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## An Infrared Spectroscopic Study of the Vapor Adsorption of Nitroglycerin and Pentaerythritol Tetranitrate on Chrysotile Asbestos

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## Foreword

This study was conducted for the Directorate of Research and Development, Headquarters, U.S. Army Corps of Engineers under 622720D048, "Industrial Operations Pollution Control (6.2 Exploratory Development), Work Unit U19, "Alternatives for Removal of Hazardous Materials in Combination." The technical reviewer was Chris Vercautren, Industrial Operations Command.

The work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The CERL Principal Investigator was Michelle J. Hanson. Dr. Roger L. Schneider is a contractor with Rho Sigma Associates, a scientific and engineering consulting firm. The technical editor was Linda L. Wheatley, Information Technology Laboratory. Dr. Ilker Adiguzel is Chief, CN-E, and Dr. John T. Bandy is Chief, CN. The Acting Director of CERL is Dr. Alan W. Moore.

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# 1 Introduction

## Background

The Construction Engineering Research Laboratory (CERL) is developing technologies for the safe, economically advantageous, and environmentally benign assessment, decontamination, and disposal of excess energetic material (EM) processing buildings at U.S. Army Ammunition Plants (AAPs). More than 20 AAPs are currently in an inactive or excess status. These facilities each have hundreds of buildings that are inactive. Some buildings have not been used since the end of the Vietnam conflict, and some since the end of World War II. They were used to manufacture EM (propellants, explosives, and pyrotechnics) and their precursors. Many of the buildings at these AAPs are contaminated with EM and/or EM residues. The EMs are present primarily as surface residues, but bulk quantities can be concealed in processing equipment. Many buildings also contain considerable quantities of asbestos containing building materials (ACBMs), and many are structurally unsound.

On 10 July 1996, an inactive processing building at the Sunflower Army Ammunition Plant (SFAAP) was intentionally set on fire to destroy the structure as part of a scheduled demolition program. Considerable ACBM and what was thought to be small amounts of residual nitrocellulose (NC) were in the building. The decision to burn the building was based on an evaluation of its structural integrity. It was determined the building's dilapidated condition would pose unacceptable hazards to workers engaged in conventional asbestos removal and/or EM decontamination. Soon after fires were set, an explosion occurred, which destroyed the structure and propelled ACBM debris substantial distances from the building site. This event illustrates the need to provide a means to demolish buildings in an environmentally benign and economically advantageous manner.

The ACBMs found in these facilities include pipe, boiler, and chemical reactor insulation, wall coverings and insulation, siding, flooring, and roofing. Provided a structure that contains ACBM is sound, well-established industrial procedures can be used to remove the asbestos prior to razing the facility. However, if the ACBMs are contaminated with EM, conventional abatement technologies will likely be unsuitable. Routine scraping, cutting, and pounding, the use of non-explosion-proof lighting fixtures and motors, the erection of dust-confining

structures, and the liberal use of nonconductive polymeric films for barriers, bagging, and worker's protective suits are commonplace in asbestos removal operations, but would be unacceptable practices in the presence of EMs.

Two major fibrous silicate groups are classified as asbestiforms. They are the fibrous serpentines, of which chrysotile is the principal member, and the amphiboles, which include amosite, crocidolite, anthophyllite, tremolite, and actinolite. In the United States, only chrysotile and amosite have been used in ACBM in any significant quantities, with chrysotile having been used to the greatest extent.

The surface structure of chrysotile provides adsorption sites for various types of organic compounds. Chrysotile's adsorption of benzo[ $\alpha$ ]pyrene, a component of cigarette smoke with mutagenic and carcinogenic potential, has been studied extensively (Shabad et al. 1974; Krivosheeva and Pylev 1974; Lakowicz and Bevan 1980; De Waele et al. 1983a; Menard et al. 1986a, 1986b; Gerde and Scholander 1988; De Waele and Adams 1988). The chrysotile's adsorption of other polycyclic hydrocarbons (Menard et al. 1986b; Mossman and Craighead 1981, 1982; Fournier and Pezerat 1986), both aliphatic and aromatic amines (De Waele et al. 1983a, 1983b; De Waele and Adams 1988; De Waele, Vansant, and Adams 1983), benzene (Gorski and Stettler 1975), and basic and acidic dyes — including picric acid (Valerio, Puntoni, and Santi 1979) — has also been investigated.

Collectively, these studies demonstrate the enhanced surface properties of natural chrysotile leading to the adsorption of many types of organic materials. Since significant interactions occur between natural chrysotile and both low and high molecular weight organic materials, it seems likely that EMs will interact with chrysotile in much the same manner. However, although the literature is replete with studies of the adsorption of both organic and inorganic compounds on chrysotile, no accounts could be found which address the adsorption of the typical components of EM, such as polynitroaromatics (other than picric acid), nitrate esters, and nitramines, on any asbestiform (Schneider and Spooner 1997).

## Structure of Chrysotile

Chrysotile is a hydrous magnesium silicate of empirical formula  $Mg_3Si_2O_6(OH)_4$ , with a double-layered structure as the fundamental building block. The lower layer has linked  $SiO_4$  tetrahedra. All of these tetrahedra point in one direction and join to a brucite (magnesium hydroxide,  $Mg(OH)_2$ ) layer. The inter-atomic dimensions of the tetrahedral silicate layer are about 9 percent smaller than the corresponding dimensions in the brucite layer. This mismatch is accommodated

by curving the layers in one direction, with the silicate-brucite paired layers coiling upon themselves to form concentric, tightly wrapped (convolute wound) tubes or fibrils. The outside layer of these tubes is brucite, so the external surface of the fibrils comprises a matrix of  $Mg^{2+}$  ions and terminal hydroxyl (OH) groups. The magnesium ions and hydrogens on the hydroxyls represent potential bonding sites for nucleophiles (electronegative species) such as aromatic rings or the nonbonded pair of electrons on the nitrogen of amines. The fused ring structure of benzo( $\alpha$ )pyrene, with abundant  $\pi$  electron density is thought to bond to the brucite layer of chrysotile (Deer, Howie, and Zussman 1962).

Gorski and Stettler (1975) determined select surface properties of samples of chrysotile. Samples were prepared into three groups: "as received" condition, a lightly crushed or disaggregated state, and milled into a very fine state. Brunauer-Emmett-Teller (BET) isotherms were determined at 78K using  $N_2$  as the adsorbate. Surface area measurements for these samples of chrysotile range from 15 to 48  $m^2/g$ . These data suggest that significant surface area is available on chrysotile for the bonding of EMs. Chrysotile could be an EM sink.

## Objectives

Because of a lack of information regarding the possible interactions between ACBMs and EMs, CERL began research efforts to determine the nature and extent of adsorption of common energetic compounds on chrysotile asbestos. The research addressed questions concerning (1) the possibility that ACBMs, serving as absorbents, could be contaminated with energetic compounds, such as NG and PETN, and (2) could the level of contamination be high enough to make the removal of ACBMs explosively hazardous? Understanding the interaction of these materials is essential to developing sound, comprehensive guidance for the disposal of excess AAP facilities.

## Approach

To determine the nature and extent of the interactions between EMs and chrysotile, methods were desired that were direct, simple to use, and would provide both qualitative and quantitative information on the sorption process. The analytical procedures also needed to be compatible with EMs, creating no greater safety hazard in their use.

Infrared (IR) spectroscopy was the principal analytical probe chosen for this study. This well-established instrumental technique is convenient to use, and

was expected to provide qualitative and some quantitative information on the adsorption of EMs on chrysotile. Fingerprinting, which refers to the comparison of a spectrum of an unknown substance with reference spectra of known materials, can also be done (Settle 1997) to confirm the presence of adsorbed molecules and judge the purity of reactants.

IR spectroscopy can also be used to determine the form of adsorption, that is, whether it is physical and readily reversible, or it is chemical, involving strong bonding and decomposition of the surface reactants. The ability to monitor by IR spectra adsorption and desorption processes also provided empirical rate of reaction data.

A dedicated glass high vacuum system was constructed and used for the thermal pretreatment of hydraulically pressed ultrathin chrysotile wafers. In the typical experiment, a chrysotile wafer was housed within a specially designed IR cell/reactor. While the cell/reactor was affixed to the vacuum system, the wafer was heated to 200 °C, under vacuum, to clean the surface of physically adsorbed water and organics. The cell/reactor was then detached from the vacuum system and placed in the sample compartment of the IR spectrometer. With the chrysotile wafer in the beam and still under vacuum, a source of PETN or NG vapors was opened and the adsorption of the energetic compound was monitored with absorbance band development during sequential recordings of spectra.

Untreated chrysotile wafers, under ambient laboratory conditions, were spotted with solutions of PETN and NG. The solvents were allowed to evaporate and the IR spectra of the spotted wafers were then recorded. These spectra were used as references and to provide information on the interaction of chrysotile with PETN or NG at levels which could be encountered if a chrysotile ACBM was the receptor of an accidental spillage of the energetics.

### **Mode of Technology Transfer**

Findings from this study will be incorporated into ongoing research efforts involving the assessment, decontamination, and disposal of excess EM processing buildings at U.S. AAPs.

Results were presented at the October 1999 Federation of Analytical Chemistry and Spectroscopy Studies (FACSS) Conference in Vancouver, British Columbia, Canada. Also, a paper specifically addressing the adsorption of NG on chrysotile has been accepted for publication in the proceedings of the 27<sup>th</sup> International Pyrotechnics Seminar, Grand Junction, CO, July 2000.

## 2 Experimental Apparatus

### Borosilicate Glass High Vacuum System

A general purpose, glass high vacuum system capable of maintaining an equilibrium pressure of  $10^{-6}$  torr had been constructed for a previous investigation. With modifications it was also used in this research. The main manifold (30 mm outside diameter [OD]) and a submanifold (15 mm OD), and all connecting tubing were Pyrex 7440. The stopcocks were either high vacuum glass (Ace Glass, Inc., Vineland, NJ) or high vacuum Teflon/glass (VM Glass Co., Vineland, NJ). The system is serviced by a glass, 4-in. diameter, air-cooled, three-stage high vacuum oil diffusion pump (Dow Corning 704 pump fluid [Dow Corning, Midland, MI]), backed by a Welch 1400 Duoseal fore pump (Welch Vacuum Technologies, Inc., Skokie, IL). The "Wheeler" diffusion pump was manufactured by Custom Glassblowing, Chandler, AZ. Its pumping speed is claimed to be 375 l/s with a capability of achieving a pump fluid limited ultimate vacuum of  $5 \times 10^{-8}$  torr. This pump replaced a damaged and considerably less efficient glass, two-stage pump, which had serviced the system. The system pressure was measured with cold cathode and thermal conductivity pressure gauges. Cold traps for the diffusion pump and fore pump were maintained at 77K with  $\text{LN}_2$ .

### Infrared Cell/Reactor

Figure 1 (page 14) depicts the IR cell/reactor used in this work. The cell enables a pressed wafer of chrysotile to be subjected to several treatments, including vacuum heating (quartz limit) and exposure to vapors of EMs while monitoring the results of each treatment with IR spectroscopy. Except for the quartz oven section (A), the cell components are made of borosilicate glass. For high temperature oven processing of samples, the carriage (B) can be constructed of quartz.

The oven section is joined to the upper and lower borosilicate sections through graded seals (a). The heating source for the oven is a coil of 22-gauge chromel (Nichrome) wire, which runs the length of the 17 mm OD quartz tubing and terminates at the ends with simple loops for attachment of leads from a 110 VAC variac power supply. The oven insulation (C) is Refrasil, a fibrous silica cloth

manufactured by the H.I. Thompson Co (Guelph, Ontario, Canada). It is sealed with an external coating of GE-RTV108 silicone sealant (General Electric, Schenectady, NY), which prevents unraveling or flaking. The RTV108 will resist short-period heatings at 260 °C and a continuous operating temperature of 205 °C. The oven jacket will have (in quiescent air) an external surface temperature of about 100 °C when the center of the oven sections is 500 °C. A thermocouple (b) housed in a quartz tubing well (c) is used to measure the oven temperature. The true temperature at the center of the oven, under vacuum, is typically 5 percent higher than the thermocouple reading over the range of 100 to 300 °C. For the heating of the chrysotile wafers, the oven temperature was maintained at set point with an Omega Engineering model CN6072A temperature controller, configured with a Type K (chromel-alumel) thermocouple temperature probe.

The IR wafer holder or carriage (B) comprises an encased Alnico V cylindrical magnet (f), an extension rod, a pair of links, and the wafer cradle (d). The foot (g) is for positioning purposes. The arrows indicate the point of insertion for the pressed rectangular wafer. In this research, oven temperatures below 500 °C were used; therefore, a borosilicate carriage was adequate. If asbestos wafers are to be heated at temperatures above 550 °C, the carriage must be made entirely of quartz.

The sublimator (D) is a modified, size 0-3, high vacuum Teflon/glass stopcock. The NG is contained in the bulb (h), the wall thickness of which is blown thin to improve thermal conductivity.

The cell ports (E) have ground flat frames (i) around the two rectangular openings. These roughened flat surfaces are necessary for strong, vacuum tight bonding of the salt (potassium bromide, KBr) windows, not shown in Figure 1. The KBr windows are 41-mm long, 23-mm wide, and 6-mm thick. They were Catalog No 0002C-99, obtained from International Crystal Laboratories (Garfield, NJ). A two-part epoxy resin (Borden Chemicals, Morganton, NC) was used to cement the windows to the frames.

The three-way "tee" high vacuum stopcock allows for the evacuation of the cell and the introduction of a gas contained in the storage bulb (F). The bulb provides a convenient way to introduce a reactant gas into the cell while the wafer sample is fixed within the beam of the IR spectrophotometer. The storage bulb was not used in the work reported here.

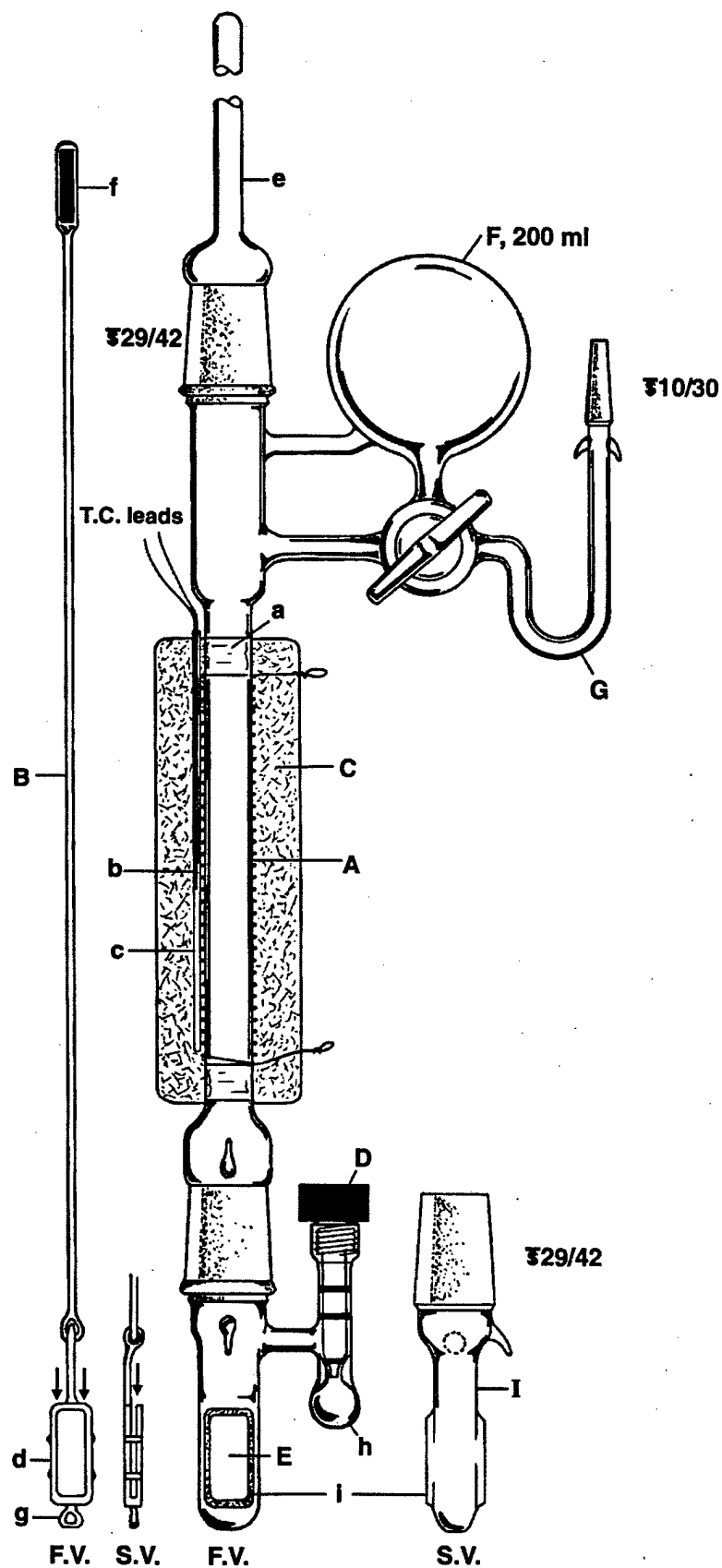


Figure 1. IR cell/reactor.

## **Infrared Spectrophotometer**

A 1980's vintage Polaris brand, Fourier transform infrared (FTIR) spectrophotometer (Mattson Instruments, Madison, WI) was used for the recording of all spectra to  $0.5 \text{ cm}^{-1}$  resolution. Data were collected and digitally encoded with WinFIRST (Windows Fourier Infrared Software Tools) software, produced by Analytical Technology, Inc. (Oaks, PA). Typically, for each IR spectrum, 256 interferograms or scans were recorded, co-added, Fourier transformed, and plotted as absorbance versus wave numbers. Although the capability existed, background spectra of the neat chrysotile were not subtracted from spectra of adsorbed NG.

## **Gas Chromatograph-Mass Spectrometer**

Samples were processed with a model 5890 gas chromatograph (GC) coupled to a model 5970 quadrupole mass spectrometer (MS) (Hewlett-Packard, Palo Alto, CA).

### 3 Reactants

#### Chrysotile

A clean, white, naturally occurring chrysotile was obtained from the Geology Department of the Milwaukee Public Museum, where it was labeled as having come from the Jeffrey Mine, Quebec, Canada. Slightly dampened with water, this chrysotile was easily pressed hydraulically at 10-20 Kpsi (69-138 MPa) into thin self-supporting, irregularly shaped wafers. Rectangular samples, measuring typically 11 by 28 mm and suitable for the wafer cradle of the IR cell, were prepared by trimming the wafer with a razor blade. The wafers had a "thickness" of 10 mg/cm<sup>2</sup>.

#### Brucite

A clean, white, naturally occurring crystalline brucite was obtained from Ward's Natural Science Establishment, Inc. (Rochester, NY). It was labeled as having come from Cedar Hill, Lancaster Co., PA. This crystalline material was ground to a fine powder with a synthetic sapphire (Diamonite) mortar and pestle. Self-supporting wafers were prepared by pressing the powder at 10 Kpsi (69 MPa) to a thickness of about 10 mg/cm<sup>2</sup>.

#### Pentaerythritol Tetranitrate

The PETN was removed from Ensign-Bickford (Simsbury, CT) Primacord, E-Cord, and used without further purification.

#### Nitroglycerin

NG was prepared using an adaptation of published procedures (HQDA 1984; Pinchas 1951). Mixed acids comprising 56.5 ml of 70% w/w nitric acid (SpG =1.42 g/ml, JT Baker 9601-04, Lot L19028 [Fisher Scientific, Pittsburgh, PA]) and 43.5 ml of 96% w/w sulfuric acid (SpG =1.84 g/ml, VWR 6840-3, Lot 4171

[VWR Scientific Products, West Chester, PA]) was prepared and allowed to cool to room temperature in a sealed bottle.

A 16-g (10 mL) portion of the mixed acids was transferred to a 100 mL, tall form, Berzelius beaker [Corning (Pyrex) No. 13922-029] and a Teflon-coated magnet stir bar was added. The beaker was placed in a shallow ice bath, which was atop a magnetic stirrer. A lead donut held the beaker submerged to about half its height in the ice water. A mercury-in-glass thermometer was clamped into position with its bulb immersed in the mixed acids. With moderate stirring, 2.7 g of glycerin (JT Baker 1-2136, anhydrous, Lot 517051 [Fisher]) was added to the mixed acids by drops over a period of 30 minutes with the rate adjusted to ensure the reaction temperature remained below 5 °C. Salt and ice were added periodically to the bath to maintain a temperature near 0 °C.

Ten minutes after the addition of the last drop of glycerin, the milky reaction products were transferred to a 25-mL graduated cylinder. After standing for a few minutes, the NG separated from the spent acid, forming a clear layer at the top. With a pipette, the NG was carefully transferred from the cylinder into a beaker containing 200 mL of deionized wash water at 40 °C. The mixture was stirred vigorously for several seconds. The NG was then allowed to settle out as cloudy coacervated globules (NG/water emulsion). The wash water was decanted and replaced with a 2 percent solution of sodium carbonate (Fisher) at room temperature, which was stirred and then decanted. As a desiccant, 2 g of anhydrous sodium sulfate was added to the moist NG, followed by 50 mL of diethyl ether. The ether solution of NG was decanted from the hydrated sodium sulfate (Fisher) and transferred to a polypropylene bottle fitted with a rubber stopper.

This synthesis was performed three times, with the NG produced in each reaction later combined. The combined NG was judged to be reasonably pure by GC-MS and IR spectroscopy (Pristera 1953). The weight ratio of mixed acids to glycerin was 6:1.

## 4 Exposure of Chrysotile to Pentaerythritol Tetranitrate

Approximately 200 mg of PETN was loaded into the cell's sublimator. The Teflon plug was then replaced and seated. The cell was attached to the vacuum system and evacuated to  $10^5$  torr. The sublimator was slowly opened to allow trapped air within the bulb to be removed. With a vapor pressure of  $\sim 10^{-10}$  torr at room temperature (RT), there was little concern any significant amount of PETN would be lost from the bulb. After 15 minutes, the sublimator was closed and the cell pumped until a system pressure of  $10^6$  torr was achieved. The cell was then detached and opened to allow for the loading of a chrysotile rectangular wafer in the cradle. The cell was reassembled and attached to the vacuum system. The chrysotile was raised into the oven section, and under vacuum, heated to  $100^\circ\text{C}$  for 8 hr. Once the chrysotile wafer was cooled to RT, it was lowered to the windowed section and the cell was detached.

The cell was positioned within the sample cavity of the IR spectrometer, so the IR beam passed through the centers of the two parallel KBr windows. The cavity was purged with dry nitrogen, the chrysotile raised a few centimeters out of the windowed section, and a background spectrum recorded. The chrysotile was then lowered into the beam and its spectrum recorded. The absorbance spectrum in Figure 2 is typical for the chrysotile used in this work, after it had been pretreated in vacuo at  $100^\circ\text{C}$ . The lattice vibrational bands centered at  $604$ ,  $965$ ,  $1018$ , and  $1076\text{ cm}^{-1}$  are qualitative for chrysotile. The band centered at  $3685\text{ cm}^{-1}$  and its shoulder at  $3652\text{ cm}^{-1}$  are assigned to the O-H stretch of surface water and the magnesium hydroxyls in the brucite layers. The chrysotile spectra recorded with the Polaris FTIR closely match spectra recorded by others (Rajhans and Sullivan 1981).

The sublimator with the PETN at RT was opened and spectra were recorded periodically over a 7-hr period. No bands attributable to adsorbed PETN developed. The cell remained in the spectrophotometer, with the sublimator open, over a weekend. The first spectrum recorded showed no change in the chrysotile nor any PETN bands. The bulb of the sublimator was then immersed for nearly an hour in a  $60^\circ\text{C}$  oil bath, with expectations that the higher vapor pressure of

the PETN would manifest a detectable quantity of adsorbate. None was detected. Heating the PETN to 100 °C effected no change.

One might argue that PETN vapor was more strongly, perhaps even selectively, adsorbed onto the glass and quartz interior surfaces of the cell, to the exclusion of the chrysotile wafer in the IR beam. In other words, the glass and quartz surfaces acted as a PETN "getter" or "sink." No convincing argument can be made that the chrysotile wafer lacked sufficient surface area to accumulate a detectable concentration of PETN. As stated earlier, surface area measurements (BET) for chrysotile range from 15 to 48 m<sup>2</sup>/g. These measurements mean that the 150-mg chrysotile wafer in the cell exposed to PETN vapor likely had a surface area of 1 or 2 m<sup>2</sup> (or more). If so, the surface area of the chrysotile for PETN adsorption was about 30 times the interior surface area of the glass and quartz components of the cell.

The PETN was removed from the sublimator, the chrysotile wafer removed from the cradle, and the interior of the cell was cleaned with acetone. Figure 3 is a spectrum of PETN, recorded as a thin film on a KBr window. The thin film was created by allowing the acetone, in an acetone solution of PETN, to evaporate on the KBr window, leaving behind a film of microcrystalline PETN.

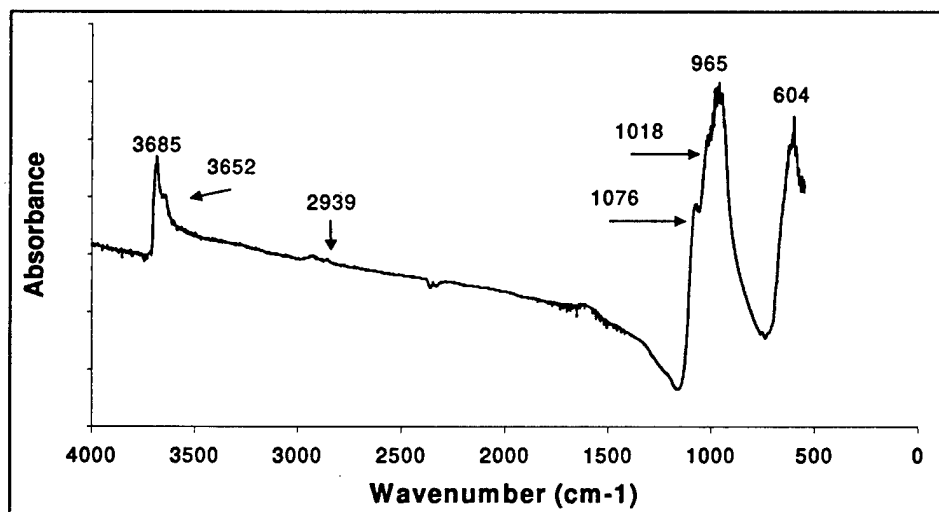


Figure 2. FTIR spectra of chrysotile.

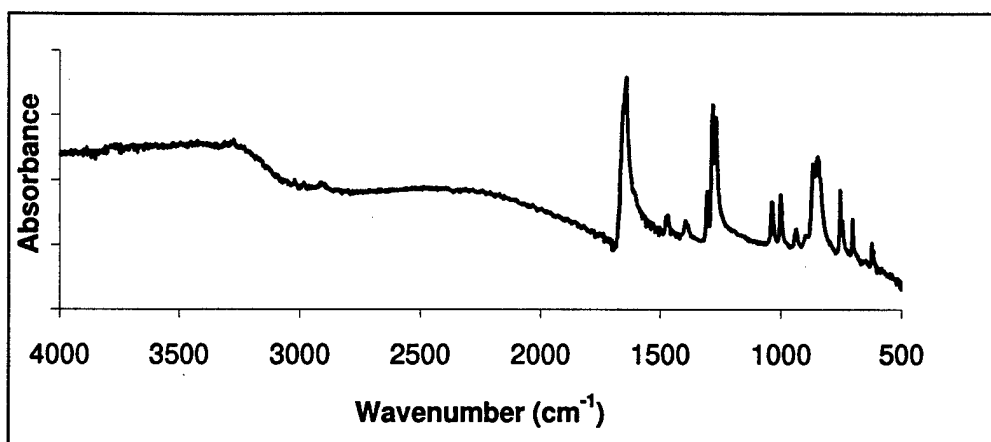


Figure 3. PETN solution on a KBr window.

## 5 Exposure of Chrysotile to Nitroglycerin

### Basic Adsorption Experiment

A few drops of the diethyl ether solution of NG were placed in the sublimator/vaporizer bulb of the cell/reactor. Using a gentle stream of nitrogen flowing through a glass capillary, the ether was purged. The process was repeated until readily noticeable droplets of NG were visible as a viscous, colorless liquid in the bulb. After the Teflon plug was replaced and seated, the cell was attached to the vacuum system and evacuated. Once the system pressure reached  $10^{-5}$  torr, the vaporizer was opened for about 15 seconds to de-gas the NG. Although some NG was undoubtedly lost from the vaporizer in the process, the amount was negligible. With the vaporizer closed, the cell was opened to allow the insertion of the carriage with a fresh chrysotile wafer in the cradle. The chrysotile was heated in vacuo at 100 °C for 2 hr. The chrysotile was cooled to RT and lowered into the windowed section of the cell, which was positioned in the spectrophotometer.

The cell was positioned within the sample cavity of the IR spectrometer so the IR beam passed through the centers of the two parallel KBr windows. The cavity was purged with dry nitrogen, the chrysotile raised a few centimeters out of the windowed section, and a background spectrum recorded. The chrysotile was then lowered into the beam and its spectrum recorded.

The vaporizer was opened. Over 4 to 6 hr, IR bands, indicative of physically adsorbed NG, developed slowly. Overnight (18 hr) exposure of the chrysotile to the NG vapor increased the loading of adsorbed NG, as evidenced by the growth in intensity of the bands. Figure 4 shows the two strong bands assigned to stretching modes of the nitrate  $\text{NO}_2$  groups. One is centered at  $1647 \text{ cm}^{-1}$  (asymmetric stretch) and the other at  $1277 \text{ cm}^{-1}$  (symmetric stretch). The spectrum of neat NG, smeared on a KBr window, is shown for comparison in Figure 5. This experiment was repeated four times with identical results.

The temperature of the NG was increased to 60 °C by immersing the vaporizer bulb in an oil bath. The concomitant increase in vapor pressure ( $\sim 0.02$  torr [AMCP 706-177, 1963]), effected over a period of 5 hr, caused significantly greater loading of the chrysotile, as shown in Figure 6. A shoulder is present at about  $860 \text{ cm}^{-1}$ . It is assigned to the O-N stretch, and a shallow band centered at

2900  $\text{cm}^{-1}$  is attributable to the C-H stretch. A similar spectrum is produced (Figure 7) when a wafer of chrysotile in open air was spotted with NG. The NG was transferred to the surface as a diethyl ether solution with the ether allowed to simply evaporate.

The cell was reattached to the vacuum system and the chrysotile (with adsorbed NG) was heated in vacuo for 15 minutes. The temperature was ramped up to 100 °C in 5 minutes and held at set point for an additional 10 minutes. After cooling to RT, the chrysotile produced a spectrum indicative of the loss of adsorbed NG. Treating the sample to vacuum heating at 200 °C for 15 minutes effected the nearly complete desorption or decomposition of the NG, as manifested by the spectrum shown in Figure 8. The chrysotile had also become light grey, suggesting pyrolysis of the NG may have occurred, although some chrysotile wafers, freshly prepared and unexposed to NG also darkened following vacuum heating at 200 °C.

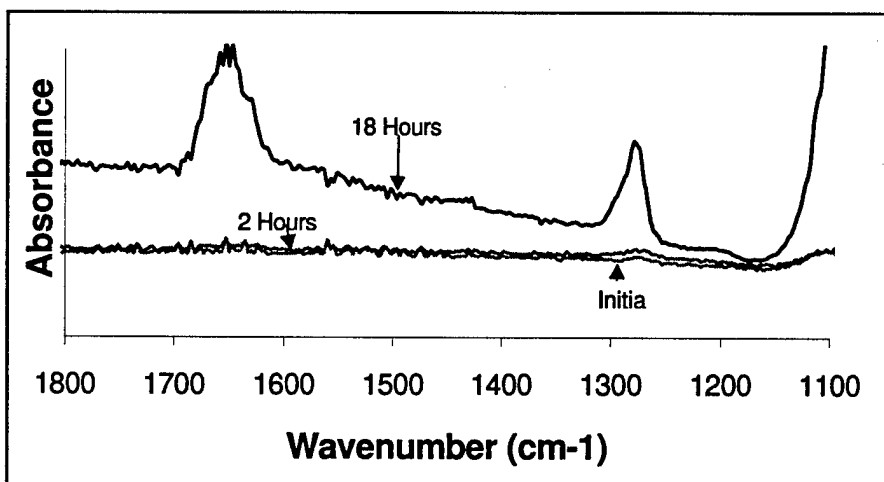


Figure 4. Development on NG bands.

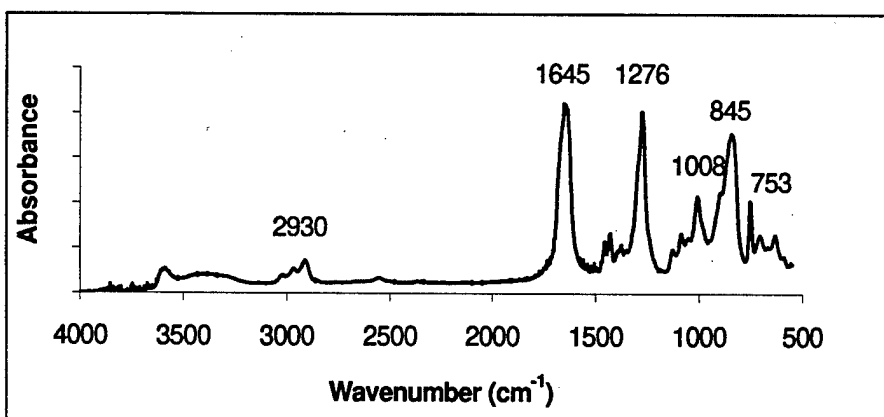


Figure 5. FTIR spectrum of NG on a KBr window.

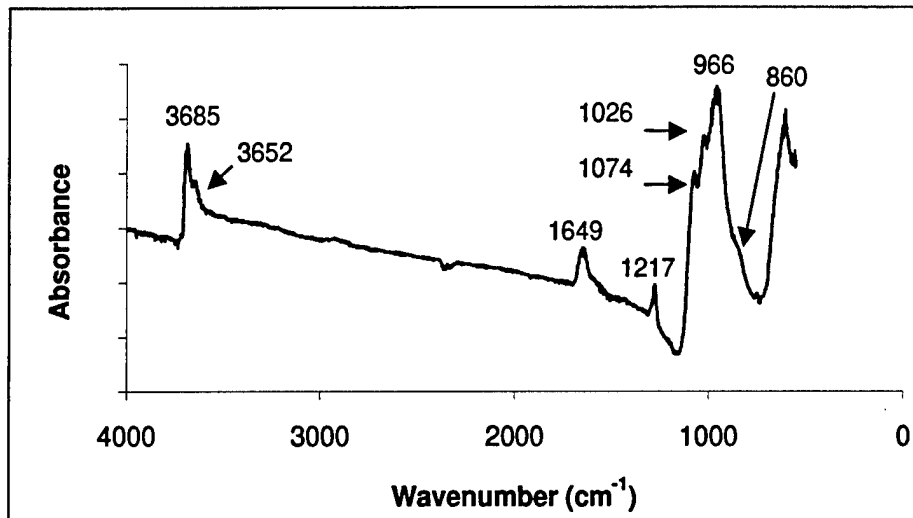


Figure 6. FTIR spectrum of NG vapor sorbed on chrysotile.

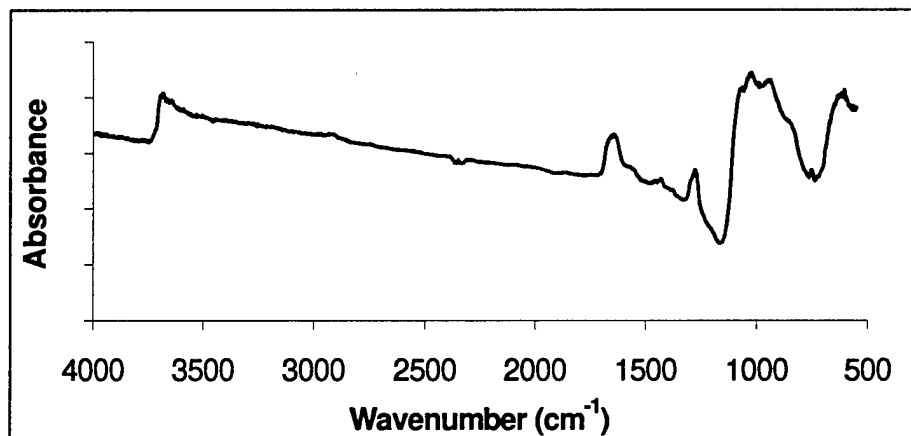


Figure 7. FTIR spectrum of chrysotile with adsorbed NG, introduced as a diethyl ether solution.

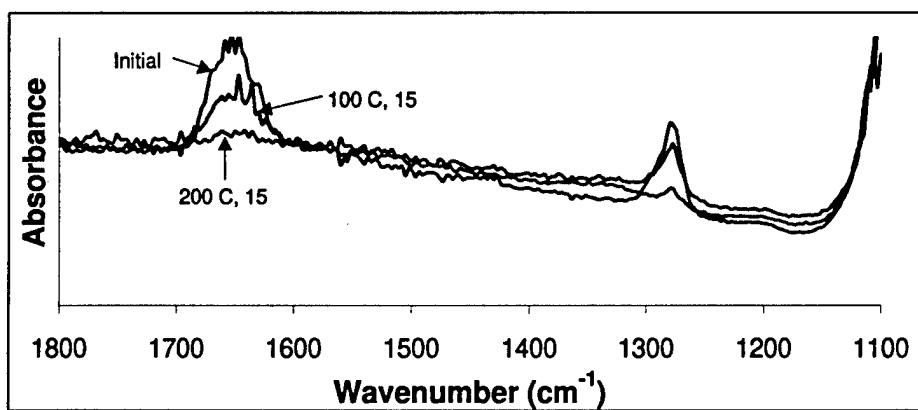


Figure 8. FTIR spectrum of NG on chrysotile before and after vacuum heating at 100 °C and 200 °C.

## A Test of Physical Adsorption

A freshly prepared chrysotile wafer was pretreated by vacuum heating for 1 hr at 100 °C. With the IR cell/reactor positioned within the spectrometer, a reference chrysotile spectrum was recorded and then, as in the basic experiment, the NG vaporizer was opened. During the next 60 hr, spectra documenting the development of bands attributable to increasing sorption of NG were recorded. An additional 10 hr of exposure resulted in no significant change in the NG band intensities and equilibrium was assumed. The NG vaporizer was closed. The cell/reactor was reattached to the vacuum system and evacuated with the NG saturated wafer at RT. Periodically throughout the next 70 hr, the cell/reactor was detached from the vacuum system and a spectrum of the wafer recorded. Diminution of the NG band absorbances was observed with complete loss of the NG bands observed after 60 hr.

## Sorption of Nitroglycerin on Untreated Chrysotile

Experiments were conducted to determine the sorption of NG on chrysotile wafers that were not dehydrated by vacuum heating above RT. A freshly prepared chrysotile wafer was inserted into the cradle of the IR cell, which was then attached to the vacuum system. The cell was evacuated to  $10^{-5}$  torr, with the wafer at RT. The cell was detached, placed in the spectrometer, and a background chrysotile spectrum recorded. Figure 9 shows, for comparison, the spectra of NG adsorbed on chrysotile, reflecting three different sample preparations (i.e., NG vapor adsorbed on dehydrated chrysotile [100 °C, vacuo]; NG vapor adsorbed on unheated [RT, vacuo] chrysotile; and NG transferred to the surface of untreated chrysotile in open air, as a diethyl ether solution).

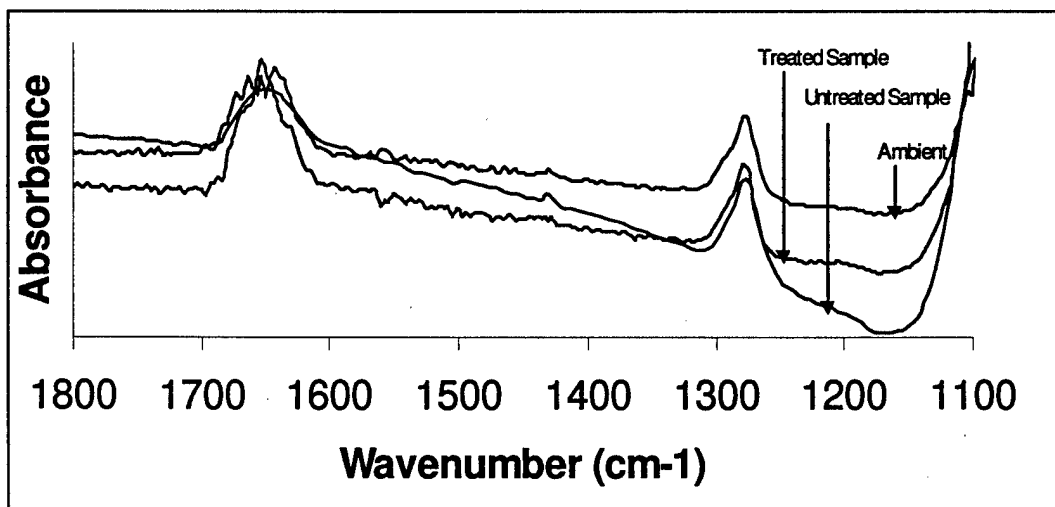


Figure 9. FTIR spectrum of NG on chrysotile — treated, untreated, and ambient conditions.

All of the spectra show the broad bands centered on 1647 and 1277  $\text{cm}^{-1}$  assigned to NG. Because the three spectra are quite similar, it may be concluded that the nature of the adsorption of NG on chrysotile is independent of the degree of surface hydration and perhaps the presence of competing solvent molecules.

### Solvent Extraction of Adsorbed Nitroglycerin

In an attempt to measure the quantity (loading) of NG on a chrysotile wafer, a "basic adsorption" sample was prepared first. The spectrum of the chrysotile wafer with sorbed NG was recorded to document the initial condition. The wafer was then removed from the cell and carefully immersed in 5 mL of a 50:50 v/v% mixture of diethyl ether-acetone. The integrity of the wafer was retained after immersion, but the solubilization/extraction of the NG was affected. The wafer was treated with a second 5 mL aliquot of the solvent mixture and then removed. The two 5-mL extractions were combined. The intact wafer was returned to the cell, the cell evacuated to  $10^{-6}$  torr, detached from vacuo, and a spectrum then recorded. The extraction process was repeated with two additional 5-mL aliquots of the solvent mixture and a third spectrum subsequently recorded. Figure 10 shows the three spectra. The four aliquots were combined, reduced in volume, and an NG concentration estimated by GC/MS. It was concluded that about 350  $\mu\text{g}$  of NG was adsorbed initially on the 30-mg chrysotile wafer, providing a 1% w/w loading.

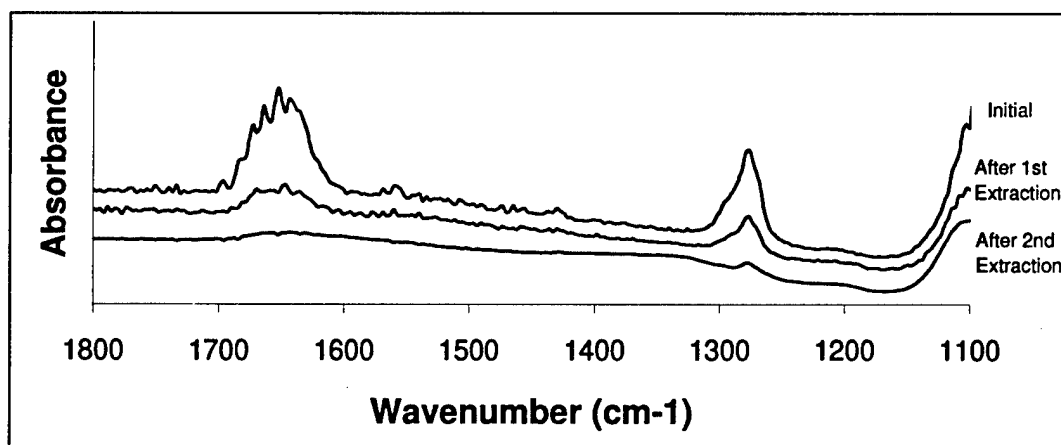


Figure 10. FTIR spectrum of NG on chrysotile — before and after solvent extractions.

Based upon the crystallographic data shown in the appendix, the projection area for the NG molecule is about  $80 \text{ \AA}^2$ . Projection area is the area occupied by an adsorbate molecule on a substrate. The BET surface area of chrysotile of the form used in this work has been estimated as  $30 \text{ m}^2/\text{g}$ . Using this figure, it can be shown that monolayer coverage of NG can be effected at 1% w/w loading, or 10 mg NG/g chrysotile. If the results of the extraction are valid, it would suggest that NG adsorbs on the chrysotile to produce monolayer coverage. However, it is more likely that the NG pools as microdroplets at certain sites on the surface, rather than as a uniform layer one molecule thick.

### Sorption of Nitroglycerin on Brucite

A brucite [ $\text{Mg}(\text{OH})_2$ ] wafer was pretreated by vacuum heating for 1 hr at  $100 \text{ }^\circ\text{C}$ , and a reference spectrum then recorded. The most distinctive feature of the brucite spectrum is a strong broad band centered at  $1452 \text{ cm}^{-1}$ . Other broad, less intense bands are observed, centered at 864 and  $600 \text{ cm}^{-1}$ . Fairly sharp hydroxyl bands are found at  $3276(\text{m})$  and  $3376(\text{w}) \text{ cm}^{-1}$ . NG adsorbed on the brucite after 30 hr of exposure produced bands centered on 1649 and  $1275 \text{ cm}^{-1}$ . These bands are lost following RT vacuum treatment of the wafer for 30 hr.

## 6 Conclusions

The apparent lack of adsorption of PETN vapor on clean chrysotile under high vacuum suggests either a low affinity or that the very low vapor pressure of PETN, even at 100 °C, produces surface concentrations too low to detect with the equipment used in this research. If the only form of PETN available to have contaminated ACBM in AAP processing buildings was its equilibrium vapor, it is very unlikely such contamination would be at a level high enough to warrant any disposal action.

At RT, chrysotile can adsorb NG vapor to loadings perhaps as high as 1% w/w, or a mass loading of 10 mg NG/g of chrysotile. This level corresponds to monolayer coverage, although it is more likely that NG pools as microdroplets on the chrysotile surface.

The adsorption is physical, with the level dependent upon the equilibrium vapor pressure of NG and exposure time. The 1% w/w loading is achieved in about 18 hr with the NG at RT (23 °C). The physically adsorbed NG can be desorbed from the chrysotile under vacuum at RT for the same length of time required to effect a specific loading. That is, the adsorption is truly reversible, as it should be if it is a physical adsorption.

As the temperature of NG-loaded chrysotile increases, adsorbed NG both desorbs and possibly undergoes a decomposition reaction(s) at the surface. Pyrolysis of NG may occur at 200 °C on chrysotile.

NG is physically adsorbed on brucite [ $\text{Mg}(\text{OH})_2$ ]. The FTIR bands attributable to NG sorbed on brucite are nearly identical to those observed for NG sorbed on chrysotile.

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## Appendix: Crystallographic Data

### Projection Area of Nitroglycerin

Density of NG at 25 °C is  $\rho_4^{25} = 1.5918 \text{ g/mL}$  (The Merck Index 1996)

The molecular volume is then,

$$V_m = \frac{M}{\rho N} = \frac{(227.09 \text{ g/mole})(10^{24} \text{ \AA}^3 / \text{cm}^3)}{(1.5918 \text{ g/cm}^3)(6.023 \times 10^{23} \text{ molecules/mole})} = 237 \text{ \AA}^3$$

Assuming the NG molecule lies "flat" on a substrate such as the surface of chrysotile, then the "thickness" of the molecule, based on the crystallographic data would be about 3 Å.

Then, with a volume of 237 Å<sup>3</sup>, the projection area would be about 80 Å<sup>2</sup>.

### Monolayer Coverage of Nitroglycerin on Chrysotile

For the "typical" chrysotile wafer: Area = 11x28 mm, mass = 31 mg

$$\therefore \text{"Thickness"} = 10 \text{ mg/cm}^2$$

Using a BET surface area of 30 m<sup>2</sup>/g, the

wafer surface area then is:  $A_w = (30 \text{ m}^2/\text{g})(0.03 \text{ g}) = 0.9 \text{ m}^2$  or

$$(0.9 \text{ m}^2)(10^{20} \text{ \AA}^2/\text{m}^2) = 9 \times 10^{19} \text{ \AA}^2$$

Each NG molecule occupies an area of 80 Å<sup>2</sup>, so for monolayer coverage on chrysotile, the number of NG molecules required is,

$$\frac{9 \times 10^{19} - 2}{8 \times 10^1 \text{ \AA}^2 / \text{molecule}} \approx 10^{18} \text{ molecules}$$

The corresponding mass of NG required is,

$$\left( \frac{10^{18} \text{ molecules}}{6.023 \times 10^{23} \text{ molecules / mole}} \right) 227.09 \text{ g / mole} = 3.8 \times 10^{-4} \text{ g} = 3.8 \times 10^{-1} \text{ mg} = 380 \mu\text{g}$$

Monolayer coverage represents,

$$\left( \frac{3.8 \times 10^{-4} \text{ g (mass of NG)}}{3 \times 10^{-2} \text{ g (mass of chrysotile)}} \right) 10^2 \% \approx 1 \% \text{ w/w}$$

So, monolayer coverage can be achieved with loadings of 10 mg NG/g chrysotile.

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