). In 1995 and 1996, exports of carbaryl from U.S. ports to developing countries were 1.04 and 1.42 million kilograms, respectively (22).

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) (19, 23, 24). Carbaryl is readily hydrolyzed in alkaline media, but resistant to hydrolysis at neutral and acidic pH (18, 19, 23–26). The primary hydrolysis product of carbaryl in soil is 1-naphthol (18, 19, 23–28) (Figure 1), which can be metabolized by soil microorganisms (18, 27, 29, 30). The reported persistence of carbaryl in soils is considered to be short (e.g., 2 weeks) to moderate (e.g., 16 weeks) (30), depending on environmental factors such as pH and temperature, as well as the rate of application, chemical formulation, and frequency of application (30). 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 (19, 28, 30). Small amounts of carbaryl present in soil solution may be absorbed by plant roots but are not expected to persist in the dissolved state (19, 30, 31).

Although carbaryl is not generally considered to be recalcitrant in the environment (18), its transformation products (e.g., 1-naphthol) have been found in California ground water at concentrations up to 610 $\mu\text{g/L}$ (3, 21). Howard (19) reported that carbaryl persisted in the environment (soil and water) for a few weeks up to 3 months. Carbaryl persisted for 3 weeks in mud, but 1-naphthol did not (30). Rajagopal et al. (30) 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-h laboratory exposure experiments (27, 32).

Retention of carbaryl in soils may result from sorption by clay minerals. Carbaryl sorption by bentonite clay (composed largely of smectite) was greater than that by kaolinite (30). The ability of smectite to adsorb organic contaminants and pesticides from aqueous solution is influenced by the exchangeable cation, as well as structural charge and its origin (11, 13). Aly et al. (33) studied sorption 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 (33). Sheng et al. (7) evaluated the potential contribution of smectite and organic matter to pesticide retention in soils, and they concluded that homoionic K^{+} -smectite was a more effective sorbent than muck soil for 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 (34). The initial descriptions of these materials were presented in the *Data Handbook for Clay Materials and Other Non-Metallic Minerals* (35). An updated version of this book provides descriptions of materials added

to the original reference set and additional data obtained with new analytical techniques (36). Chipera and Bish (37) established that most of the Source Clays, which are naturally occurring materials, contain discernible amounts of other materials. 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, preparing different homoionic forms of the clays or removing impurities. Preparations reported in the literature include a simple wet sedimentation, that is, gravity settling overnight to obtain the $<2\ \mu\text{m}$ fraction (7, 8, 13, 16, 17, 38–44), and Na^{+} -saturation followed by low-speed centrifugation to separate larger particles from the $<2\ \mu\text{m}$ fraction (14, 45, 46). Often, reference clays are used without previous Na^{+} -saturation, wet sedimentation, or centrifugation (11). 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 (47), prior to cation saturation, or do not have defined pretreatment procedures at all (33, 48–50). Experimental details such as dispersal method, sedimentation time, centrifugation forces, and type of membranes used in 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.

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 CMS (Columbia, MO) and has been characterized previously (36, 51–53). Four separate procedures, detailed below, were used to prepare subset fractions of 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 h. The mixture was centrifuged for 20 min at 3295g (4500 rpm) using a Sorvall GSA rotor and centrifuge (DuPont Co., Wilmington, DE). The pellet was collected and the supernatant discarded. The pellet was resuspended 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 \times 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 60g for 6 min and the supernatant discarded. The sample was quick-frozen, freeze-dried, and stored.

Clay-cent. To obtain the clay-sized particles ($<2\ \mu\text{m}$), 25 g of SWy-2 was placed in a 1 L beaker with 500 mL of d.i. water and stirred for 24 h using a magnetic stirbar 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 min at 58–60g ($\sim 600\ \text{rpm}$) using a Sorvall GSA rotor and centrifuge. The supernatant suspension containing the $<2\ \mu\text{m}$ clay-sized particles was then collected in six polyethylene centrifuge bottles and centrifuged again for 30 min at 3295g (4500 rpm). The supernatant was discarded. The clay pellet was K^+ saturated ($4\times$) 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 ($<2\ \mu\text{m}$), 25 g of SWy-2 was placed in a 2 L beaker with 1.8 L of d.i. water and stirred for 8 h using a magnetic stir bar and plate to hydrate the clay and to form a stable suspension. After overnight ($\sim 18\ \text{h}$) settling, the supernatant suspension containing the $<2\ \mu\text{m}$ clay-sized particles was poured into 12 polyethylene centrifuge bottles and then centrifuged for 30 min at 3295g (4500 rpm). The supernatant was discarded. The clay pellet was K^+ saturated ($4\times$) 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 h of ethylene glycol vapor saturation at $40\ ^\circ\text{C}$. The XRD patterns were recorded using $\text{Cu K}\alpha$ 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 $60^\circ\ 2\theta$, in steps of $0.02^\circ\ 2\theta$, at $2\ \text{s/step}$.

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 a high-performance liquid chromatograph (HPLC). Carbaryl-naphthalene- $1\text{-}^{14}\text{C}$ with a specific activity of $8.4\ \text{mCi/mmol}$ and a radiochemical purity of 97% was obtained from Sigma-Aldrich. Solutions of $40\ \mu\text{g/mL}$ of carbaryl in 0.01 M KCl solution at ambient pH 6.5, protected from light, were prepared and used immediately for the sorption/degradation experiments. In some instances, the $40\ \mu\text{g/mL}$ carbaryl solution was amended with the ^{14}C -ring-labeled carbaryl. The labeled $[^{14}\text{C}]$ carbaryl solution was prepared as follows: $100\ \mu\text{Ci}$ of $[^{14}\text{C}]$ carbaryl ($\sim 2.4\ \text{mg}$ of $[^{14}\text{C}]$ carbaryl) was dissolved in 1 mL of methanol, and then 100 mL of $40\ \mu\text{g/mL}$ unlabeled carbaryl solution was amended with $10\ \mu\text{L}$ ($\sim 1\ \mu\text{Ci}$) of ^{14}C -labeled carbaryl stock solution. The final carbaryl solution contained $\sim 0.01\ \mu\text{Ci/mL}$.

Kinetics. Kinetic 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 $40\ \mu\text{g/mL}$ 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 ($23 \pm 1\ ^\circ\text{C}$). Vials were then centrifuged at $\sim 3500g$ for 20 min (whole clay and heavy fraction) or for 40 min (light fraction and clay-cent.) to separate solid and liquid phases. Centrifugation occurred after 2, 4, 8, 12, 16, 24, 48, 72, and 96 h 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 the residual ^{14}C activities, the extracted clays were air-dried and combusted at $900\ ^\circ\text{C}$ in an OX-300 Harvey biological oxidizer. The $^{14}\text{CO}_2$ 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. Whole clay, light fraction, clay-sed., and heavy fraction slurries were determined to be alkaline, but the pH of clay-cent. was neutral. To investigate the pH impact of clay impurities on carbaryl hydrolysis, 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 of (5.0 mL) of a $40\ \mu\text{g/mL}$ carbaryl solution (in 0.01 M KCl, pH 6.5) was 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 (53). 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 (54) 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 $150 \times 4.6\ \text{mm}$ Supelcosil-C₁₈ column ($5\ \mu\text{m}$ particle size and $120\ \text{\AA}$ pore size). The mobile phase was a mixture of 71% methanol and 29% $0.025\ \text{M}\ \text{KH}_2\text{PO}_4$ solution at pH 3.2. The injection volume was $25\ \mu\text{L}$, and the flow rate was $1.0\ \text{mL/min}$. 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

$$\ln(M_0/M_t) = k_{\text{obs}}t \quad (1)$$

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 (55). 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_{obs}). The half-life ($t_{1/2}$) for the dissipation of carbaryl was estimated by assuming first-order processes (56) using k_{obs} from the eq 1.

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

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 pale yellow with a gel-like consistency. It comprised $\sim 20\%$ (w/w) of the whole clay. The second band in the pellet was dark yellow, and a third (bottom) one was dark brown in color. The dark-brown material comprised $\sim 14\%$ 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 3295g). This facilitated physical separation of the light and heavy fractions.

Clay-sized particles ($< 2 \mu\text{m}$) obtained from SWy-2 (prior to K^+ -saturation) by gravity sedimentation are referred to as clay-sed. According to the Stokes equation, the $> 2 \mu\text{m}$ particles should settle 23.5 cm in 18 h, which forms the basis of the gravity sedimentation procedure (57). The clay-sed. was then K^+ -saturated with 0.1 M KCl solution. Some of very fine particles were lost in the subsequent washing process. Removing excess salts by washing with d.i. water caused resuspension (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. The clay-cent. obtained from the resultant aqueous suspension corresponded to $\sim 70\%$ (w/w) of the original SWy-2. When this suspension was centrifuged at high speed (3295g), 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 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 the whole clay and the 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 the 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 2. Peaks corresponding to quartz, orthoclase and plagioclase feldspar, calcite, dolomite, and rutile

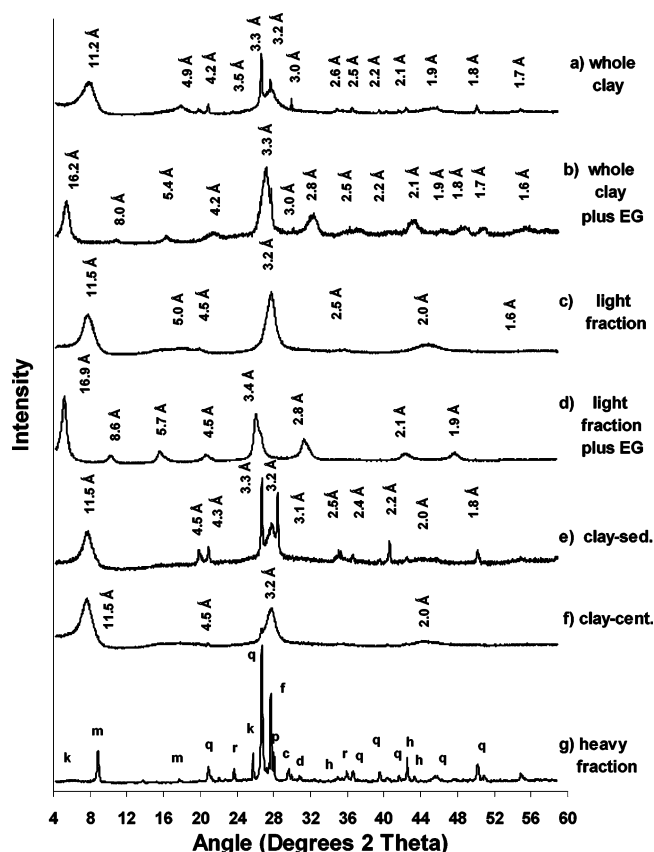


Figure 2. XRD patterns of K-SWy-2: (a) whole clay, oriented air-dried and (b) after ethylene glycol solvation; (c) light fraction, oriented air-dried and (d) after ethylene glycol solvation; (e) clay-sed., oriented air-dried; (f) clay-cent., oriented air-dried; (g) heavy fraction, oriented air-dried. 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, f = orthoclase feldspar, and p = plagioclase feldspar.

are apparent. Chipera and Bish (37) and Vogt et al. (52) 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 3). Hydrolysis of carbaryl in blanks not containing clay was minimal after 48 h, and the amount hydrolyzed remained constant at $\sim 8\%$ (of initial carbaryl concentration) between 48 and 96 h. 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 h reaction time, the rate and extent of carbaryl degradation followed the order whole clay > heavy fraction >> clay-sed. > light clay > clay-cent. Accumulation of

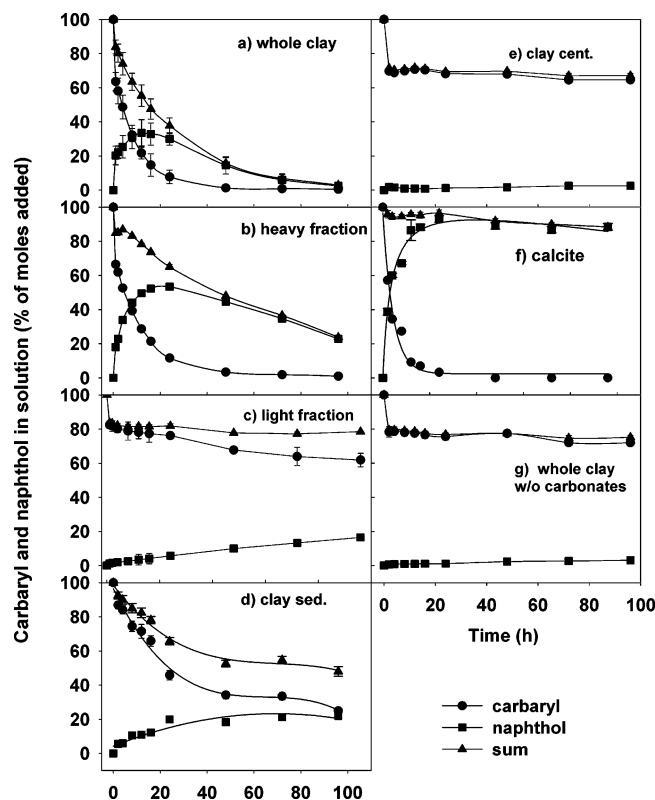


Figure 3. Hydrolysis of carbaryl by smectite clay K-SWy-2: (a) whole clay; (b) light fraction; (c) heavy fraction; (d) clay-cent.; (e) clay-sed.; (f) whole clay (now without carbonates); (g) hydrolysis of carbaryl by calcite.

1-naphthol in solution maximized at ~ 24 h 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 3c–e).

In experiments utilizing the whole clay, $\sim 80\%$ of carbaryl plus 1-naphthol (on a molar basis) had disappeared from the aqueous solution within 48 h (Figure 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 $\sim 80\%$ of carbaryl plus 1-naphthol (on a molar basis) was present in the aqueous solution after 48 h of reaction time. In these slurries, disappearance of carbaryl from solution occurred only during the first 2 h, after which its concentration remained almost constant. The calculated half-lives of carbaryl were 9 and 10 h in the presence of the whole clay and the heavy fraction, respectively. Due to the slow hydrolysis of carbaryl in the light fraction and the clay-cent. slurries, its half-life in these systems was estimated to be 204 and 770 h, 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 (Figure 4), ca. 30 and 65%, respectively. 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 the light fraction, ^{14}C -ring-labeled carbaryl was used. Total recoveries were $100 \pm 6\%$ (Tables 1 and 2). For the whole clay slurries after 48 h, ^{14}C activity in the aqueous phase was $\sim 16\%$ of the total ^{14}C activity added (Table 1). Water and methanol extracted 25% of the total ^{14}C activity added (or $\sim 29\%$ 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 h of reaction time (Table 1). For the whole clay slurries in general, the amount of solution phase activity decreased steadily over time (up to 48 h), and the amount of sorbed but not extractable activity increased. For the light fraction slurries after 48 h, ^{14}C activity in the aqueous phase was $\sim 50\%$ of the total ^{14}C activity (Table 2). Water and methanol extracted 31% of the total ^{14}C activity added (or $\sim 67\%$ 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 h 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 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 the heavy fraction (Figure 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 (54) 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, $\sim 30\%$ of carbaryl had disappeared from the aqueous solution. This corresponds to an amount sorbed of ~ 1.0 mg/g of clay (Figure 3g). There was negligible formation of 1-naphthol in this clay slurry.

DISCUSSION

The availability of specimen (or reference) clays from the CMS Source Repository and their extensive characterization (35, 37, 51, 53) 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 (54, 57) and for purifying clay samples (57), there is still no general recognition of the need to purify reference (or commercial) clays prior to use (11). 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 $<2 \mu\text{m}$ in effective spherical diameter. These are usually obtained by gravity sedimentation or by low-speed centrifugation to remove the $>2 \mu\text{m}$ 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 (52, 53). However,

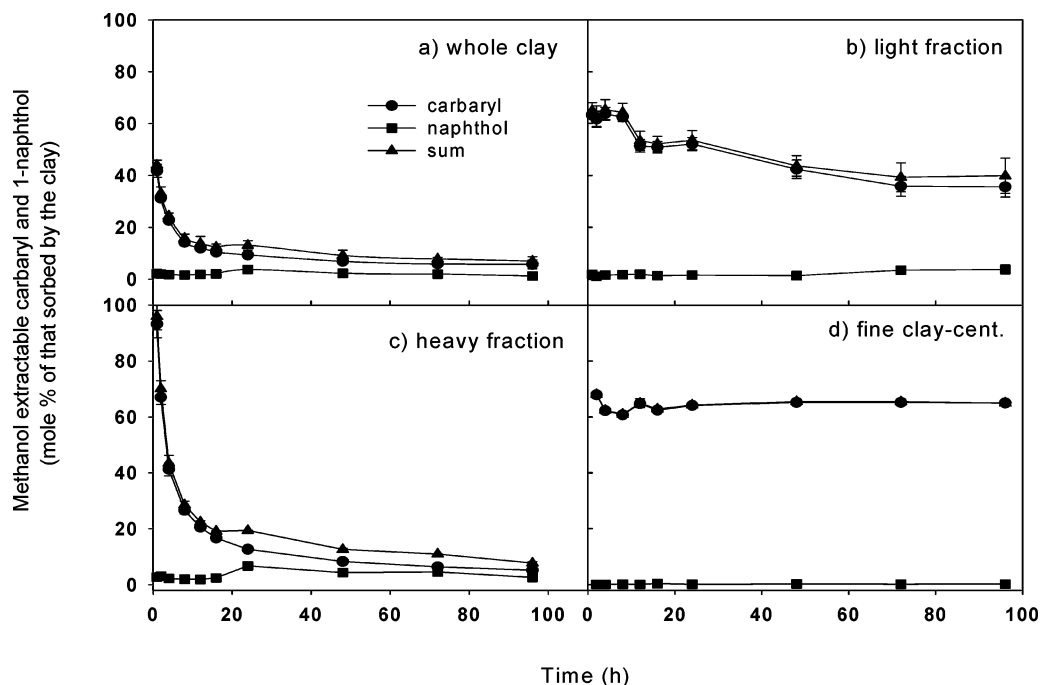


Figure 4. Amounts of methanol extractable carbaryl and 1-naphthol from K-SWy-2: (a) whole clay; (b) light fraction; (c) heavy fraction; (d) clay-cent.

Table 1. Time-Dependent Distribution of ^{14}C Activity in Whole K-Smectite (SWy-2) Slurries Amended with [^{14}C]Carbaryl

time (h)	in solution	SD	^{14}C activity ^a		SD	SD	^{14}C activity ^a		SD	SD	total recovery
			sorbed by K-SWy-2	sorbed but water extractable			sorbed but MeOH extractable	sorbed and nonextractable			
2	80	1	25.9	4.0	0.1	0.3	4.6	17.3	0.2	0.2	106
8	59	1	43	2.0	2	0.1	11.3	30	0.4	2	101
12	53	4	49	2.1	2	0.3	13.4	34	0.3	2	102
24	49	10	53	3.0	3	0.4	12	38	4	2	102
48	41	2	62	3.1	2	0.3	14.0	45	0.2	2	103
72	16	1	85.7	6.6	0.1	0.2	18.0	61.1	0.4	0.3	102

^aExpressed as a percentage of the initial added ^{14}C activity.

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

time (h)	in solution	SD	^{14}C activity ^a		SD	SD	^{14}C activity ^a		SD	SD	total recovery
			sorbed by K-SWy-2	sorbed but water extractable			sorbed but MeOH extractable	sorbed and nonextractable			
2	75	3	19	2.0	2	0.4	8.1	9	0.1	1	94
8	73	2	24	1.8	3	0.3	12.2	10	0.3	2	97
12	70	1	29	1.4	3	0.2	17.6	10	0.6	3	99
24	63	2	35	2.5	2	0.4	19	13	1	3	98
48	52	1	46	3.2	2	0.5	28	15	2	1	99
72	47	2	54	3.7	4	0.2	35.4	15	0.4	4	101

^aExpressed as a percentage of the initial added ^{14}C activity.

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 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 be-

tween 1.68 and 0.05% (52, 53); the CaO content in the bulk CMS sample of SWy-2 was higher than in the corresponding clay-sized fraction (37).

Adding carbaryl to an aqueous calcite suspension resulted in the rapid and stoichiometric hydrolysis of carbaryl to 1-naphthol (Figure 3f). Furthermore, the hydrolysis of carbaryl by whole clay suspensions was eliminated when SWy-2 was subjected to carbonate dissolution by sodium acetate buffer (54) prior to use (Figure 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 4** and **Tables 1** and **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 (7, 16, 17). 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 as 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 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 $<2\ \mu\text{m}$ 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.

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