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SULFUR MUSTARD DEGRADATION ON AMBIENT AND MOIST CONCRETE



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14. ABSTRACT The reactivity, rate, and products for sulfur mustard were measured on ambient and moist concrete using ¹³ C solid-state magic-angle-spinning nuclear magnetic resonance (SSMAS NMR). Three samples of concrete made by the same formulation, but differing in age and alkalinity, were used. A portion of sulfur mustard directly formed 8 to 31% vinyl moieties on the newer, more alkaline concrete sample. The balance of the sulfur mustard degraded to thiodiglycol and 1,4-oxathiane via the intermediate sulfonium ions CH-TG, H-TG, H-2TG, and O(CH ₂ CH ₂) ₂ S ⁺ CH ₂ CH ₂ OH on all of the concrete samples. The degradation of sulfur mustard occurred more quickly at elevated temperatures and with added water; half-lives on ambient substrates at 22 °C ranged from 3.5 to 54 weeks on ambient concrete, with no reaction on ambient limestone. On moistened substrates the degradation half-lives at 22 °C ranged from 75 to 350 hr. The Arrhenius activation energies were 47 kJ/mol on ambient concrete and 86 kJ/mol on moist concrete. The toxic sulfonium ions, which were the first product of the degradation, persisted for months to years on concrete at 22 °C and weeks to months on concrete at 35 °C.					
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PREFACE

The work described in this report was authorized under Contract No. DAAD13-03-D-0017. The work was started in November 2004 and completed in December 2006.

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SULFUR MUSTARD DEGRADATION ON AMBIENT AND MOIST CONCRETE

1. INTRODUCTION

Studies of the fate of sulfur mustard on moist and ambient sand, limestone, and asphalt have been previously reported.¹ Brevett et al. used ^{13}C SSMA NMR to show that sulfur mustard on wet sand degraded to form TDG, H-2TG, and CH-TG,² and that sulfur mustard on ambient concrete would remain as mustard for 12 weeks, but after the passage of 2 weeks, it was non-extractable.³ The ^{13}C SSMA NMR techniques were employed to study the rate of and identify the products for sulfur mustard degradation on a different grade of ambient and moist concrete, as a function of the temperature of the sample and the age of the concrete. The degradation of sulfur mustard on the moist and ambient mortar and limestone components of the concrete was also monitored.⁴ In the present document, additional kinetic data and spectra for sulfur mustard degradation on ambient and moist concrete are given.

2. EXPERIMENTAL PROCEDURES

Substrates, agent, NMR instrumentation, and GC instrumentation have been previously described.⁴

3. RESULTS

3.1 Kinetics and Products on Ambient Concrete.

The degradation kinetics of sulfur mustard at 22 °C on ambient concrete were generally first- or zero-order, and the first half-life ranged from 3 to 52 weeks (Table 1). Selected spectra are shown in Figures 1-4, product chemical shifts are given in Table 2, and the products formed for each substrate are summarized in Table 3.

Table 1. Half-lives of Sulfur Mustard Degradation on Concrete

Concrete	Temperature, °C	Ambient, weeks	Moist, hours	H ₂ O excess
C03	22	3.5 ^a	92 ^a	16
M03	22	52 ^{b, a}	75 ^c	13
C90	22	Irregular, ~30	107 ^b	16
C04a	22	15 ^c	350 ^c	14
C04b	22	45 ^{b, d}		
C04	35	7.2 ^c	23.5 ^c	20
C04	50	na	<~5 ^c	19
Limestone	22	No reaction ^c	~260 ^c	18

^a ~70% mass balance.

^b Zero-order kinetics were observed; the first half-life is recorded.

^c ~100% mass balance.

^d ~50% mass balance.

Table 2. Chemical Shifts for Mustard and Its Degradation Products

Abbreviation	Name	Formula	¹³ C Chemical Shift, ppm	Toxicity Comment ^a
H, HD, HD*	Mustard gas	(ClCH ₂ CH ₂) ₂ S bis(2-chloroethyl) sulfide	43, 35	Blister; PGI [4]
CH	Chlorohydrin	ClCH ₂ CH ₂ SCH ₂ CH ₂ OH	43, 33, 35, 61	PGI [4]
TDG	Thiodiglycol	(HOCH ₂ CH ₂) ₂ S	61, 34	Non-toxic [4]
CH-TG	-	HOCH ₂ CH ₂ SCH ₂ CH ₂ S ⁺⁻ (CH ₂ CH ₂ OH) ₂	62, 35, 27, 43, 45, 58	Toxic [2]
H-TG	-	ClCH ₂ CH ₂ SCH ₂ CH ₂ S ⁺⁻ (CH ₂ CH ₂ OH) ₂	43, 33, 29, 44, 46, 59	PGIII [4]; PGI [5]
H-2TG	-	S[CH ₂ CH ₂ S ⁺ (CH ₂ CH ₂ OH) ₂] ₂	27, 44, 46, 59	PGII [4]
HOEt-OT		O(CH ₂ CH ₂) ₂ S ⁺ CH ₂ CH ₂ OH	64, 59, 33, 46 ^b	
HOEt-dT		S(CH ₂ CH ₂) ₂ S ⁺ CH ₂ CH ₂ OH	56, 43, 37, 23	
2-CE	2-chloroethanol	ClCH ₂ CH ₂ OH	63, 47	PGIII ^d
	1,4-oxathiane	O(CH ₂ CH ₂) ₂ S	71, 32, 69, 27 ^c	Non-toxic ^d
	1,4-dithiane	S(CH ₂ CH ₂) ₂ S	33, 29 ^c	Non-toxic ^d
EG	Ethylene glycol	HOCH ₂ CH ₂ OH	63	Non-toxic ^d
CEVS	2-chloroethyl vinyl sulfide	ClCH ₂ CH ₂ SCH=CH ₂	110, 132, 34, 43	
HOEVS	2-hydroxyethyl vinyl sulfide	HOCH ₂ CH ₂ SCH=CH ₂	33, 60, 109, 138	
DVS	Divinyl sulfide	CH ₂ =CHSCH=CH ₂	114, 129	

^aToxicity ratings from 49CFR 173.133 (a)(1): Oral LD₅₀: PGI < 5mg/kg; PGII between 5 and 50 mg/kg; PGIII between 50 and 200 mg/kg for solids and 50 to 500 mg/kg for liquids.

^bCalculated using ACD Software.

^cValues on charcoal.

^dFrom MSDS.

Table 3. Products and Intermediates Formed during Sulfur Mustard Degradation on Ambient Concrete

Compound Chem shift, ppm	C90 ^a	C04, 50 °C	C04, 35 °C	C04a [*]	C04b [*]	M03 [*]	C03
CEVS 132, 112	0	Y	Y	Y	Y	Y	Y
HOEt-OH 65, 57, 46, 33	Y	0	Y	Y	0	0	Y
H-2TG 57, 46, 44, 27	0	0	0	Y	0	0	Y
TDG 61, 33	0	0	Y	0	0	0	Y
1,4-oxathiane 72, 33	0	Y	Y	Y	Y	Y	Y
1,4-dithiane 32	0	Y	Y	Y	Y	Y	0
Age of last spectrum, weeks	39	9	40	78	71	61	24

^aThe decomposition of the sulfur mustard was incomplete when the last spectrum was taken.

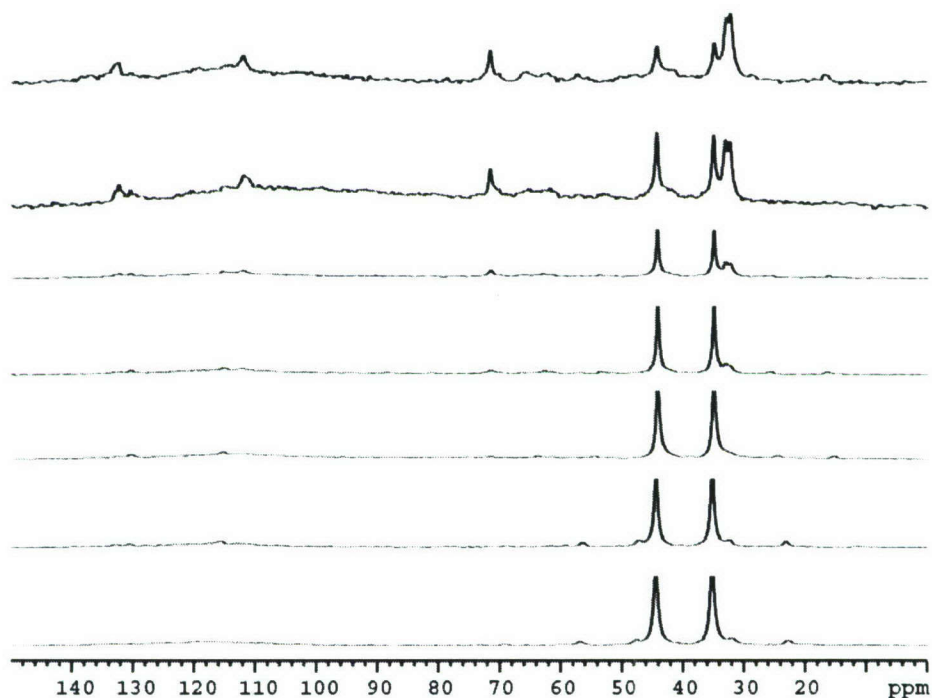


Figure 1. ¹³C SSMAS NMR Spectra of Sulfur Mustard on Ambient M03 at 22 °C. Top two spectra are x4 magnification. Times from bottom to top: initial, 4, 18, 70 days, 28 and 61 weeks.

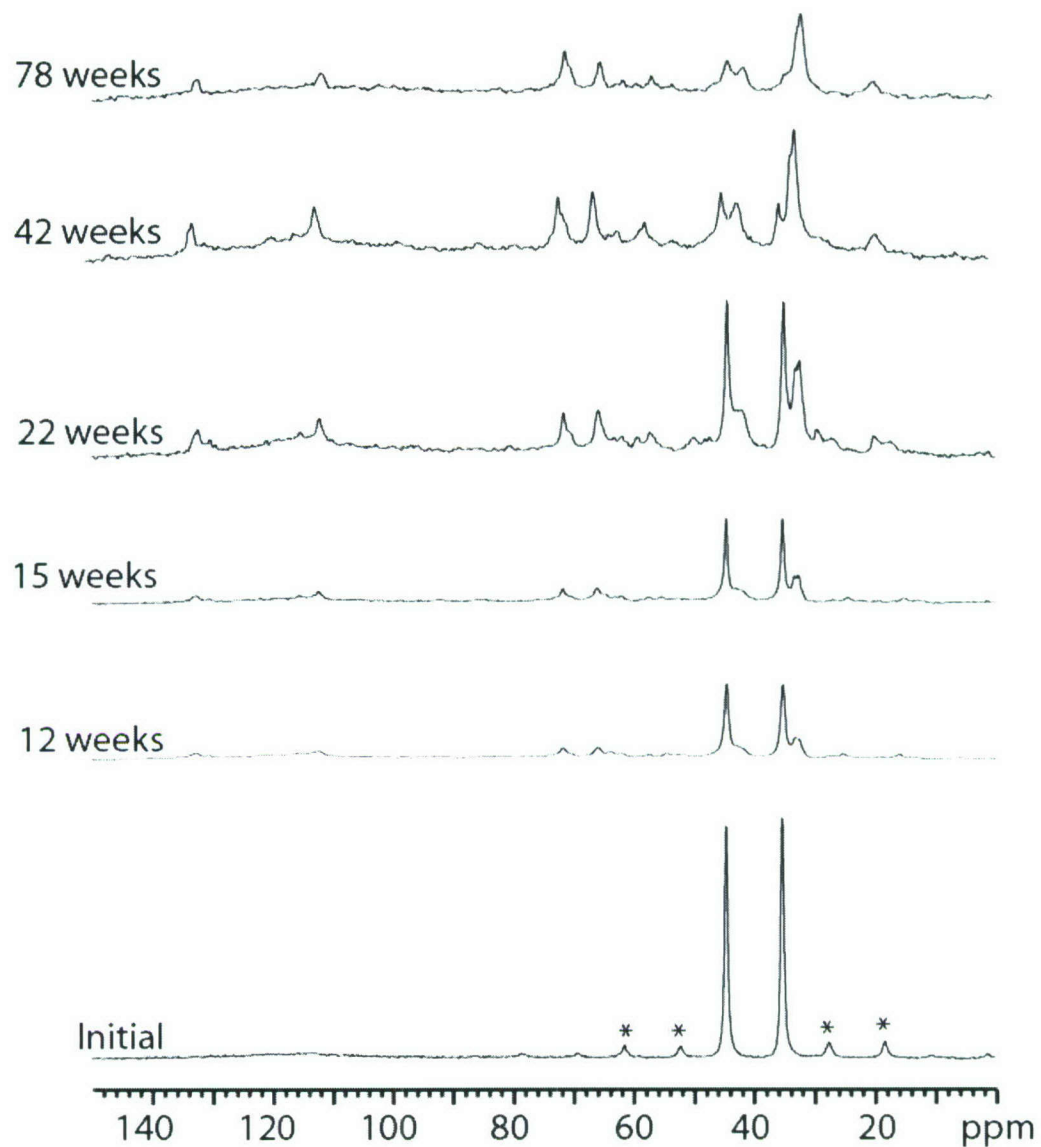


Figure 2. ^{13}C SSMAS NMR Spectra of Sulfur Mustard on Ambient Concrete, Sample C04a. The * denote spinning side bands. The top three spectra are shown at 4x the magnification of the bottom three spectra.

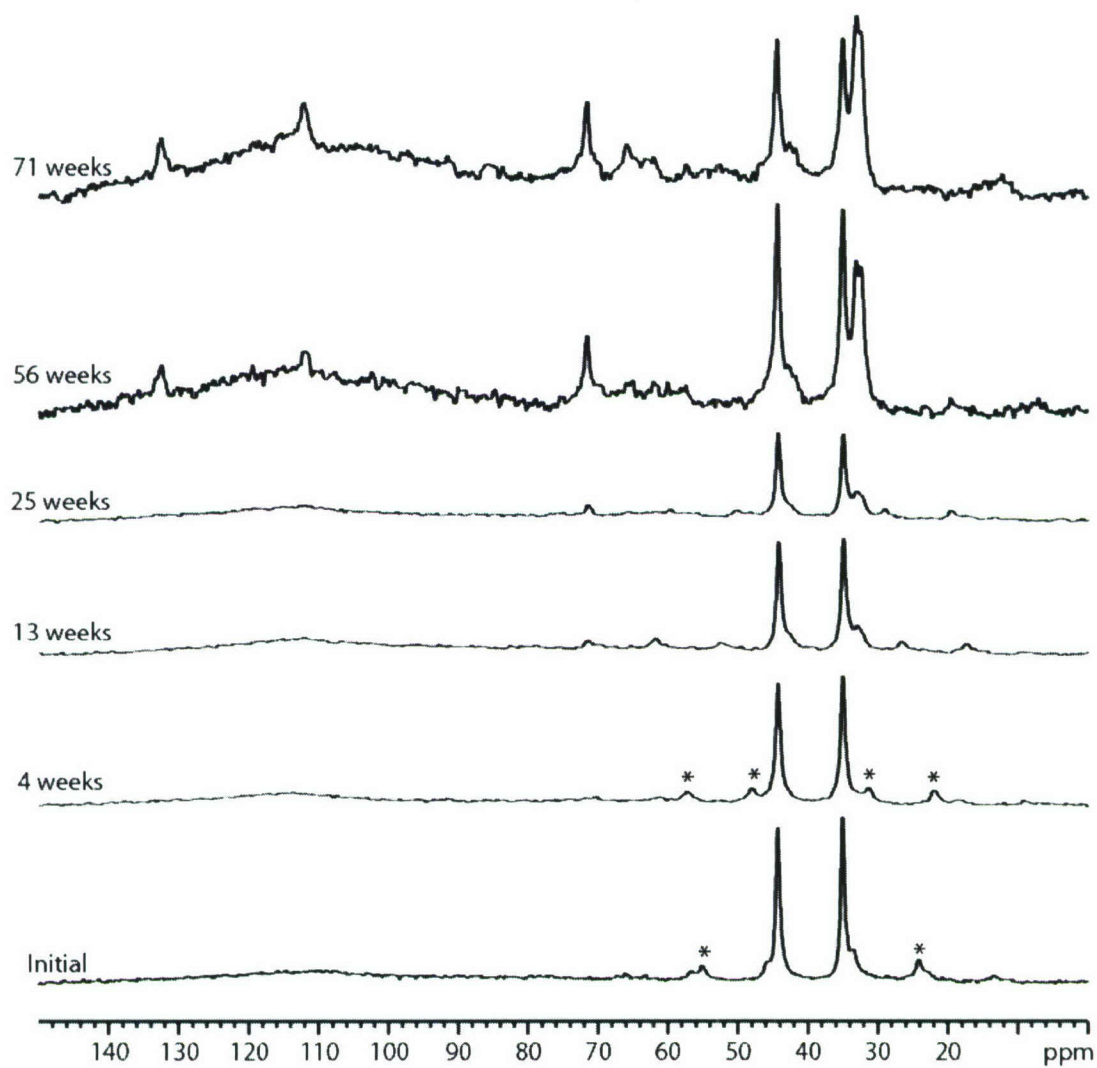


Figure 3. ^{13}C SSMAS NMR Spectra of Sulfur Mustard on Ambient Concrete, Sample C04b. The vertical scale of the last two was magnified 5-fold. The * denote spinning side bands.

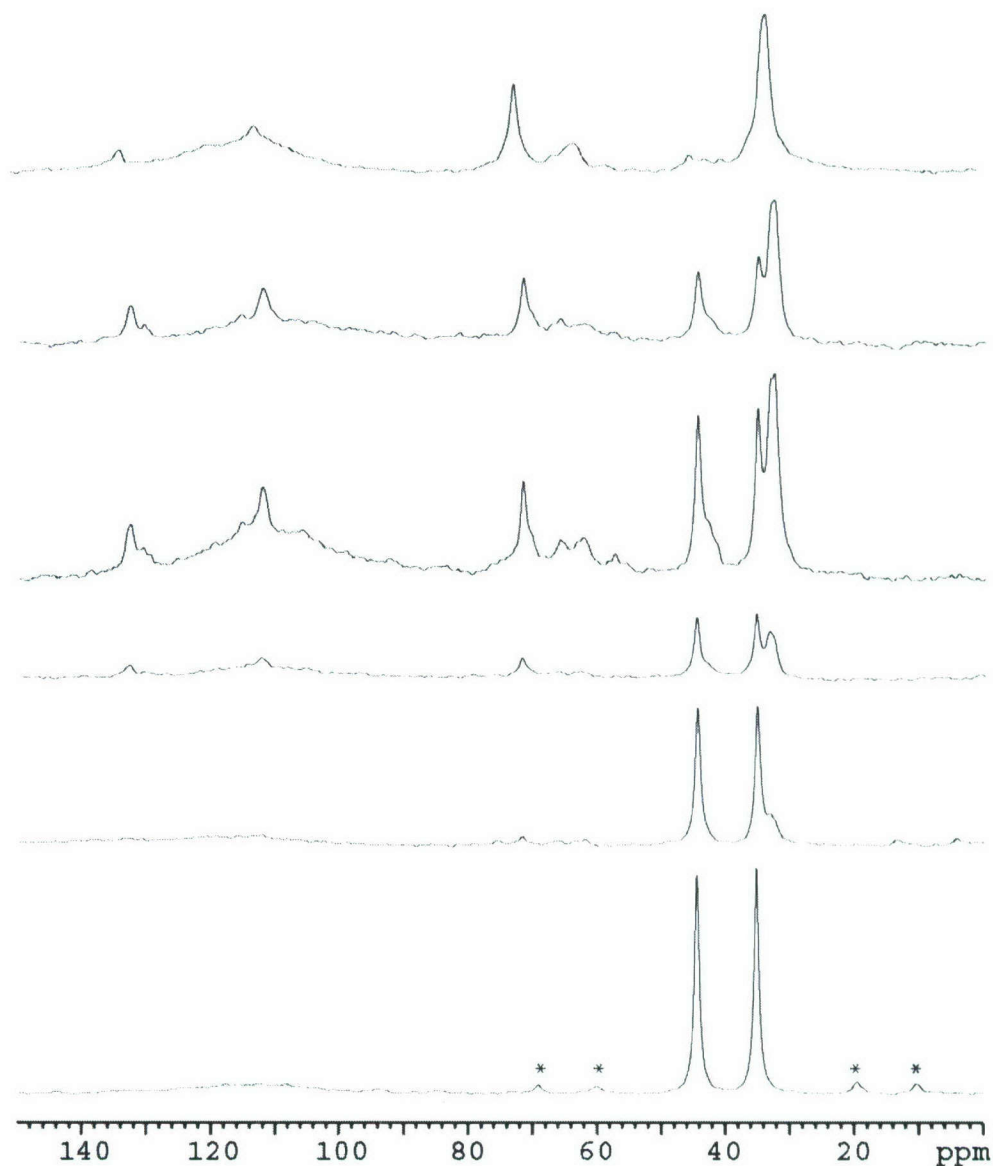


Figure 4. ^{13}C SSMAS NMR Spectra of Sulfur Mustard on Ambient C04 at 35 °C, Taken at Sample Ages of 5 hr, 3, 11, 15, 18, and 40 weeks. The last three spectra were magnified 4-fold compared to the first 3. The * denotes spinning side bands.

3.2 Kinetics and Products on Moist Concrete.

Sulfur mustard degradation on moist C03, M03 (Figure 5), C90 and C04 at 22 °C, gave similar results. The first-order kinetic plots (Figure 6) were used to calculate the rate constants for samples C03, M03, and C04, which were 92, 75, and 350 hr, respectively. Due to the paucity of data, the first-order rate constant for C90 estimated from one data point was ~107 hr. The degradation of sulfur mustard on moist C04 at 35 °C was measured using duplicate samples; the first-order half-lives were 23 and 24 hr (Figures 7 and 8). The kinetics for the degradation of the sample at 50 °C were too fast to measure accurately but were estimated to be <5 hr (Figure 9). Sulfur mustard on

moist limestone at 22 °C exhibited degradation at 6 days and was complete in approximately 7 weeks. Mass balance was maintained throughout the course of the reaction. The half-life was estimated to be 260 hr. Products formed on all of the substrates are summarized in Table 4, and the half-lives were given in Table 1. Figure 10 shows a typical evolution of integrated peak areas for the various products with time.

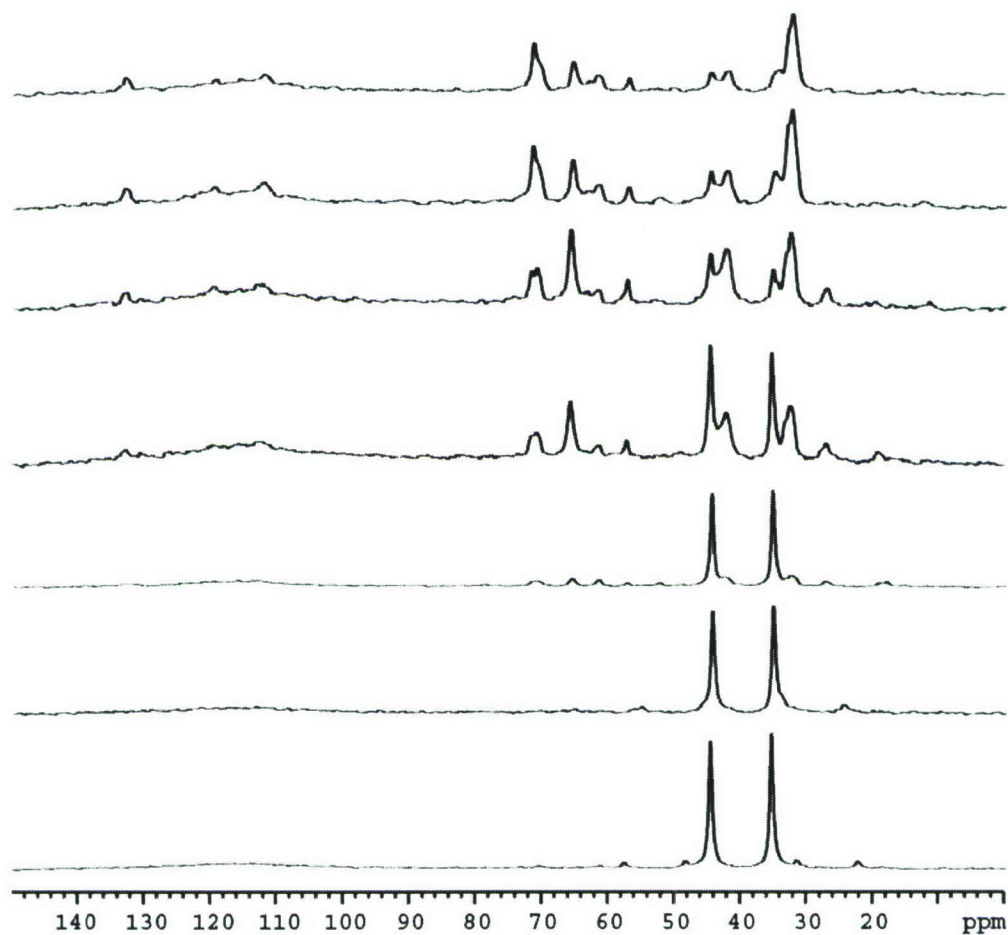


Figure 5. ^{13}C SSMAS NMR Spectra of Sulfur Mustard on Moist M03 at 22 °C. Times from bottom to top are 1, 24, 96, 216, and 336 hr, 18 and 25 days. The bottom three spectra have 1/3 the vertical scale of the upper spectra.

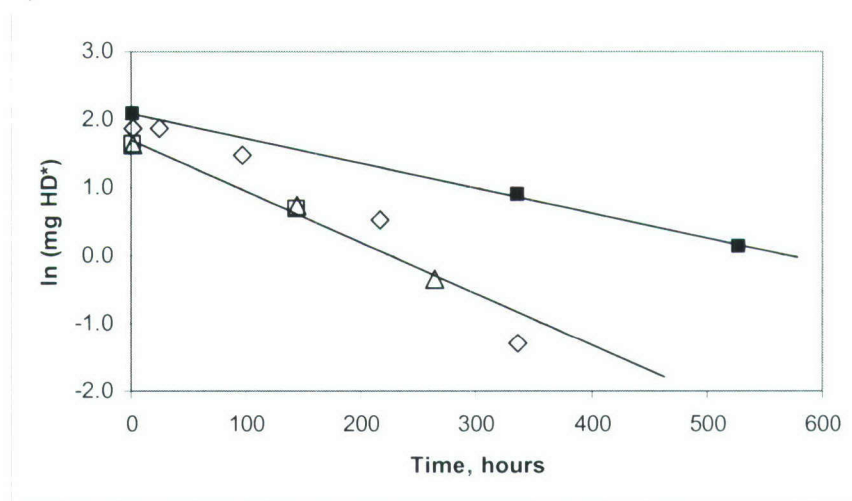


Figure 6. First-Order Kinetic Plots for HD* on Moist C03 ($\triangle$), M03 ($\diamond$), C04 ($\blacksquare$), and C90 ($\square$) Concrete Samples at 22 °C.

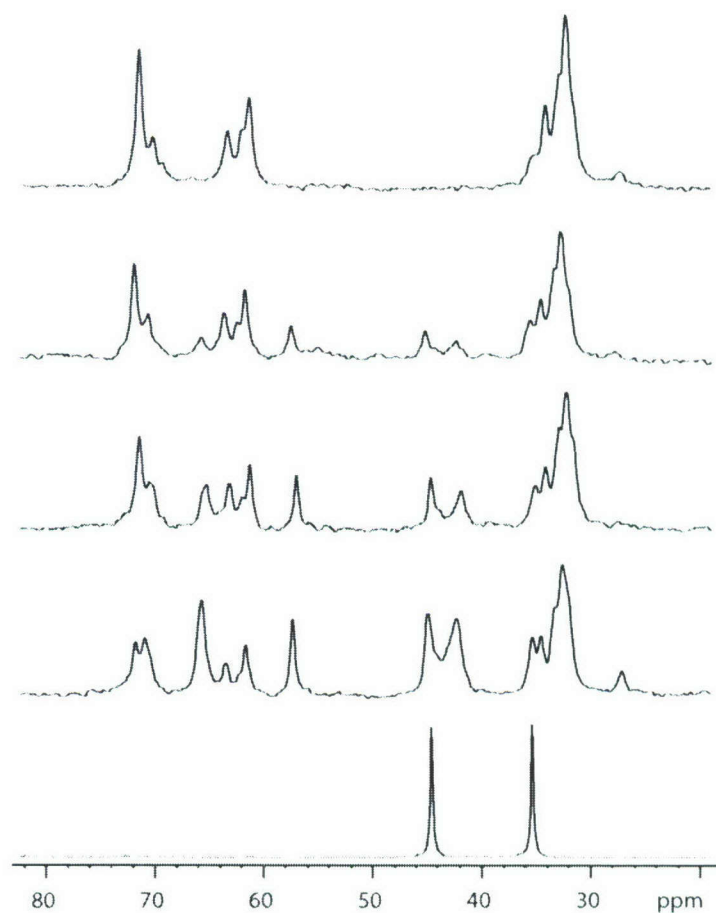


Figure 7. ^{13}C SSMAS NMR Spectra of Sulfur Mustard on Moist C04 at 50 °C. Age of sample from bottom to top: initial, 20, 45, 96 hr, and 2 months.



Figure 8. ^{13}C SS MAS Spectra of Sulfur Mustard on Moist C04 at 35 °C, Taken at 2, 23, 49, 73, 95 hr, 7, 9, 24 days, 13 and 16 weeks. The first two samples are shown at 1/10 the magnification of the subsequent samples.

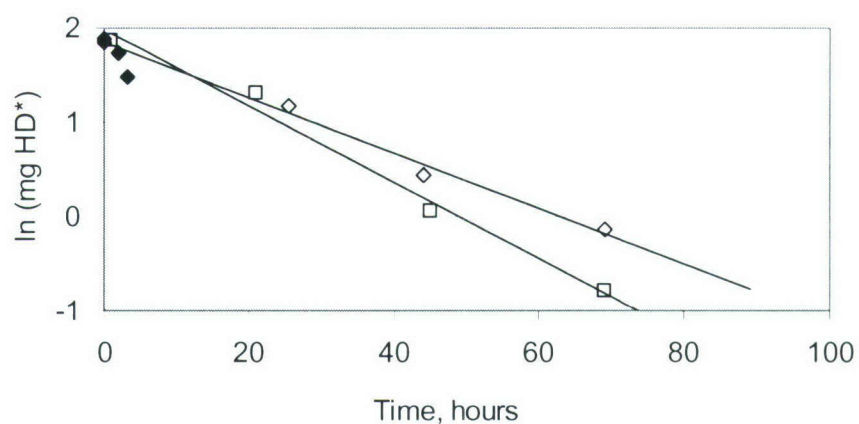


Figure 9. First-Order Kinetic Plots from ^{13}C SSMAS NMR Spectra of Sulfur Mustard Degradation on Moist Concrete C04 at 22 °C ($\triangle$), 35 °C ($\diamond$, $\square$), and 50 °C ($\blacklozenge$).

Table 4. Products and Intermediates Formed during Sulfur Mustard Degradation on Moist Concrete

Compound Chemical shift, ppm	C90 ^a	C04, 50 °C	C04, 35 °C	C04	M03 ^a	C03	Limestone [*]
CEVS 132, 112	0	y	y	y	y	y	0
HOEt-OH 65, 57, 46, 33	y	y	y	y	y	y	0
H-2TG 57, 46, 44, 27	y	y	y	y	y	y	y
TDG 61, 33	y	y	y	y	y	y	y
1,4-oxathiane 72, 33	y	y	y	y	y	y	0
1,4-dithiane 32	0	0	0	0	y	0	0
2-chloroethanol 65, 43	0	0	0	y	y	y	0
Age of last spectrum, weeks	62	9	16	22	3.5	83	7

^{*}The decomposition of the sulfur mustard was incomplete when the last spectrum was taken.

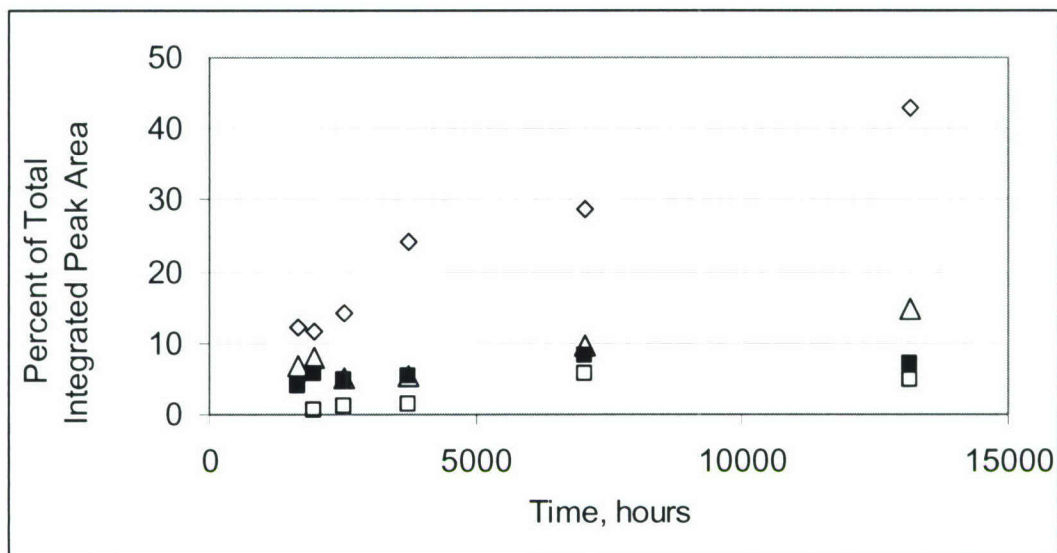


Figure 10. Evolution of Peaks in ^{13}C SS MAS NMR Spectra for Sulfur Mustard Degradation on Ambient C04a at 22 °C: 33 (◇), 57 (□), 66 (■), and (△) 72 ppm

3.3 Order of the Sulfur Mustard Degradation, Activation Energies, and Mass Balance.

An examination of the order of the degradation reaction showed that nine of the reactions examined exhibited first-order kinetics based upon a plot of $[\ln(\text{mg HD}^*)]$ versus time (Figures 6 and 9), and two ambient samples, M03 and C04b, exhibited zero-order kinetics based upon a plot of $\{\text{mg HD}^*\}$ versus time. Sulfur mustard degradation on ambient C90 displayed an irregular kinetic profile. Insufficient data were collected on the other samples to determine the order of the degradation. Neither of the samples that exhibited zero-order kinetics produced any sulfonium ions. The reason for the change in order is not well understood but may be related to the inhomogeneity of the concrete, which in turn affected the amount of entrained water and then affected the product distribution.

Because the majority of the samples that gave good kinetic plots exhibited first-order kinetics, the data from the other samples were used to calculate the half-life assuming first-order kinetics. The calculated half-lives were used to make an Arrhenius plot to calculate the Energy of Activation, E_a and the pre-exponential factor, A , according to the Arrhenius equation. The E_a was 47 kJ/mol for sulfur mustard degradation on the ambient concrete and 86 kJ/mol on the moist concrete (Figure 11). The pre-exponential factor, A , was 6.3×10^9 for sulfur mustard degradation on the ambient concrete and 7.9×10^{12} on the moist concrete (calculated from Figure 11).

$$k = A e^{-E_a/RT} \quad (1)$$

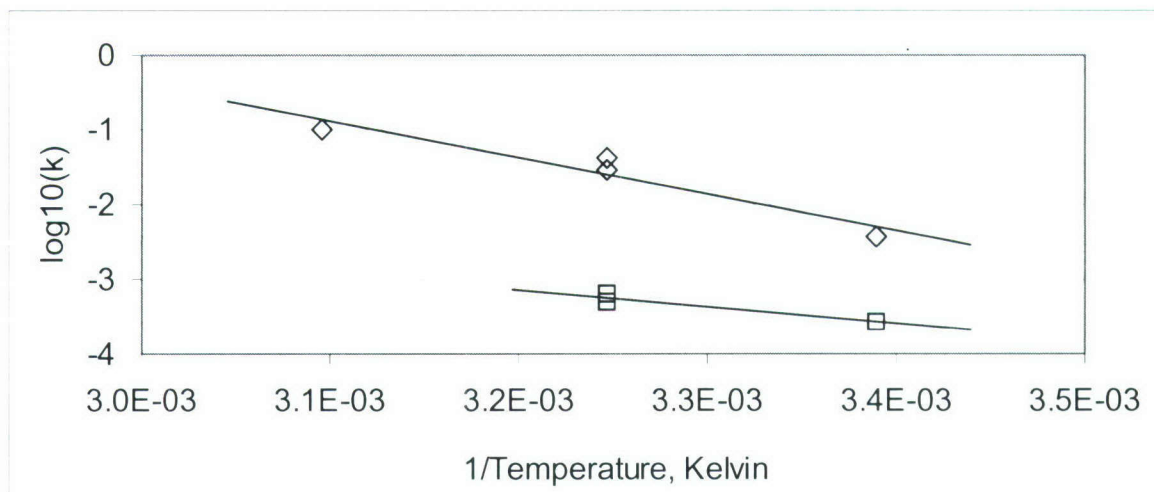


Figure 11. Arrhenius Plots for Sulfur Mustard Degradation on Ambient (□) and Moist (◇) C04

4. DISCUSSION

The sulfur mustard degradation occurred faster with the addition of water and with increasing temperature. It was noted that the vinyl species (CEVS) (Table 5) were only formed on the newer, more alkaline concrete samples, and did not form on the aged C90 concrete. The reason for the change in order of the reactions is not well understood, but may be related to the heterogeneity and moisture content of the samples. The products formed on the M03, C04, and C03 concrete samples in this study are similar to each other. The products, sidebands, and loss of intensity for C90 were similar to that observed in the previous work³ with the C00 concrete. The HOEt-OH sulfonium ion was observed on concrete but not on moist sand or asphalt.

Many of the reactions were, in fact, incomplete when the last spectrum was taken; in some cases, this was at 84 weeks. The ultimate products were 1,4-oxathiane, 1,4-dithiane, and thiodiglycol; sulfonium ions were intermediates. Due to the overlap of peaks and the fact that the chemical shifts varied within a few ppm, it was difficult at times to determine if the 65-63 ppm peak was due to 2-CE, HOEt-OH, or both. It was also difficult to determine conclusively which vinyl species were present (CEVS, HOEVS, or DVS) and to determine if small amounts of CH-TG and H-TG occurred.

Table 5. Percent Vinyl Moieties for Sulfur Mustard Degradation on Concrete

Concrete	Temperature, °C	Ambient	Moist
C03	22	10	10
M03	22	31	8
C90	22	0	0
C04a	22	13	10
C04b	22	13	n/a
C04	35	18, 19	11, 12
C04	50	16	13

5. CONCLUSIONS

The kinetics and products of the degradation of sulfur mustard on three samples of airport runway concrete were studied. The first half-lives for the degradation of sulfur mustard at 22 °C on moist concrete fell within a narrow range, between 70 and 350 hr, whereas on ambient concrete the range was broad, ranging from 25 days to 52 weeks. The rate was slower on the older, less alkaline concrete. Increasing the temperature also resulted in a faster degradation rate. The wide range of decomposition rates on ambient concrete samples indicated that it would be difficult to accurately predict degradation rates in an environment where the age and degree of hydration of the concrete are unknown.

The degradation immediately produced the minor product 2-chloroethyl vinyl sulfide on the younger, more alkaline concrete samples but not on the aged sample. The other immediate products were the sulfonium ions 4-(2-hydroxyethyl)-1,4-oxathian-4-ium, toxic H-2TG, and 2-chloroethanol. The sulfonium ions decomposed to form predominantly 1,4-oxathiane and 1,4-dithiane on the ambient concrete samples and 1,4-oxathiane and thiodiglycol on the moist samples. The formation of only non-toxic products would take years on some samples at 22 °C. The products observed were consistent with those observed on alkaline metal oxides and with those observed during the thermal degradation of mustard.

In the event of contamination of concrete with sulfur mustard, the production of toxic intermediates would lead to a condition in which air monitors would not detect any mustard, but vesicant materials would still be present in the concrete. Thus, the concrete would need to be tested for the presence of sulfur mustard and toxic sulfonium ions.

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