

VOC immobilization in soil by adsorption, absorption and encapsulation

Marco A. Arocha, Ben J. McCoy^{*}, Alan P. Jackman

Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA

Received 13 December 1995; accepted 3 June 1996

Abstract

Immobilization of volatile organic compounds (VOCs) in contaminated soils by solidification/stabilization (S/S) processes is an attractive potential remediation process. The objectives of this study were as follows: to evaluate S/S procedures, including a new process with a VOC adsorbent and silica coatings; to apply a straightforward and inexpensive analytical technique for characterizing VOC behavior during processing; and to propose the expanded use of waste materials such as contaminated soil, rice hulls, and shredded-tire particles. We investigated how the adsorbents, absorbents and encapsulating agents can be combined to retard volatilization and resist acidic aqueous leaching of toluene. The toluene released at each step of the S/S process was determined by an accurate headspace analysis method. Results showed that combining shredded-tire particles for absorption and sodium silicate for encapsulation is a promising method for immobilization of toluene in soil.

Keywords: VOC immobilization; Soil remediation; Adsorption and absorption; Encapsulation; Solidification/stabilization; Headspace analysis

1. Introduction

Solidification/stabilization (S/S) processes with cement have been widely applied for the treatment of wastes containing toxic heavy metals before landfilling [1,2]. This technology works satisfactorily for liquid and sludge wastes with up to 15% by volume of organic contaminants [3]. Contaminated soils containing toxic metals can be treated successfully with a cement-based S/S process. Toxic metals are chemically transformed to harmless compounds, such as insoluble salts and hydroxides, which have slower leaching rates than the original species [4]. After the cement sets, insoluble species are

^{*} Corresponding author.

microencapsulated in a solid mass, and the product can be used as construction material, such as road fill, hence eliminating disposal expenses.

Volatile organic compounds (VOCs) are frequently encountered in contaminated soils where nonpolar VOCs are sorbed to the clay and organic matter [5]. Exposed to ambient air, VOCs readily evaporate. Less reactive than metals in cement-based treatments, VOCs are difficult to immobilize and can interfere with cement setting [6]. As a preventive measure, organophilic clays and other patented materials are added as presolidification agents [3,7,8]. Organic binders are used for physical encapsulation of organic liquid waste and sludge, such as asphalt, polyethylene, polyesters, polybutadiene, epoxide, acrylamide gel, and polyolefins [9].

Ordinary Portland cement (OPC) is widely used as the encapsulating agent for inorganic (liquid and sludge) waste. When this technique is applied to VOC-contaminated soils, a minimum of 0.4 water/cement ratio [10] water must be available for OPC hydration. If the original soil water content is less than the OPC requirement and water is added, a significant amount of the adsorbed VOCs may be released to air because water displaces VOCs from adsorption sites [11]. Adsorbents may improve VOC adsorption, and decrease VOC desorption upon soil wetting. We have investigated how various adsorbents, absorbents, and encapsulating agents immobilize VOCs in S/S processes. In this study, OPC was tested as a VOC encapsulating agent. The low-cost adsorbent, rice hull ash (RHA), was also tested as a presolidifying agent to improve VOC retention and to avoid cement–VOC interaction during setting.

We propose a new approach to VOC immobilization wherein a low-cost VOC absorbent, shredded-tire particles, is substituted for adsorbents. With such an absorbent, VOC releases upon wetting are avoided. We suggest replacing the slow-setting OPC commonly used as the encapsulating agent by an instantaneous silica precipitation from sodium silicate solutions. Precipitated silica acts in two ways, as a particle coating agent and as an adhesive that forms soil agglomerates.

Used tires are a national problem because about 240 million worn-out tires are discarded in this country each year [12]. There is an urgent need for developing applications to use such waste material. For instance, about 3 million scrap tires are used as asphalt additives for road applications nationwide [13]. In a similar application, contaminated soil is used with asphaltic emulsions for cold-process paving [14]. An S/S treated product incorporating both contaminated soil and shredded-tire waste is, therefore, attractive for such applications.

The waste treatment industry has tried with limited success to apply S/S processes with a variety of additives for immobilization of VOCs in contaminated soils [8,15]. Conner [10] reports that “virtually no credible data are available” for VOC immobilization. Evaluation of immobilization of VOCs is difficult because of the volatility of these compounds, and few data are available on VOC losses during processing. Leachability of VOCs is often measured by the toxicity characteristic leaching procedure (TCLP) [16], but seldom are data reported on the VOC content prior to S/S processing [8,10]. Weitzman et al. [17] measured the VOCs emitted to air by a cement-based S/S process. It was observed that VOC emissions occurred mainly during mixing of waste and additives, and that emissions during curing time (30 days) were the same regardless of treatment.

Equilibrium headspace analysis is an effective analytical tool to measure VOCs in gas, liquid and sludge. Concentration of VOCs in leaching fluids from soil extraction can also be determined by this method. A headspace gas chromatographic technique, developed as a screening method for total VOC analysis in contaminated soils, was comparable to a more expensive and tedious purge-and-trap gas chromatographic method [5]. Lincoff and Gossett [18], using headspace gas chromatography, showed that equilibrium partitioning in closed systems (EPICS) is an accurate technique to determine Henry's constant of VOCs in water. Garbarini and Lion [19] developed an equilibrium headspace technique in closed systems to determine sorption of toluene and trichloroethylene from aqueous solution. In the current work, headspace analysis was applied as a method to follow VOC behavior through each S/S step. The S/S procedures are evaluated by measuring VOCs released to air in equilibrium with the treated waste, and by determining the VOCs extracted from treated and untreated soil with an acidic solution simulating acid rain and/or organic acids formed in landfills. We also applied headspace analysis with EPICS to construct equilibrium adsorption and absorption isotherms for gas and liquid phases.

The objectives of this study were (i) to evaluate a S/S procedure—commonly used for toxic heavy metal—when applied to VOCs, (ii) to test a new approach using a VOC absorbent and silica coatings, (iii) to apply a direct analytical technique for characterizing VOC behavior during processing, and (iv) to suggest the expanded beneficial use of waste materials such as contaminated soil, rice hulls, and shredded tires.

2. Materials and methods

Yolo silt loam (Table 1) was adopted as the soil model for this study. A sample was obtained from Horizon A of a UC Davis field location and dried in a greenhouse for 2 days. After drying, the soil was ground to 2 mm particle diameter. The resulting sample was milled through a No. 10 ASTM standard sieve, and plant residues were eliminated. Toluene, a common VOC soil contaminant, was chosen as the model contaminant (Table 2). Shredded tire particles 2 mm diameter size with particle density 0.95 g/ml were provided by Champion Recycling Inc., Apple Valley, CA. A typical tire contains 62% (w/w) styrene-butadiene copolymer rubber, 31% carbon black (used to reinforce the rubber), and small amounts of other components, such as extender oils, sulfur, zinc

Table 1
Physical characteristics of Yolo silt loam

| | |
|------------------|--------------------------------------|
| Surface area | 80.60 m ² g ⁻¹ |
| Organic carbon | 1.05% |
| pH | 7.9 |
| Sand | 33% |
| Silt | 49% |
| Clay | 18% |
| Particle density | 2.65 g cm ⁻³ |

Table 2
Physical properties of toluene

| | |
|--|---|
| Boiling point ^a | 111 °C |
| K_{ow} (at 20 °C) ^a | 490 ml ml ⁻¹ |
| Water solubility (at 20 °C) ^a | 515 mg l ⁻¹ |
| Henry's law constant ^b (at 25 °C) | 0.0067 atm m ³ mol ⁻¹ |
| Vapor pressure (at 25 °C) ^b | 28.44 mmHg |

^a [30]. ^b [25].

oxide, and stearic acid [20]. Properties of the sodium silicate solution are in Table 3, and characteristics of rice hull ash are in Table 4.

Sorption experiments for aqueous and vapor phases at 24 °C were conducted to evaluate VOC sorbents. The evaluation involved the construction of sorption isotherms that were applied to VOC mass balances in headspace analysis. The volatility of VOC compounds makes these chemicals difficult to quantify in experimental work, and several replicate samples were needed for all the experiments.

2.1. Vapor-phase sorption experiments

To construct toluene vapor sorption isotherms, known amounts of toluene and sorbent were combined in air-filled glass vials and allowed to equilibrate. Toluene headspace concentration was analyzed at equilibrium by gas chromatography. Control samples with various amounts of toluene and with no sorbent were used to construct a GC-response calibration curve. VOC mass balances comparing the GC-response calibration curve from empty vessels with sample vessels of the same internal surface area accounted for toluene sorption to vial walls. The amount of toluene sorbed was found by subtraction of the toluene in the headspace vapor from the original toluene added as:

$$X = M^i - V^g C^g \quad (1)$$

where X = mass (mg) of VOC sorbed, M^i = mass (mg) of VOC added to the vial, V^g = headspace volume (ml), and C^g = headspace concentration (mg ml⁻¹) calculated from the calibration curve.

A rough estimate of VOC adsorption to vial walls was made from data for adsorption on Pyrex[®] [21] for the worst-case scenario of relative vapor pressure (actual vapor

Table 3
Properties of sodium silicate solution ^a

| | |
|---|-------------------------|
| SiO ₂ | 28.7% |
| Na ₂ O | 8.9% |
| Ratio SiO ₂ /Na ₂ O | 3.22 |
| H ₂ O | 62.4% |
| Density | 1.38 g cm ⁻³ |
| Viscosity | 180 cp |
| pH (1% solution) | 11.3 |

^a PQ Corporation, Valley Forge, PA.

Table 4
Representative characteristics of rice hull ash ^a

| | |
|--------------------------------|----------------------------|
| SiO ₂ | 93.1% |
| K ₂ O | 2.3% |
| MgO | 0.5% |
| Al ₂ O ₃ | 0.4% |
| CaO | 0.4% |
| Fe ₂ O ₃ | 0.2% |
| Na ₂ O | 0.1% |
| Ignition loss | 2.77% |
| Carbon | 2–40% |
| Particle density | 1.5–2.3 g cm ⁻³ |
| Bulk density | 2–4 g cm ⁻³ |

^a OEC Corp., Williams, CA.

pressure/saturation vapor pressure, p/p°) equal to 0.95 (equivalent to 5800 μg toluene/42 ml vial). For these conditions the mass of toluene adsorbed on the internal surface of a 42 ml vial was conservatively estimated to be 3 μg . The VOC adsorbed to vial walls was only 0.05% of the amount added, and therefore adsorption to vial walls was neglected.

The sorbents rice hull ash, tire particles, and Yolo silt loam were compared with a strong adsorbent, activated carbon (S51 Darco, American Norit Company). Amber glass vials (42 ml, Fisher Scientific) were capped with septum-featured Teflon valves (no. 614163, 24 mm, Mininert[®] valve, Dynatech Precision Sampling, Co.). Various amounts of liquid toluene (1–35 μl) were added with a Gastight[®] microsyringe to vials containing a carefully measured mass of sorbent (about 2 g). Vials were slowly tumbled end-over-end at 1 rpm for 48 h to equilibrate [22]. Samples of the headspace vapor were withdrawn with a Gastight[®] microsyringe and analyzed by direct injection into a gas chromatograph (8500 series Perkin Elmer) equipped with a 30 m \times 0.53 mm Megabore[®] column (no. 125-1334, DB-624, J and W Scientific) and a flame ionization detector (GC-FID). An adsorption experiment was also conducted to confirm that no toluene adsorbed on dried powder OPC.

2.2. Aqueous-phase sorption experiments

Similar to the vapor sorption experiments, we conducted measurements for toluene sorption from an aqueous phase. Glass vials with known volumes of liquid and air, and known mass of sorbent were injected with various amounts of liquid toluene. Control experiments with the aqueous phase but no sorbent, and with no aqueous phase or sorbent, were also conducted to construct a calibration curve. The VOC sorbed was calculated in terms of M^t , the total mass of VOC added, V^l and C^l , the volume and concentration of the aqueous phase, and V^g and C^g , the volume and concentration of the gas phase,

$$X = M^t - V^l C^l - V^g C^g \quad (2)$$

Table 5
Characteristics of the pyrolyzed tire carbon ^a

| | |
|-----------------------|---|
| Carbon | 85.78% |
| Ash | 8.46% |
| Volatile matter | 5.31% |
| Moisture | 0.45% |
| Specific surface area | 45.8 ± 0.5 m ² g ⁻¹ |

^a Champion Recycling Inc. (Apple Valley, CA).

where C^l (mg ml⁻¹) was calculated from the dimensionless Henry's constant (H_t) for toluene,

$$C^l = C^g / H_t \quad (3)$$

Experiments with rice hull ash, tire particles, and Yolo silt loam were carried out in 42 ml amber glass vials loaded with various amounts of each sorbent (up to 5 g) and 20 ml of the aqueous phase. About 2 ml of headspace was allowed in each of the vials, which were capped with Mininert[®] valves. The aqueous phase solution was prepared with 5.7 ml glacial acetic acid and 64.3 ml of 1.0 N solution of NaOH, diluted to 1.00 l with reagent-grade water. This solution (pH = 4.93 ± 0.05) in TCLP [16] is known as extraction fluid no. 1 (EF no. 1). A volume of 14 μl of toluene was added to each vial with a Gastight[®] microsyringe. The vials were rotated end-over-end at 30 rpm for 24 h to achieve equilibrium [16], and samples of the vapor headspace were analyzed by GC-FID. For the aqueous-phase adsorption experiments on soil, less than 3 μl of toluene were added because wet soil is a poor adsorbent. Pyrolyzed tire carbon (Table 5), an adsorbent produced by heat treatment of shredded-tire particles, was also tested for comparison with the tire particles. Henry's constants for toluene were calculated from control samples containing either EF no. 1 or water, but not sorbents.

3. Stabilization / solidification procedures

3.1. Analysis technique

Headspace analysis was used to follow the behavior of VOCs during each step of the fixation process. The analyses were performed to determine contaminant spiking level in soil mixture, contaminant losses resulting from moisture and curing reactions, and contaminant concentration in extract. The procedure was as follows.

3.2. VOC spiking level

Oven-dry samples of soil and dry additives, such as tire particles or rice hull ash, in vials of known volume were spiked with a given amount of toluene. The amount of contaminant sorbed was calculated by headspace analysis after 24 h of end-over-end tumbling at 1 rpm as

$$X_1 = M^t - V_1^g C_1^g \quad (4)$$

where X_1 = mass of VOC sorbed, M^t = mass of VOC added, V_1^g = headspace volume, and C_1^g = headspace concentration. Subscript 1 stands for the initial spiking step. The mass of VOC sorbed at this step, X_1 , was used to normalize the results at each subsequent step of the S/S procedure.

3.3. VOC evaporation resulting from liquid additives and curing reactions

Water for cement hydration was added via microsyringe, and samples were allowed to set. Headspace analysis gave the amount of VOC remaining in the soil after cement curing,

$$X_2 = M^t - V_2^g C_2^g \quad (5)$$

where subscript 2 stands for the analysis after water addition and cement curing. The VOC volatilized by water addition and cement curing was calculated as

$$\% \text{VOC volatilized} = [(X_1 - X_2)/X_1] 100 \quad (6)$$

3.4. VOC leached

The leaching procedure was accomplished by opening the vial, adding a volume V_3^l of extraction fluid, flushing out vapor in the headspace with compressed air, and capping immediately. The total amount of toluene in the vials at the start of the leaching was the amount X_2 sorbed by the soil in the spiking procedure. The samples were tumbled end-over-end for 18 h at 30 rpm. The headspace volume V_3^g during extraction was about 25% of the vial volume. The amount of contaminant released to the gas phase was measured by headspace analysis and VOC mass balance,

$$X_3 + V_3^l C_3^l + V_3^g C_3^g = X_2 \quad (7)$$

where subscript 3 refers to the analysis after the extraction procedure. The extract concentration C_3^l was calculated by Eq. (3). The VOC retained by the treated soil was calculated from Eq. (7) by solving for X_3 . The percent of VOC retained and the percent of VOC leached out by the extraction procedure were calculated as follows:

$$\% \text{VOC retained} = (X_3/X_1) 100 \quad (8)$$

$$\% \text{VOC leached} = [(X_2 - X_3)/X_1] 100 \quad (9)$$

To calculate the extracted amount by Eq. (9), the VOC released to both air and aqueous phases were added, i.e. $X_2 - X_3 = V_3^l C_3^l + V_3^g C_3^g$. The amount of VOC released to the gas phase during the extraction was about 10% (w/w) of the amount released to the liquid phase.

The aim of the evaluation of VOC immobilization by equilibrium headspace analysis was the comparison of the equilibrium partition coefficients, K_d (VOC concentration in the solid matrix/VOC concentration in the aqueous phase), for the treated soil and the control samples. A larger difference between K_d for the treated and untreated soils implies a more effective immobilization process. The larger the value of this parameter for the treated soil, the more likely the contaminant will be retained by the solid matrix.

In S/S processing, waste isolation is not perfect because of the porosity and imperfections of the encapsulating materials. During a leaching test, a fraction of the total VOC present in the S/S product is isolated from leaching and does not participate in the sorption–desorption equilibrium process during the aqueous extraction. This fraction is either irreversibly sorbed to the solid matrix or is isolated from leaching by the encapsulating agent. VOC retention is a consequence of the sorption capacity of the solid matrix and physical isolation of the contaminant by the soil–fixative structure. The apparent partition coefficient for the treated soil mixture, K_d^{app} , is a measure of partitioning of the sorbed species between extract and solid matrix. The sorbed species can be divided into two fractions, one in equilibrium with the extract and one of immobile species retained by chemical reaction or physical encapsulation,

$$K_d^{app} = \frac{(x_i + x_s)/m}{C_L} = \frac{x_i/m}{C_L} + \frac{x_s/m}{C_L} \quad (10)$$

where x_i = mass of immobile species by encapsulation, x_s = sorbed species in equilibrium, m = mass of soil mixture, C_L = contaminant concentration in the liquid phase at equilibrium.

Because physical adsorption is a reversible process, we wish to know how much VOC retention after the leaching test is a result of the physical sorption capacity of the sorbents. For this purpose, a sorption partition coefficient K_d^{sorp} , resulting from *reversible* physisorption, can be calculated,

$$K_d^{sorp} = \frac{x_s/m}{C_L} \quad (11)$$

where x_s = calculated mass of VOC sorbed by the mixture, m = total mass of soil mixture, C_L = experimental contaminant concentration in the extract at equilibrium. The mass of VOC sorbed by the mixture, x_s , is calculated from the sorption isotherm or from the sorption equation for the particular sorbate–sorbent. For a linear sorption isotherm, the usual case for sorption in aqueous systems in small concentrations, Eq. (11) applies. Combining Eq. (10) and Eq. (11) gives

$$K_d^{app} = \frac{(x_i + x_s)/m}{C_L} = \frac{x_i/m}{C_L} + K_d^{sorp} \quad (12)$$

which allows a comparison of K_d^{sorp} and K_d^{app} and shows the effect of reversible physical sorption on the total VOC retention.

4. Treatment with cement and rice hull ash

Two treatment experiments were undertaken for two conceptual models of encapsulation in cement-based treatment processes. The first model was based on occlusion of soil pores by a small amount of ordinary Portland cement (4% w/w). The second was based on forming a uniform coating on soil surfaces by a large amount of cement (20% w/w).

4.1. Small cement content

4.1.1. Spiking step

A 2 g sample of air-dried soil (about 2% moisture content) was weighed and loaded into 42 ml amber glass vials. Ordinary Portland cement and rice hull ash were mixed with the soil and the vials were capped with Mininert® valves. For all the S/S procedures described below, samples were spiked with 4 μ l (3460 μ g) of liquid toluene and slowly tumbled for 24 h at 1 rpm to achieve toluene vapor–soil adsorption equilibrium. After this period, headspace analysis was performed to determine the amount of toluene adsorbed by the mixture, which depends on soil and rice hull ash content.

4.1.2. Soil sterilization and fixatives mixing

The porosity of the cured-cement layers on soil particles is affected by the amount of water available. The effect of water content on toluene fixation was evaluated by analyzing toluene leached in mixtures where 4, 7 and 10% water was added (the air-dried soil already contained 2% moisture). Water was added as a 2.5% mercuric chloride (HgCl_2) solution to prevent toluene biodegradation [23]. In one sample set, water without mercuric chloride was used to study the possibility of toluene biodegradation and/or mercuric chloride–cement setting interaction. The samples were hand-shaken after the addition of each drop to minimize the formation of soil aggregates. After all fixatives were added, the samples were tumbled overnight and then allowed to stand for different periods of time (7, 14 and 28 days) to study the effect of setting time. Toluene photodegradation was prevented by keeping soil samples in a closed box during setting time to avoid ultraviolet light exposure.

4.1.3. Soil leaching

TCLP is the standard leaching procedure to test immobilization of organic (VOCs and nonvolatile compounds) and inorganic analytes in liquid, solid and multiphasic wastes [16]. This procedure was not applicable in the present study because TCLP cannot be used to monitor VOC behavior through each step of S/S. An evaluation of TCLP to test VOC immobilization was described by Arocha [22]. We adopted a headspace gas chromatography procedure. After the required setting time, samples were leached with EF no. 1. Treated soil (2.2 g) in the original 42 ml vials was mixed with 30 ml of extraction fluid to allow 10 ml of headspace. After extraction fluid was added as described above, samples were mixed vigorously by hand for a minimum of 3 min and tumbled end-over-end at 30 rpm for 18 h. Analysis of the headspace yielded the amount of toluene released to the vapor phase. The percent of toluene leached was calculated by Eq. (9). In this procedure extract is not filtered from the soil sample and the three phases—air, extraction fluid, soil mixture—interact. When Henry's constants for the VOCs in the extraction fluid are known or can be estimated, this extraction procedure is an attractive alternative to the more complex purge-and-trap GC analysis.

4.2. Large cement content

Experiments with 20% cement were similar to those described above. Five replicates were tested with 66.9% oven-dried Yolo silt loam, 20.1% cement, 5% rice hull ash, and

8% water. After initial mixtures were spiked with 4 μ l toluene, samples were allowed to set 28 days to cure the cement.

5. Treatment with sodium silicate and shredded-tire material

We considered how a silica coating could be formed on soil and rubber surfaces to encapsulate sorbed VOC. Silica coatings can be deposited on substrates by acid neutralization of soluble potassium and sodium silicate solutions [24]. The approach was to mix shredded-tire particles (10% w/w) with contaminated soil (90%) so that VOCs would absorb into the tire particles and desorption would not occur during subsequent wetting. After VOC absorption was completed, we applied a silica coating to soil and tire particles with 30% by weight of a sodium silicate solution (14.35% w/w as silica). Because water does not wet rubber surfaces, a 10% dilute solution of ionic surfactant was initially applied to facilitate ST wetting, and to furnish the acidic medium for silica precipitation from the sodium silicate solution. The surfactant formulation used throughout this work was citric acid 4%, dodecyl benzene sulfonic acid 5%, and ethanol 4%, all dissolved in water [24]. To complete the experiment, the treated soil samples were leached with EF no. 1 by the same procedure described above. Control experiments were also done with soil or tire particles only.

An experiment was conducted to measure the effect of the surfactant on the toluene Henry's constant using the same ratio (surfactant/EF no. 1) as in the leaching experiments. The aim was to determine whether toluene partitioned into the organic constituents of the surfactant, particularly into a micelle phase. If toluene solubility increases as a result of the surfactant, a decrease in VOC might be expected in the headspace volume, which could be erroneously attributed to VOC fixation in the soil matrix.

6. Is the silica coating impermeable to VOC transport?

To answer this question, soil and ST particles were coated with silica from a sodium silicate solution and a sorption experiment was conducted to study the coating permeability of the solidified layer to VOC vapors. Coated soil and ST particles were compared to untreated samples. In this sorption measurement, VOC was added to the headspace above the coated particles and the headspace was sampled to determine uptake of VOC.

Two methods were used to coat soil particles (0.833–1.168 mm diameter) by silica precipitation from a sodium silicate solution. In the first, an application of 20% (w/w) of surfactant was followed by the application of 30% of a sodium silicate solution (29% as silica). The surfactant formulation was the same as described above. The second method used 20% of an acetic acid solution (50% by volume acetic acid dissolved in water) followed by 60% of a sodium silicate solution (14% as silica). In both cases, the amount of sodium silicate applied (calculated as dried silica) was the same (8.6%). Coated and uncoated particles were oven dried for 24 h at 50°C to evaporate ethanol,

acetic acid and water, and allowed to cool overnight to achieve air-dried soil moisture conditions. Samples placed in two 42 ml amber bottles with Mininert[®] valves were equally spiked with 4 μ l of toluene and tumbled for 24 h at 1 rpm. Vapor headspace was analyzed by GC-FID. Tire particles were treated by one and three surfactant–silicate applications.

7. Results and discussion

With the exception of Yolo silt loam, the tested materials were good sorbents for toluene (Figs. 1 and 2). At low relative vapor pressure, p/p° , rice hull ash showed better sorption for toluene vapor than did tire particles, but at large relative vapor pressure, tire particles were the superior sorbent. The isotherm for tire particles was linear up to $p/p^\circ = 0.45$, and its slope decreased at higher p/p° (not shown in Fig. 1). The shredded-tire particles showed a larger toluene sorption capacity than did the pyrolyzed tire carbon. The low toluene sorption from an aqueous phase by Yolo silt loam alone is significant evidence that adding VOC sorbents can decrease leaching and emission. The toluene partition coefficient for tire particles in the air phase was $1.03 (\pm 0.12) \times 10^3 \text{ ml g}^{-1}$ (average \pm standard deviation), and in the acetic acidic solution, $277 \pm 14 \text{ ml g}^{-1}$. The dimensionless Henry's constants for toluene at 25°C were 0.288 ± 0.006 for air/EF no. 1, and 0.267 ± 0.007 for air/water. Hine and Mookerjee [25], and Garbarini and Lion [19] reported similar values of 0.274 and 0.261, respectively.

Cement in the S/S process might block soil pores or form a coating on soil and rice hull ash particles and thus retard VOC desorption. The results, however (Fig. 3), show toluene retention was mainly a result of the rice hull ash adsorption capacity rather than cement encapsulation. Rice hull ash by itself under equilibrium conditions retained about

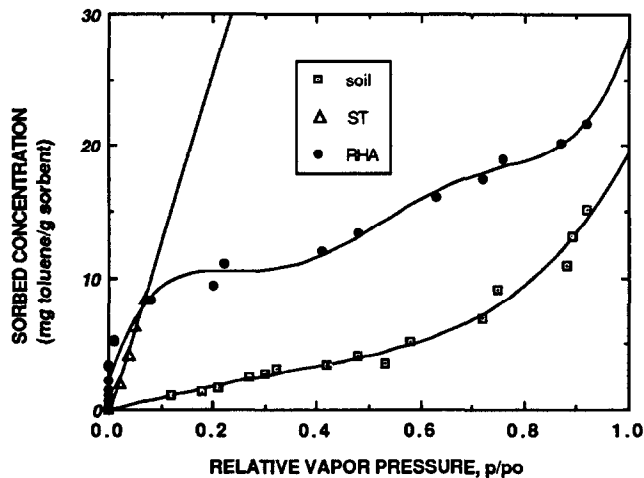


Fig. 1. Toluene vapor sorption on various sorbents. ST = shredded tire particles, RHA = rice hull ash. Experimental data for ST sorption greater than 30 mg g^{-1} are not plotted, but are indicated by the straight line.

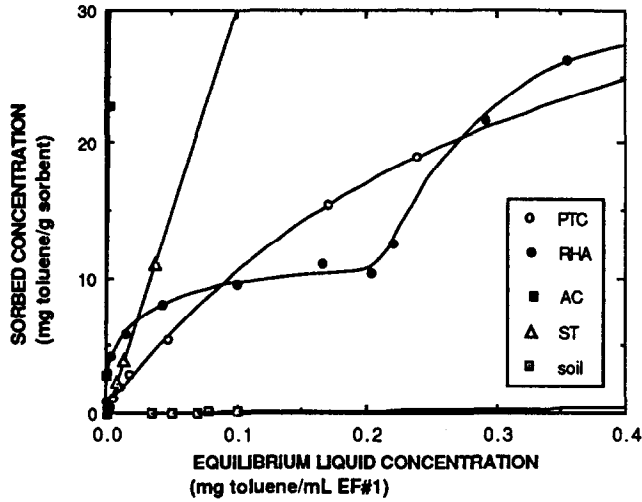


Fig. 2. Toluene sorption on various sorbents from an aqueous phase. Values for activated carbon (AC) were obtained from [31]. PTC = pyrolyzed tire carbon, RHA = rice hull ash, ST = shredded tire particles. Experimental data for ST sorption greater than 30 mg g^{-1} are not plotted, but are indicated by the straight line.

30% of the toluene. For samples after 7 days setting time, the results suggested that cement was detrimental to toluene retention because the total toluene retained was less than 30%. Toluene retention increased in the soil mixture with increasing setting time (Fig. 4). After 28 days setting time, the total toluene retained reached 39%, which was

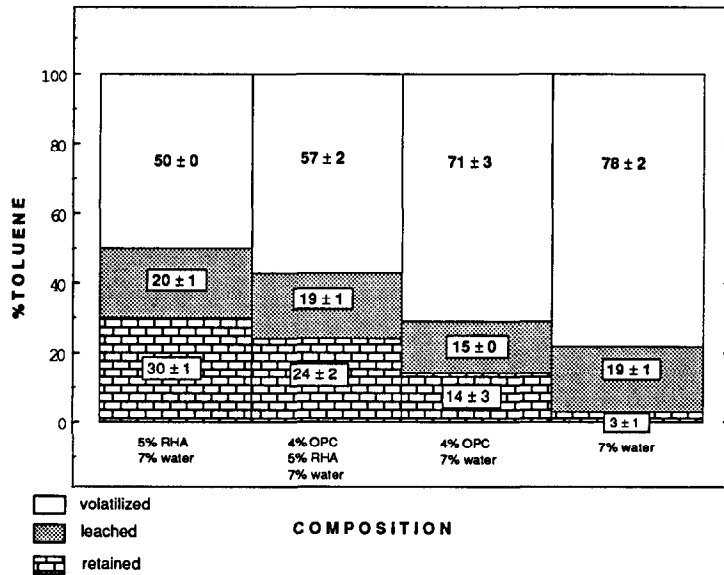


Fig. 3. Effect of composition; samples set for 7 days.

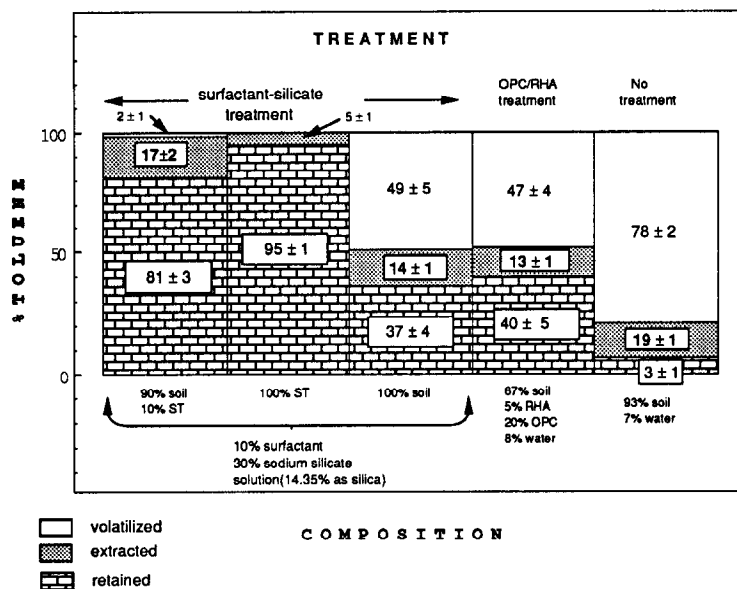


Fig. 4. Effect of setting time; samples were prepared as 5% RHA, 4% OPC and 7% water.

9% more than rice hull ash adsorption. This indicates that toluene was re-adsorbed and immobilized by cement during the curing process. For long curing times, the cement appears to act as a barrier to VOC desorption. The mixture water content did not have an effect on VOC immobilization (Fig. 5). Initially water displaced a significant amount of toluene from adsorption sites (about 50%, according to the mass balance), but a further increase in water content did not cause greater toluene volatilization nor improvement of toluene retention. The presence of mercuric chloride as a biocide had no significant effect on sorption.

Increasing cement from 4 to 20% did not improve toluene retention (Fig. 6). Portland cement improved retention by about 10% when compared with treatment by sorbents alone. Toluene retention during wetting was the result of rice hull ash, and not related to cement (Fig. 3). Adding rice hull ash or other suitable adsorbents will increase toluene holding capacity, both during soil treatment and during leaching tests. These results, indicating that cement is limited in preventing leaching and emissions of VOCs, supported the findings of Weitzman et al. [17] on VOC air emissions from contaminated soils treated with a cement-based S/S process.

The VOC releases during addition of water in the cement-RHA treatment were up to 50% for a 1500 mg kg^{-1} toluene-contaminated soil with 2% initial moisture. We considered that these large releases could be avoided by using a VOC adsorbent such as tire particles instead of a VOC adsorbent such as RHA or activated carbon. VOCs absorbed by tire particles are not desorbed during soil wetting because they are dissolved in the rubber matrix instead of adsorbed at surface sites where they can be displaced by water. This was demonstrated by allowing toluene to absorb into ST particles in a 42 ml vial, and then adding water. The amount of toluene in the headspace

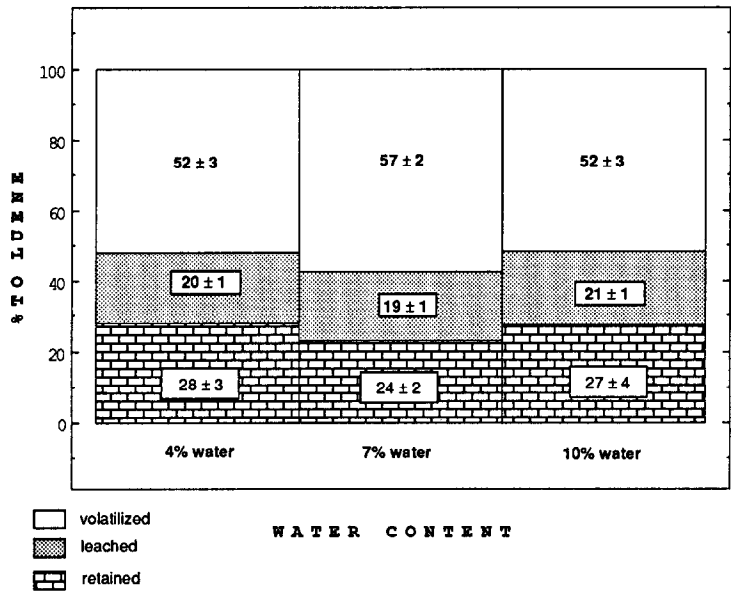


Fig. 5. Effect of water content; samples were prepared with 5% RHA and 4% OPC; samples set for 7 days.

(measured by GC-FID) did not change upon addition of water. In contrast to adsorbent behavior, no VOC desorption occurred upon wetting of the tire particles. These findings were further confirmed by the evaluation of the silica–tire particles treatment.

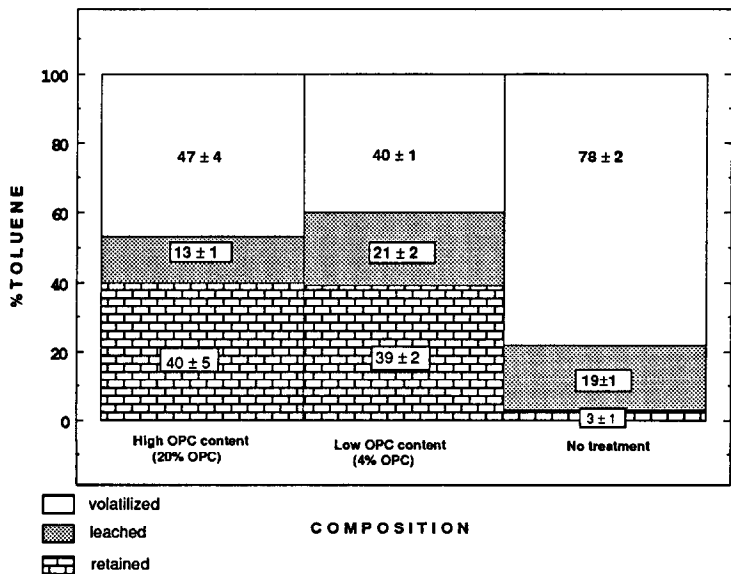


Fig. 6. Comparison of low and high cement content; samples set for 28 days.

The comparison of the sodium silicate–shredded tire process with the cement-based treatment (Fig. 7) showed little desorption resulting from surfactant and sodium silicate addition to the samples containing tire particles. Desorption was greater in the samples containing no ST. The small amount of toluene desorbed (2%) from the samples containing soil and ST was from toluene sorbed to the soil matrix. A calculation based on the ST/EF no. 1 partition coefficient shows that 31% of the toluene retained by the soil–tire particles mixture results from toluene absorption capacity of the tire material. The 50% difference between 81% (total toluene retained) and 31% (calculated toluene absorbed by shredded tire particles) was attributed to encapsulation by the silica coating. The soil without shredded tire particles, processed with the surfactant–silica treatment, had significantly improved retention (37%) compared to soil with no treatment (3%). Silica precipitation on soil particles can form a silica coating on soil and rubber particles, or it can cause particle agglomeration by adhesion to form larger particles.

The permeation of toluene through silica layers was reduced, so that coated soil samples showed less toluene adsorption than did untreated samples (Table 6). Relative to the uncoated material, a single silica application decreased the VOC adsorption by 50%, and two applications decreased toluene adsorption to less than 25%. The acetic acid solution alone sufficiently wetted the soil surfaces to allow silica encapsulation, verifying that surfactant addition was unnecessary. Also, treatment with acetic acid formed larger agglomerates than the soil clusters obtained with the surfactant treatment. Toluene uptake was unaffected after one and three surfactant–silicate treatments on tire particles in the absence of soil (Table 7). The silica-coated tire particles, when viewed

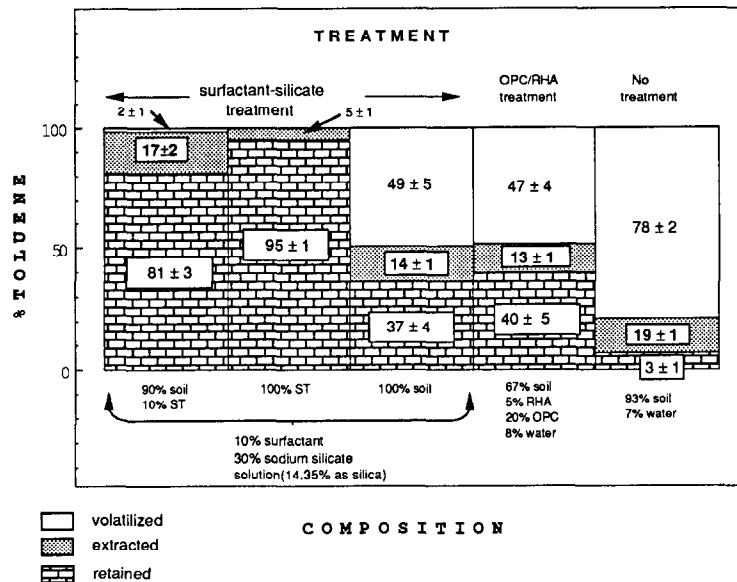


Fig. 7. Evaluation of the shredded tire waste and sodium silicate process. Sample set for 28 days for the OPC treatment and 24h for samples with the silica treatment.

Table 6
Toluene adsorption on silica(SiO₂)-coated soil particles

| Treatment | (SiO ₂ + soil)/soil w/w | Percent toluene adsorbed ^b |
|--|------------------------------------|---------------------------------------|
| 20% surfactant | 1.1 ± 0.0 | 44 ± 4 |
| 30% sodium silicate (28.70% silica) | | |
| 20% acetic acid (50% conc.) | 1.2 ± 0.0 | 32 ± 4 |
| 60% sodium silicate(14.35% silica) | | |
| 20% acetic acid (50% conc.) ^a | 1.3 | 17 |
| 60% sodium silicate(14.35% silica) | | |
| No treatment | 1.0 ± 0.0 | 73 ± 3 |

^a A single sample was treated with two sodium silicate applications.

^b Samples were spiked with 4 μl toluene and analyzed by GC-FID after 24h.

through a light microscope, showed some uncoated regions. These regions were probably caused by crazing and shrinkage [26] of the silica layers, or by regions where no reaction occurred on the rubber surface. This demonstrated the importance of satisfactory adhesion to the rubber surfaces for the silica to provide an impermeable barrier to VOC.

Recommendations [27] for preparing solid layers from organic solutions, such as silica layers from methyl or ethyl orthoesters in alcohol, apply to silica layers formed from aqueous sodium silicate solutions. To prepare a solid homogeneous layer from organic liquid films, the soil and rubber particles must be wetted by the solution. Even with the addition of wetting agents, this condition is met only if the substrate surfaces are sufficiently clean. The tire particles used in our experiments were ground from original tires without removing oil and impurities. Surface substrate roughness can also prevent a consolidated layer, for example, substrate surface scratches having an average depth of more than 10 μm can cause disturbances in the silica layer [27]. Another possible problem is the drying of the silicic acid gel film to form a nonhomogeneous

Table 7
Toluene absorption into silica-coated shredded tire particles

| Treatment | One coating | | Three coatings | |
|--|--------------------------------|---------------------------------------|--------------------------------|---------------------------------------|
| | (SiO ₂ + ST)/ST w/w | Percent toluene absorbed ^a | (SiO ₂ + ST)/ST w/w | Percent toluene absorbed ^a |
| 20 wt.% surfactant, 30 wt.% sodium silicate solution with 28.70 wt.% silica | 1.1 ± 0.0 | 97.8 ± 0.1 | 2.3 ± 0.3 | 96.8 ± 0.6 |
| No treatment | 1.0 | 98.2 | 1.0 | 97.8 |

^a Samples were spiked with 4 μl and 5 μl toluene for the one-coating and the three-coating procedures, respectively.

coat of SiO_2 . Moreover, silica layers deposited on some substrates, such as glass, are porous [28,29]. Porous films are, therefore, expected for silica coatings on soil and rubber particles. These potential difficulties suggest that in the silica-shredded tire treatment, silica reduces the available surface area for VOC desorption by closing soil pores and by particle agglomeration rather than by forming a VOC-impermeable capsule around individual particles. Tire rubber particles, which are the actual VOC reservoirs after VOCs migrate from soil, were observed trapped among soil clusters during treatment. Therefore, improving mechanical strength of silica–soil–rubber agglomerates should lead to slower leaching rates.

Two idealized goals motivated this study: VOCs should not be emitted to air during and after solidification/stabilization processing of contaminated soils, and VOCs should not be released during the acidic extraction of treated soils. Both conditions are idealizations because of the volatility of VOCs, but they suggest a practical question. How much of the toluene initially present in the contaminated soil can be released during treatment and leaching for a process to be considered acceptable? An equilibrium analysis of the leaching process allows an estimate to be made by considering the toluene partitioning between the treated soil and the extraction fluid. For waste extraction, the US EPA regulatory limit for toluene is 14.4 mg l^{-1} of extract by TCLP [10]. The soil agglomerates with 14% of dried additives (10% shredded tire particles and 4.3% silica coating) from an initial 1600 mg kg^{-1} toluene-contaminated soil (1400 mg kg^{-1} toluene–soil mixture) had a partition coefficient (soil mixture/extract) of $72 \pm 11 \text{ ml g}^{-1}$ (Table 8). The extract concentration was 16 mg l^{-1} toluene, slightly beyond the regulatory limit of 14.4 mg l^{-1} . For these conditions, the partition coefficient of the treated soil would have to be *greater* than 77 ml g^{-1} to meet the TCLP extract concentration regulatory limit. Increasing the fraction of shredded tire particles in the given mixture would easily allow US EPA limits to be met. As shown in Table 8, the soil sample without treatment had a small partition coefficient (2.7 ml g^{-1}), while the silica-treated soil with and without tire particles had values of 72 and 43 ml g^{-1} , respectively. Thus the silica–tire particle treatment shows promise as a solidification/stabilization process for VOCs in contaminated soils.

Table 8
Solid–liquid partition coefficients, K_d , for leaching experiments

| Treatment | Toluene spiking level before the extraction step (ppm) | C_1 ($\mu\text{g tol ml}^{-1}$ extract) | K_d (ml g^{-1}) ^a | K_d^{sorp} (ml g^{-1}) | K_d^{app} (ml g^{-1}) |
|-------------------------------|--|--|---|--|---|
| Low OPC content (4% OPC) | 1680 ± 17 | 17.6 ± 1.6 | 2.7 | 26 | 28 ± 4 |
| High OPC content (20% OPC) | 1230 ± 60 | 12.9 ± 0.1 | 2.7 | 39 | 44 ± 10 |
| Silica–surfactant (10% ST) | 1405 ± 5 | 16.0 ± 0.2 | 2.7 | 28 | 72 ± 11 |
| Silica–surfactant (100% soil) | 708 ± 38 | 12.4 ± 1.4 | 2.7 | 2.7 | 43 ± 6 |

^a Distribution coefficient for the plain soil without treatment.

8. Conclusions

Most of the current immobilizing and encapsulating agents in solidification/stabilization processing require water (e.g. cementitious and pozzolanic materials) or are dissolved in water (silicate solution, asphalt emulsion, etc.). The problem is that water displaces VOCs adsorbed on soil. Shredded tire waste, which has excellent sorption properties for VOCs, is an inexpensive sorbent that can immobilize VOCs during treatment of contaminated soil with an encapsulating material. Encapsulation by silica, an economic and environmentally safe material whose physical and chemical characteristics resemble soil, provides a VOC impermeable coating of the soil-sorbent mixture. Headspace analysis is a straightforward, accurate and inexpensive method to test VOC immobilization and evaluate VOC retention in S/S processes.

References

- [1] R.B. Pojasek, *Toxic and Hazardous Waste Disposal*, Vol. 1, Ann Arbor Science, Ann Arbor, MI (1979).
- [2] US EPA, *Guide to the Disposal of Chemically Stabilized and Solidified Waste*. SW-872 Revised. Municipal Environmental Research Laboratory, Office of Research and Development. US Environmental Protection Agency, Cincinnati, OH (1982).
- [3] D.M. Montgomery, C.J. Sollars, T.S. Sheriff and P. Perry, *Environ. Technol. Lett.*, 9 (1988) 1403.
- [4] H. Akhter, L.G. Butler, S. Branz, F.K. Cartledge and M.E. Tittlebaum, *J. Hazard. Mater.*, 24 (1990) 145.
- [5] A.D. Hewitt, P.H. Miyares, D.C. Leggett and T.F. Jenkins, *Environ. Sci. Technol.*, 26 (1992) 1932.
- [6] M.J. Cullinane and R.M. Bricka, in P.T. Kostecki and E.J. Calabrese (eds.), *Petroleum Contaminated Soil*, Vol. I. Lewis Publishers, Chicago (1989).
- [7] S.J.T. Pollard, C.J. Sollars and R. Perry, *Environ. Technol.*, 11 (1990) 1113.
- [8] US EPA, *Applications Analysis Report*, HAZCON Solidification Process, Douglassville, PA. Risk Reduction Engineering Laboratory. Office of Research and Development. US Environmental Protection Agency, Cincinnati, OH. EPA/540/A5-89/001 (May 1989).
- [9] US EPA, *Handbook for Stabilization/Solidification of Hazardous Waste*. US Environmental Protection Agency, Cincinnati, Ohio. EPA/540/2-86/001 (June 1986).
- [10] J.R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York (1990).
- [11] S.G. Donaldson, G.C. Miller and W.W. Miller, *J. Environ. Qual.*, 21 (1992) 94.
- [12] N.N. Eldin and A.B. Senouci, *J. Construct. Engng Mgmt*, 118 (1992) 561.
- [13] K. Eklund, in: P.T. Kostecki and E.J. Calabrese (eds.), *Petroleum Contaminated Soils*, Vol. I, *Remediation Techniques, Environmental Fate, Risk Assessment*, Lewis Publishers, 1989.
- [14] M.H. Blumenthal, *BioCycle* (October 1991) 47, 86.
- [15] US EPA, *Bench Scale Study Final Report*. Chemical Control Corporation Superfund Site. Elizabeth, New Jersey. Prepared by Law Environmental Inc., Government Service Division (LEGS) Kennesaw, GE. Project Number 11-9551, EPA/DACW41-89-C-0095 (September 1990).
- [16] US EPA, Method 1311. Toxicity characteristic leaching procedure (TCLP), in *US EPA. Test Method for Evaluating Solid Waste*, SW-846, Washington, DC Office of Solid Waste and Emergency Response, 1986 (Revision July 1992).
- [17] US EPA, *Volatile Emissions from Stabilized Waste*. Final Report. Prepared by L. Weitzman, L.R. Hamel and S.R. Cadmus, Acurex Corporation, Environmental Systems Division, Mountain View, CA 94039, EPA/68-02-3993, Work Assignments nos 32 and 37 (May 1989).
- [18] A.H. Lincoff and J.M. Gossett, in W. Brutsaert and G.H. Jirka (eds.), *Gas Transfer at Water Surfaces*, Reidel, Dordrech, 1984, pp. 17–25.
- [19] D.R. Garbarini and L.W. Lion, *Envir. Sci. Technol.*, 19 (1985) 1122.

- [20] A.A. Merchant and M.A. Petrich, *Envir. Energy Engng*, 39 (1993) 1370.
- [21] S.J. Gregg and K.S.W. Sing, *Adsorption, Surface Area, and Porosity*, Academic Press, New York, 1967, p. 187.
- [22] M.A. Arocha, *Ph.D. Dissertation*, Department of Chemical Engineering and Materials Science, University of California, Davis, 1995.
- [23] D.C. Wolf, T.H. Dao, H.D. Scott and T.L. Lavy, *J. Envir. Qual.*, 18 (1989) 39.
- [24] *US Patent 2,366,516* to Schott and Genossen (1939).
- [25] J. Hine and P.K. Mookerjee, *J. Org. Chem.*, 40 (1975) 292.
- [26] I.M. Thomas, *Appl. Opt.*, 28 (1992) 6145.
- [27] H. Schroeder, Oxide layers deposited from organic solutions, in G. Hass and R. Thun (eds.), *Physics of Thin Films*. Academic Press, New York, 1969.
- [28] R.K. Iler, *Colloid Chemistry of Silica and Silicates*, Cornell University Press, Ithaca, NY, 1955.
- [29] R.K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979.
- [30] K. Verschuren, *Handbook of Environmental Data on Organic Chemicals*, Van Nostrand Reinhold, New York (1983).
- [31] K.A. Peterson, M.S. Thesis, Department of Chemical Engineering, University of California, Davis, 1991.