

Degradation of the blister agent sulfur mustard, bis(2-chloroethyl) sulfide, on concrete

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Abstract

The products formed from the degradation of the blister agent sulfur mustard [bis(2-chloroethyl) sulfide] on concrete were identified using gas chromatography with mass spectrometry detection (GC/MSD), ¹H NMR, 2D ¹H–¹³C NMR and ¹³C solid state magic angle spinning (SSMAS) NMR. In situ and extraction experiments were performed. Sulfur mustard was detected in the in situ ¹³C SSMAS samples for 12 weeks, whereas less than 5% of the sulfur mustard was detected in extracts from the concrete monoliths after 8 days. Sulfonium ions and (2-chloroethylthio)ethyl ether (T) were observed on the in situ samples after a period of 12 weeks, whereas vinyl species and bis(2-chloroethyl) sulfoxide were observed in the extracts of the concrete monoliths within 24 h. The differences between the extraction and the SSMAS data indicated that the sulfur mustard existed in the concrete in a non-extractable form prior to its degradation. Extraction methods alone were not sufficient to identify the products; methods to identify the presence of non-extractable degradation products were also required.

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1. Introduction

Knowledge of when a Chemical Warfare Agent (CWA) no longer poses a hazard – that is, when a contaminated area is safe to enter without protective clothing – is of major concern for battlefield commanders. Decisions must be made whether to decontaminate an area, or allow resumption of normal operations after an acceptable waiting period. The correct assessment of the amount of agent in the air, in nearby water, on equipment, and on the ground (substrates such as soil, grass, concrete and asphalt) is critical to making correct decisions about the need for decontamination. Therefore, testing methods that detect both the CWA and its degradation products, some of which may be toxic, are needed.

Abbreviations: ¹³C, Carbon-13; 1D, 1-dimensional; ¹H, proton; ¹H–¹³C, proton–carbon correlated; 2D, 2-dimensional; NMR, nuclear magnetic resonance; SSMAS, solid state magic angle spinning

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The chemistry of decontamination has been studied and reviewed [1]. Bleach and other decontamination solutions and mixtures containing the hypochlorite ion, OCl[−], reacted with sulfur mustard to form sulfoxide derivatives, which then formed sulfone derivatives, which then formed the corresponding elimination products 2-chloroethyl vinyl sulfide (CEVS) and divinyl sulfide (DVS) [2] were seen immediately with the use of DS2, an alternative decontamination solution containing CH₃-OCH₂CH₂O[−], that was developed to avoid the corrosiveness of bleach.

Although sulfur mustard exhibited low solubility in water, forming droplets within it, reactions occurred at the water–sulfur mustard interface to form the hydrolysis products chlorohydrin (CH) and thiodiglycol (TDG), which subsequently formed the toxic sulfonium ions H-2TG and CH-TG [1].

Environmentally, sulfur mustard has been observed to persist for 4 years in soil [3]. Wagner and MacIver [4] used ¹³C SSMAS (solid state magic angle spinning) NMR to show that sulfur mustard persisted for several weeks on dry soil, but hydrolyzed and polymerized to form toxic CH-TG and H-2TG sulfonium ions within 1 week when water was added. Liquid chromatography followed by electrospray ionization mass spectrometry

of acetonitrile extracts was used to confirm the presence of the sulfonium ions.

Similarly, when sulfur mustard was placed on MgO or CaO, the products thiodiglycol (TDG), CEVS and DVS were formed [5]. Degradation of sulfur mustard on CaO also led to minor amounts of sulfonium ions [6]. On the surface of ambient alumina, sulfur mustard reacted to give mostly thiodiglycol with minor amounts of CEVS and DVS. When excess water was added, the sulfonium ions H-2TG and CH-TG were formed, and $\text{Al}(\text{H}_2\text{O})_6^{3+}$ was liberated from the surface [7].

CWAs and their degradation products have been removed from solid matrices using solvents and then analyzed by Hooijschuur, Kientz and Brinkman [8]. Davis, Jensen, McGuire, Skoumal and Fagan [9] extracted sulfur mustard from concrete after a 30-min contact time using isopropanol and acetonitrile; GC/MS analysis of the solvent showed 2–68% recovery of sulfur mustard when isopropanol was used and 7–21% recovery of sulfur mustard when acetonitrile was used. Decomposition products were not detected. Tomkins, Sega and Mcnaughton [10] developed an extraction and GC method for analyzing the breakdown products of sulfur mustard on soil and concrete. The substrates were spiked and extracted immediately, yielding a total recovery of the analyte. Wils, Hulst, and de Jong [11] used thermal desorption followed by headspace analysis to monitor the recovery of sulfur mustard from rubber over a period of 6 weeks. The 30 min recovery was 86%; the six week recovery was 57%.

In the current study, both extraction and SSMAS techniques were employed to study the persistence and reactivity of sulfur mustard on concrete quantitatively. The sulfur mustard and its degradation products were extracted from concrete monoliths with chloroform and analyzed using both GC/MSD and liquids NMR. For the SSMAS studies, a sample of sulfur mustard on the same concrete was sealed in a SSMAS rotor and monitored over a period of 12 weeks. In addition, sulfur mustard was placed onto concrete, which was then crushed, studied using SSMAS, and subsequently extracted for GC/MSD; this procedure enabled side-by-side comparison of the SSMAS and extraction methods.

2. Experimental

2.1. Substrates

The concrete was made in the year 2000 using Portland cement, ~3 mm silicate filler, and a 0.32 water-to-concrete ratio. All samples were used under ambient conditions (about 21 °C and 20% RH). The concrete had a surface area of 7.8 m²/g and 17% porosity (four samples) as measured by mercury intrusion porosimetry (MIP). Nitrogen gas adsorption with BET surface area (SA) calculations gave a value of 9.0 m²/g for a small monolith; a sample of the concrete that was finely ground with a mortar and pestle had a surface area of 6.3 m²/g. MIP and SA data were collected by Micromeritics Inc., Norcross, GA.

2.2. Agent

Two different sources of sulfur mustard were used: munitions grade (H), which was shown to be 85% pure by GC/MSD

and ¹³C labeled (HD*), which was shown to be 99.5% pure by GC. The HD* was 50% labeled at each carbon position, such that two ¹³C would not be adjacent. This allowed for good detection of the ¹³C signal, but avoided the ¹³C–¹³C couplings that would be present if 100% labeling were used. Caution: sulfur mustard, bis(2-chloroethyl) sulfide is a potent vesicant, and care must be taken to prevent exposure to liquid or vapor. It should only be manipulated by trained personnel employing appropriate engineering controls and personal protective equipment.

2.3. Extractions

Four 1 μL drops of sulfur mustard ($\text{ClCH}_2\text{CH}_2)_2\text{S}$) weighing approximately 6 mg total, were placed onto monoliths of ambient concrete that were about 3 mm thick, 15 mm long and 9 mm wide. Typical concrete samples weighed 1.3 g, (concrete:sulfur mustard ratio = 220:1), although experiments with 0.3 and 0.6 g monoliths were also performed (concrete:sulfur mustard ratios of 50:1 and 100:1, respectively). The concrete samples were stored in 20 mL glass vials that were sealed with GC septum caps. After a specified exposure time at 21 °C, the samples were crushed in the vial using pliers, and extracted once with 2 mL CDCl_3 . The extracts were analyzed using GC/MSD and liquids ¹H NMR. Typical sulfur mustard concentrations in solution were 2 mg/mL. All concrete samples were made in duplicate; the NMR and GC/MSD of the extracts were run once.

2.4. NMR instrumentation

¹H NMR liquids spectra were collected at 9.4 T using a Varian Inova NMR spectrometer equipped with a Varian 5 mm liquids probe. All spectra were obtained using direct polarization; delay times between pulses were at least five times the measured T_1 , and the chemical shift reference was internal chloroform. Quantification of the sulfur mustard extracted was obtained by comparing total integrated peak areas between an external standard that was approximately 2 mg/mL sulfur mustard in chloroform and the extract. The vinyl compounds 2-hydroxyethyl vinyl sulfide (HOEVS, 5.35 and 6.45 ppm) and 2-chloroethyl vinyl sulfide (CEVS, at 5.22 and 6.28 ppm) were detected by ¹H NMR; quantification was based upon the vinyl resonance at ~5.3 ppm. The aliphatic protons were observed as small peaks adjacent to the much larger sulfur mustard resonances.

¹³C SSMAS (solid state magic angle spinning) spectra were collected at 9.4 T using a Varian Inova NMR spectrometer equipped with a Doty Scientific 7 mm standard series VT-MAS (variable temperature magic angle spinning) probe. The spectra were obtained using direct polarization at spinning rates of ~2000 Hz. Delay times between pulses were at least five times the measured T_1 , and spectra were referenced to external tetramethylsilane. Alternatively, the ¹³C SSMAS spectra were measured at 7.0 T using a Varian Inova NMR spectrometer equipped with a Doty Scientific 7 mm high-speed VT-MAS probe and spinning at 3000 Hz.

Two-dimensional COSY, HMBC and HMQC spectra were collected at 25 °C at 14.1 T using a Varian Inova NMR spectrometer equipped with a Varian 5 mm ‘HCN’ indirect detection liquids probe, and the chemical shift reference was internal chloroform. The pulse sequences used were those supplied by the manufacturer. Typical parameters for the HMQC experiment were: 32 transients, 128 increments of the t_1 evolution period, scalar coupling constant of 144 Hz, and a recycle time of 1.5 s. Typical parameters for the HMBC experiment were 96 transients, 256 increments of the t_1 evolution period, scalar coupling constant of 144 Hz, long-range spin coupling constant of 7 Hz and a recycle time of 1.5 s. Typical parameters for the COSY experiment were 16 transients, 512 increments of the t_1 evolution period and a recycle time of 2 s.

2.5. GC instrumentation

An Agilent Technologies 6890 Series gas chromatograph equipped with a 5973 mass selective detector (MSD) was used for all mass spectral analyses. Ultra-Pure helium (99.999%) was used as the carrier gas with an average linear velocity of 36 cm per second in the splitless-constant flow mode. The inlet temperature was 250 °C, the inlet mode was splitless (purge on at 0.1 min, flow 50 mL/min), the inlet pressure was 7.3 psi (constant flow at 1 mL/min) and a 1 μ L sample volume was used. The oven temperature profile was 45 °C for 5 min, then increasing to 250 °C at the rate of 10 °C/min with no final hold time. The GC column was an HP-5MS, 30 m \times 0.25 mm \times 0.25 μ m film thickness. The mass range for the MSD was 40–350 amu. The sulfur mustard was 85% pure (retention time 13.32 min); Q (1,2-bis(2-chloroethylthio) ethane, ClCH₂CH₂SCH₂CH₂SCH₂CH₂Cl, 20.05 min) was a major impurity, present at about 11% of the total. 1,4-Dithiane (C₄H₈S₂, 11.32 min) was present at 2.6%; all other impurities, including S₈, were present at less than 1% by GC area. The GC data were considered semi-quantitative since standards were not available for the products; the percent products were calculated by normalizing to the amount of sulfur mustard present in the standard. The products found in the GC (retention time, minutes) were 2-chloroethyl vinyl sulfide (CEVS, 7.92), 2-hydroxyethyl vinyl sulfide (HOEVS, 8.34), 1,2-bis(vinylthio)ethane (BVTE, CH₂=CHSCH₂CH₂SCH=CH₂, 13.02), and (2-chloroethylthio)ethyl vinyl sulfide (CETEVS, ClCH₂CH₂SCH₂CH₂SCH=CH₂, 16.74).

3. Results

3.1. Extraction of sulfur mustard from concrete monoliths

3.1.1. Contact time

When the samples were extracted after 1 h, the percentages of sulfur mustard recovered were 90–100%. The NMR and GC percent recoveries were generally within 10% of each other for any given extract; sample-to-sample variation of the duplicates was also generally within 10%. As the contact time of sulfur mustard on concrete was increased, the percent sulfur mustard extracted decreased; about 40% of the sulfur mustard was extractable after

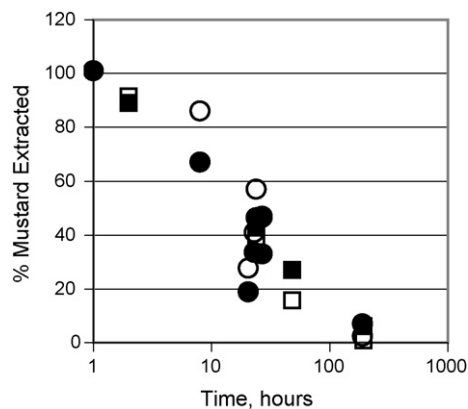


Fig. 1. Percent sulfur mustard extracted from concrete as a function of contact time, concrete:sulfur mustard ratio = 220:1. (●) H via NMR; (○) H via GC; (■) HD* via NMR and (□) HD* via GC.

24 h (Fig. 1). The concrete:sulfur mustard ratio for these samples was 220:1.

Products were observed after a 24 h contact time by using both NMR and GC/MSD. ¹H NMR was used to quantify the CEVS and HOEVS products (Fig. 2). The GC/MSD was not quantitative for the products since standards were not available. CEVS and/or HOEVS were present in all of the samples that gave products; a variety of other compounds was occasionally detected. Compounds that were detected in some, but not all samples were bis(2-chloroethyl) sulfoxide, TDG, chlorohydrin (CH), and (2-hydroxyethylthio)ethyl ether (HOCH₂CH₂SCH₂CH₂)₂O. These products were identified using 2-dimensional ¹H–¹³C NMR and GC/MSD because the product chemical shifts in the 1D ¹H NMR were too close to the much more intense sulfur mustard peaks for good identification. The sum of products and reactant extracted was less than 100% after a 24-h contact time based on the ¹H NMR data.

3.1.2. Concrete:sulfur mustard ratios

The concrete:sulfur mustard ratios varied from 50:1 to 250:1; at a ratio of 50:1, the concrete was almost saturated with sulfur

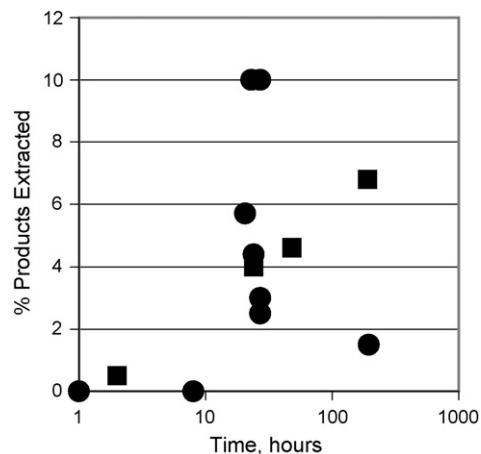


Fig. 2. ¹H NMR measurement of percent products extracted from concrete as a function of contact time, concrete:sulfur mustard ratio = 220:1. (●) H; (■) HD*.

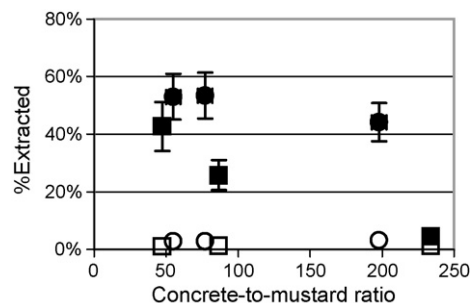


Fig. 3. Percent sulfur mustard and vinyl products extracted from concrete as a function of concrete:sulfur mustard ratio. (●) H after 24 h; (○) vinyl products after 24 h; (■) H after 192 h; (□) vinyl products after 192 h.

mustard. Extractions were performed after 24 and 192 h. The percent sulfur mustard extracted after 24 h remained relatively constant at ~50% regardless of the concrete:sulfur mustard ratio; after the 192-h contact time the percent sulfur mustard extracted decreased from ~40 to ~5% as the ratio increased from 47:1 to 234:1 (Fig. 3).

In addition to the sulfur mustard, the vinyl compounds 2-hydroxyethyl vinyl sulfide (HOEVS) and 2-chloroethyl vinyl sulfide (CEVS) were detected by ^1H NMR. Both vinyl species were seen in the 24-h concrete:sulfur mustard ratio of 198:1 sample, and in all of the 192-h contact time samples. Only CEVS was seen in the 24-h samples with concrete:sulfur mustard ratios of 55:1 and 77:1.

The products identified by GC/MSD were CEVS, HOEVS, 1,2-bis(vinylthio) ethane (BVTE) and (2-chloro-ethylthio)ethyl vinyl sulfide (CETEVS). The relative amounts of product present (Table 1) were based on the normalized responses of the compounds in the GC to sulfur mustard; since standards were not available, it was not possible to quantify the products. The GC data showed that the amount of sulfur mustard decreased with contact time, the relative amount of products increased, and the impurities remained constant. The occurrence of the products depended upon the concrete:sulfur mustard ratio. After a 24-h contact time CEVS was formed when only a small amount of surface was available for the sulfur mustard (55:1), whereas HOEVS was produced when more surface area was available (77:1 and 198:1). Comparison of the products after 24 and 192-h contact times also showed that CEVS formed first, followed by HOEVS. Thus, the elimination occurred before the hydrolysis. Divinyl sulfide (DVS) was not seen. CETEVS and BVTE, which both contain two sulfur atoms, were likely formed by the degradation of Q on the concrete.

Table 1

Products and the normalized response observed in the extracts of different concrete:sulfur mustard ratio samples via GC/MSD

Products and the normalized response observed via GC/MSD	24 h contact time			192 h contact time		
	55:1	77:1	198:1	47:1	86:1	234:1
2-Chloroethyl vinyl sulfide (CEVS)	2.3	3.3	4.0	1.3	3.7	4.9
2-Hydroxyethyl vinyl sulfide (HOEVS)		0.3	1.7	0.1	0.4	5.8
1,2-Bis(vinylthio) ethane (BVTE)			0.6		0.5	1.7
(2-Chloroethylthio)ethyl vinyl sulfide (CETEVS)				3.1	4.3	8.8

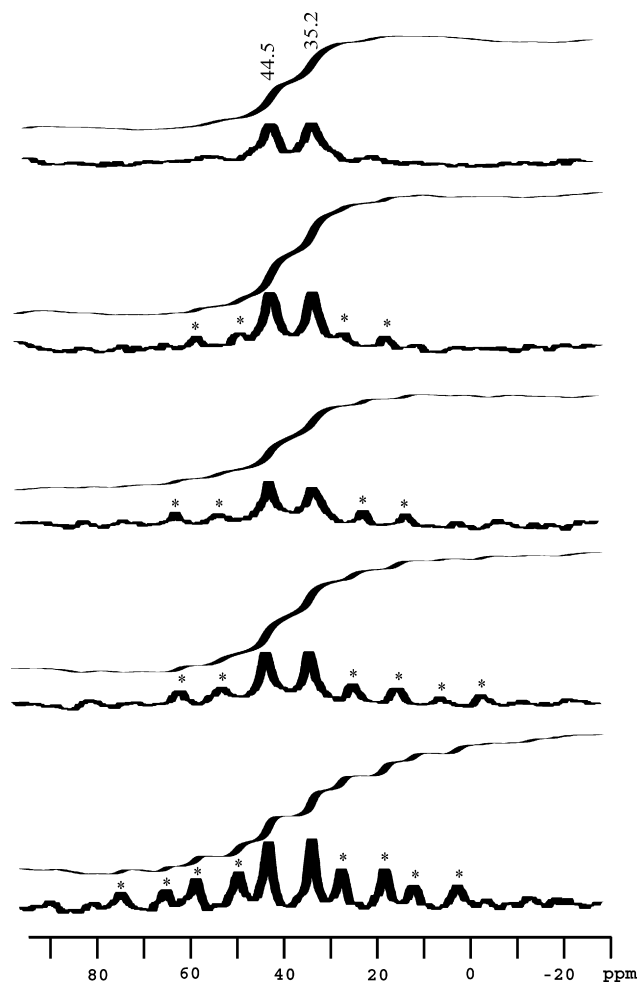


Fig. 4. ^{13}C SSMAS spectra of HD^* on concrete. Age of spectra from bottom to top: initial, 2, 4, 7, and 12 weeks.

3.2. SSMAS studies

^{13}C -labeled sulfur mustard was placed onto finely ground concrete (concrete:sulfur mustard ratio=40:1) and sealed in a rotor for SSMAS experiments. Initially, numerous spinning sidebands were observed for the HD^* on the concrete (Fig. 4). However, after 12 weeks very few spinning side bands were seen, the total integrated peak area had gradually decreased to 60% of its original value, and the peak widths had increased from 200 to 500 Hz (Fig. 5). The chemical shifts of sulfur mustard, at 34.1 and 43.4 ppm were unchanged during this process.

The final spectrum was acquired with a one-second recycle time. This experiment was performed based on the observation

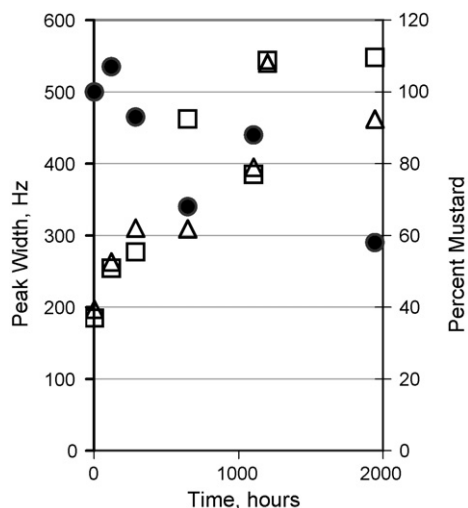


Fig. 5. Summary of SSMAS spectra of HD* on crushed concrete. Left axis: peak widths at 35 ppm (□) and 44 ppm (△) in Hz. Right axis: normalized total integrated peak area for sulfur mustard (●) in percent.

that the T_1 became shorter for products on a different concrete. The short recycle time had the net effect of enhancing the intensity of any short T_1 product peaks relative to the longer T_1 background and reactant peaks (Fig. 6). The total integrated peak area was larger than observed in the initial spectrum, because the shorter T_1 affected the baseline on which the integral was calculated.

In addition to the sulfur mustard peaks, the spectrum had peaks at 19.3, 57.3 and 72.2 ppm that were about 500 Hz wide, and shoulders at 29.5 and 48.8 ppm. The chemical shifts at 29.5, 48.8 and 57.3 were consistent with the presence of the sulfonium ion H-2TG; CH-TG has similar chemical shifts but has an additional peak at 62 ppm, which was not seen. Another product, (2-chloroethylthio)ethyl ether, (T, $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$, the ether of two hydrolyzed sulfur mustard molecules) was identified by its peak at 72.2 ppm; its other resonances were at 43, 35 and 32 ppm, all of which were observed in the spectrum. The 19.3 ppm peak has not yet been identified. Thus, after 12 weeks, a combination of sulfur mustard, H-2TG and T were present on the concrete.

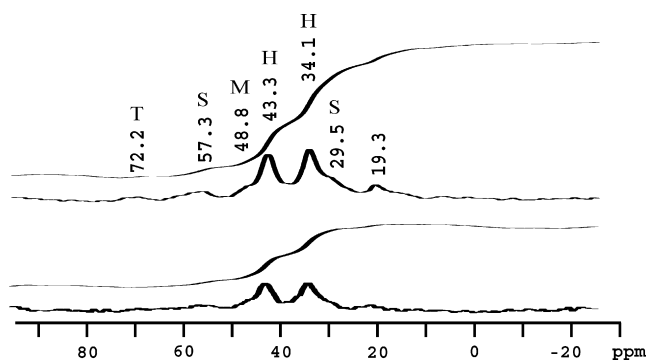


Fig. 6. ^{13}C SSMAS spectra of HD* on concrete after 12 weeks. Recycle times: bottom -10 s and top -1 s . H represents sulfur mustard, T is for (2-chloroethylthio)ethyl ether, S is for sulfonium ion and M represents multiple species.

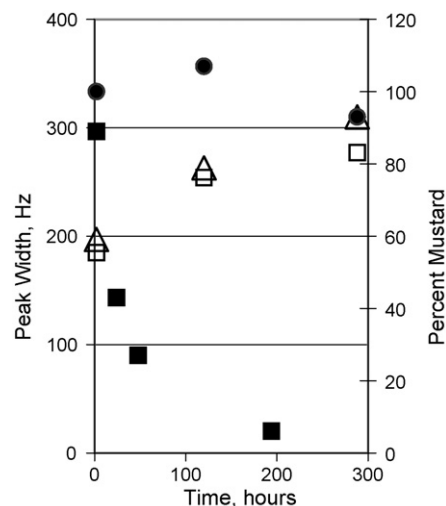


Fig. 7. Comparison of SSMAS spectral data for HD* on crushed concrete with extraction data. Left axis: peak widths at 35 ppm (□) and 44 ppm (△) in Hz. Right axis: percent sulfur mustard recovered from extraction (■) and normalized total integrated peak area for sulfur mustard via SSMAS (●).

3.3. Comparison between SSMAS studies and extractions

The timescale progression of the SSMAS sample was compared to that of the extracted monoliths (Fig. 7). After 192 h, the amount of sulfur mustard that was detected in the extracts from the monoliths was approximately 5%, yet the SSMAS spectra showed no decrease in the percentage of sulfur mustard that was present. The sulfur mustard peak widths in the SSMAS sample increased from 200 to 300 Hz over this period. Liquid sulfur mustard that was not interacting with a surface would demonstrate a peak width of 20–50 Hz under the same conditions. Thus, adsorption of the sulfur mustard to the surface may have begun within the one-hour time frame that it took to acquire the initial spectrum, and continued with time, as evidenced by the increasing peak widths.

In order to investigate the apparent dichotomy between the SSMAS and extraction results, a few monoliths were spiked with sulfur mustard, finely ground after the specified contact time, measured by SSMAS, and then extracted. The SSMAS total integrated peak areas were quantified by comparison to a freshly made standard of sulfur mustard on finely ground concrete. The SSMAS and extraction data pairs were compared to the previously obtained extraction data of percent sulfur mustard extracted versus concrete:sulfur mustard ratio and the trendlines that joined those data (Fig. 8).

At a concrete:sulfur mustard ratio of 91:1, and a 24-h contact time, more sulfur mustard was seen in the SSMAS spectra than was extracted. However, when typical error bars of 15% were added to all of the data, the SSMAS and extracted data were seen to fall within the range of the previous extraction data for the 24-h samples. The 192-h sample at a concrete:sulfur mustard ratio of 77:1 exhibited more sulfur mustard in the SSMAS than was extracted even after considering the experimental error.

At a concrete:sulfur mustard ratio of ca. 155:1 and a 24-h contact time the percent sulfur mustard observed by SSMAS and that extracted were very similar, 43 and 40%, respectively. At

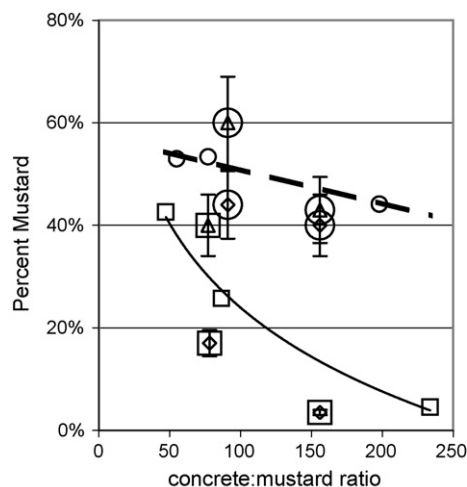


Fig. 8. Percent sulfur mustard extracted after 24 h (○) and 192 h (□). Percent sulfur mustard observed using SSMAS (△) followed by extraction (◇).

a concrete:sulfur mustard ratio of ca. 155:1 the sulfur mustard was not detected in the SSMAS spectra after a 48-h contact time, probably due to its low concentration and the numerous spinning side bands that were typical for this system. Only 4% of the original sulfur mustard was extracted.

4. Discussion

The observed decline in the extraction efficiency of sulfur mustard from concrete as the contact time increased was similar to the trends seen in prior investigations [9–11]. Beck, Carrick, Cooper and Muir [12] used pressurized liquid extraction to remove thiodiglycol from two soils and one type of sand; their percentage recovery ranged from 56 to 89 after 24 h depending upon the substrate, and declined over a period of 1–28 days.

The concrete:sulfur mustard ratio affected the rate of product formation. A concrete:sulfur mustard ratio of 170:1 corresponded to a monolayer of sulfur mustard coverage based on a sulfur mustard molecular area of 38 \AA^2 [4], a 1.3 g monolith with a surface area of $8.4 \text{ m}^2/\text{g}$ spiked with 6 mg sulfur mustard. At a concrete:sulfur mustard ratio of 55:1, some of the sulfur mustard was not in contact with the concrete but in a more liquid-like state in the pores of the concrete. This sulfur mustard would be less reactive than that in contact with the concrete surface, and hence react more slowly.

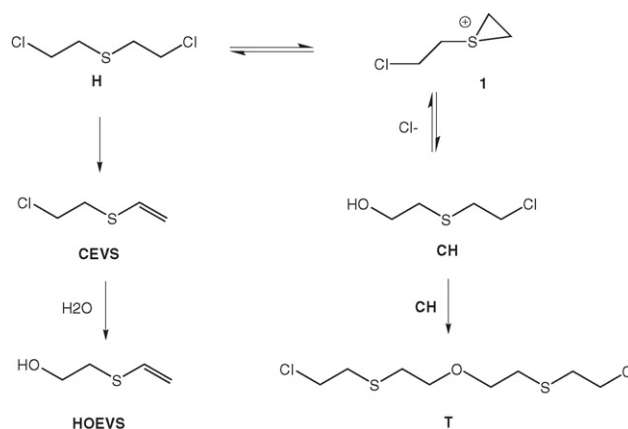
The initial SSMAS measurements of sulfur mustard on ground concrete showed multiple spinning side bands; these indicated a high degree of order of the sulfur mustard on the concrete, and implied that the sulfur mustard was bound to the surface rather than remaining as mobile droplets within the matrix. Initially, the spinning side bands accounted for ~50% of the total peak intensity, and thus precluded use of higher concrete:sulfur mustard ratios in the SSMAS experiments (the use of 2 mg sulfur mustard with 200 mg finely ground concrete in the rotor would barely be above the detection limit). The continuous broadening of the peaks in the SSMAS spectra indicated that the sulfur mustard and its products were binding more tightly to the concrete over time. The peak width data were consistent with

the observations that less sulfur mustard was extracted as the surface areas and contact times increased. These results were in contrast to the results in soil, in which the peaks remained narrow throughout the reaction [4]. Thus, the peak widths observed in this work were 200 Hz wide, compared to the 20–50 Hz peak widths that were typically seen for non-adsorbed liquid droplets in the SSMAS experiment.

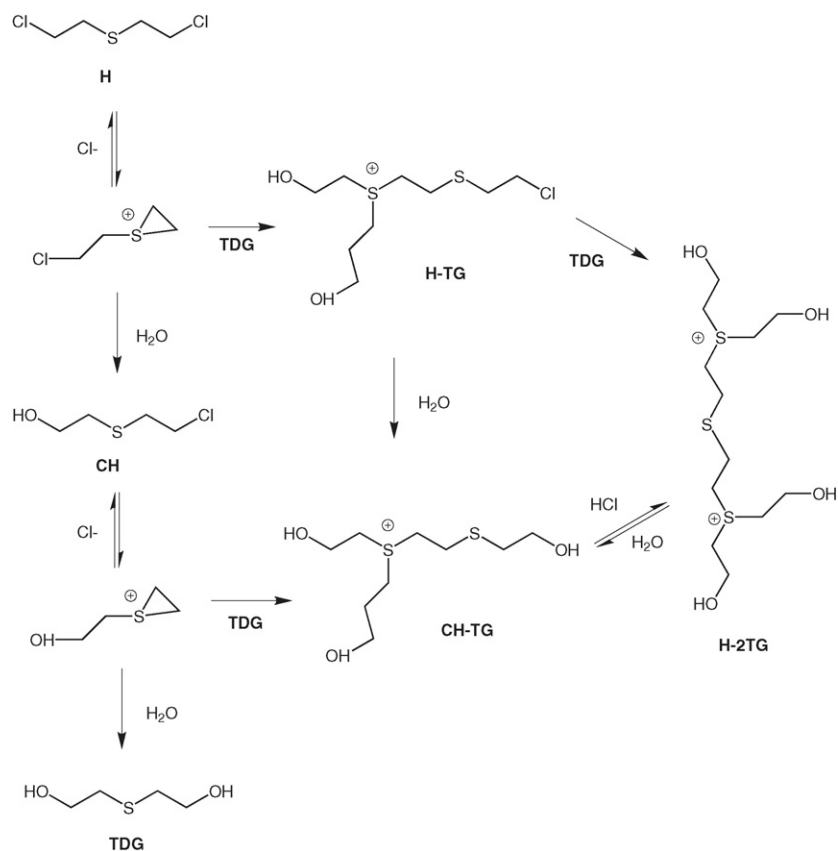
Performing SSMAS experiments on monolithic samples that were spiked, aged, and then ground immediately prior to extraction indicated that approximately half of the sulfur mustard was not seen in the SSMAS spectra. The interpretation of this data was that the sulfur mustard adsorbed onto the concrete and bound to it more tightly with time, resulting in peaks that were too broad for detection. Grinding the sample simultaneously removed existing pores and created new surfaces onto which any liquid sulfur mustard could adsorb. As the sulfur mustard adsorbed onto and then bound with the concrete, the peaks broadened and thus became difficult to detect. Hence, only half of the sulfur mustard that was put onto the monolithic sample was detected in the SSMAS spectra. All of the sulfur mustard that was observed in the SSMAS after a 24-h contact time was detected in extracts; the extractability decreased as the contact time increased to 192 h.

The products observed depended upon whether extraction or SSMAS methods were used to detect the products. A combination of sulfur mustard, H-2TG and T were detected on finely ground concrete after a 12-week contact time by SSMAS. The data from the extracts of the monoliths showed ~3% elimination products after 1 week, with ~5% sulfur mustard remaining, and the bulk of the material was not detected. These results are consistent with a mechanism in which most of the sulfur mustard bound tightly to the concrete and reacted over a period of 12 weeks, eventually forming H-2TG and T. Approximately 5% of the sulfur mustard formed elimination products; S-oxidized products and hydrolysis products were only detected occasionally. Since small samples of a heterogeneous substrate were used, slight variations in the products detected were not surprising.

The elimination pathway proceeded first followed by hydrolysis, as evidenced by the order of appearance of CEVS and HOEVS in Table 1. More HOEVS was present on the samples



Scheme 1. Formation of T, CEVS and HOEVS in concrete.



Scheme 2. Reactions of sulfur mustard with water.

that had a higher concrete:sulfur mustard ratio; this result was consistent with the fact that a larger sample of concrete would have more surface adsorbed water than a smaller sample. The formation of T, which occurred via hydrolysis of sulfur mustard to chlorohydrin followed by dimerization (Scheme 1) has not been seen in any other schemes for sulfur mustard degradation. The formation of H-2TG, according to Scheme 2, required the hydrolysis of the sulfur mustard and the formation of TDG; yet TDG was only seen in one sample by GC/MSD and was not seen by NMR. This lack of detection of major amounts of TG and CH indicated that they reacted rapidly to form H-2TG or T. Consideration of the pathways for the formation of H-2TG indicated that at some point either H-TG and/or CH-TG must have been formed, yet they were not detected as isolated species.

The sulfonium ion products generated by the degradation of sulfur mustard on concrete indicated a similarity to the reaction in water and on wet soil. This was not surprising, since concrete is porous and hygroscopic, and in equilibrium with the environmental moisture present.

The elimination product CEVS indicated that the reaction also had a component similar to that seen on CaO, MgO and alumina, all of which formed elimination and hydrolysis products (DVS, CEVS and TDG). TDG and DVS were not seen on the concrete; formation of sulfonium ions from the TDG dominated the products. Elimination, hydrolysis and sulfoxide products were also detected in extracts of soil samples from the Iran–Iraq war [13,14].

5. Conclusions

After 200 h very little mustard was extracted from the concrete monoliths, but the SSMAS spectra of crushed samples showed clearly that it was still present. This difference suggested that the mustard existed in the concrete in a non-extractable form prior to its degradation.

The degradation of the sulfur mustard as observed via ^{13}C SSMAS NMR progressed similarly to that in water or on wet soil, yielding mostly sulfonium ion products, with a minor component of the reaction yielding elimination products as observed on metal oxides. In addition, the degradation on concrete yielded T, a product that had not been previously observed.

Given a scenario in which the sulfur mustard on concrete is non-extractable with organic solvents, and not water soluble, its bioavailability is brought into question. However, the sulfur mustard will eventually degrade to form sulfonium ions; these can be extracted with both acetonitrile and water, and hence may become bioavailable [4,17]. Therefore, sulfur mustard bound in a matrix must be regarded as a future source of toxic, extractable, potentially bioavailable sulfonium ions.

Three of the degradation products—CEVS, CETEVS and T contained a 2-chloroethyl moiety. This moiety is generally related to vesicant action, and thus these three products may be considered potential vesicants [15]. The intraperitoneal LD_{50} of H-2TG in mice was 50 mg/kg; the oral LD_{50} in rats was 250 mg/kg. These LD_{50} were lower than the desired “non-toxic”

degradation products of thiodiglycol and 1,4-oxathiane that had oral LD₅₀ values of 6.6 and 3.0 g/kg in rats, respectively [15]. H-2TG was less toxic than sulfur mustard itself, which had human LD₅₀ values of 0.7 mg/kg (oral) and 20 mg/kg (skin) [16]. No toxicity data were found for HOEVS [15] or BVTE.

The potential vesicant and moderately toxic compounds observed in the degradation of sulfur mustard on concrete indicated that measuring the disappearance of sulfur mustard from concrete is not sufficient to declare an area safe for re-entry and re-use. In order to declare an area safe for subsequent activities, the degradation products formed must be identified, and their propensity to transfer onto skin and equipment must be evaluated in light of their toxicities. Thus, studies of the toxicity of a surface that has been contaminated with sulfur mustard and aged must be performed in order to determine the suitability of the area for a variety of future uses.

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