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### DEGRADATION OF MUSTARD ON MOIST SAND, ASPHALT, AND LIMESTONE USING $^{13}\text{C}$ SSMAS NMR

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## PREFACE

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# DEGRADATION OF MUSTARD ON MOIST SAND, ASPHALT, AND LIMESTONE USING $^{13}\text{C}$ SSMAS NMR

## 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.

Environmentally, mustard has been observed to persist for four years in soil.<sup>1</sup> Wagner and MacIver<sup>2</sup> used  $^{13}\text{C}$  SSMAS (solid state magic angle spinning) NMR to show that mustard persisted for several weeks on dry soil, but hydrolyzed and polymerized to form toxic CH-TG and H-2TG within one week when water was added. Other studies showed that although mustard has low solubility in water, forming droplets within it, reactions occurred at the water-mustard interface to form the hydrolysis products chlorohydrin (CH) and thiodiglycol (TDG), which subsequently formed the sulfonium ions H-2TG and CH-TG<sup>3-5</sup>.

In the current study,  $^{13}\text{C}$  SSMAS NMR techniques were employed to quantitatively study the degradation of mustard on moist sand, limestone and asphalt.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Substrates.

#### 2.1.1 Sand.

The sand used was obtained from three sources. Foundry Sand Washed 0-17 was produced by Moravske Keramicke Zavody A. S. in Europe; AFS-50 Fine Sand was produced by Warmwell Quarry in the United Kingdom; and Filter Sand #2 was produced by Southern Products & Silica Co., Hoffman, NC, USA, via the distributor Charles Reade Co. in Providence, RI, USA. The particle sizes and elemental compositions, based on the specifications sheets of the suppliers, are compared in Table 1. The surface area measurements were made by Micromeritics Inc., Norcross, GA using the 5-point BET method.

### 2.1.2 Limestone.

The finely ground limestone, labeled Caldera, was obtained from the Army Corps of Engineers (ACE). Larger pieces of the same composition were aggregate in the asphalt and concrete that had been supplied by ACE.

Table 1. Physical Properties of the Sand and Limestone Samples used

Property	European Foundry Sand Washed 0-17	UK Sand Warmwell Quarry AFS-50	US Filter Sand#2, Southern Products	Caldera Limestone
Predominant particle size (mm)	0.14 - 0.2	0.25 - .50	0.8 -1.2	<0.1
Sand Type	fine	medium	coarse	very fine
Silica (SiO <sub>2</sub> ) %	97.0	98.6	99.8	16.4
Aluminum oxide %	-	0.39	0.04	0.92
Ferric oxide %	0.3	0.09	0.05	0.67
Calcium Carbonate, %	-	-	-	75.7
Surface Area, m <sup>2</sup> /g	0.14	-	-	2.2

### 2.1.3 Asphalt.

The asphalt samples were obtained from Europe and from ACE. The samples were completely ground using a mortar and pestle, and sieved through a 0.1 mm sieve before use.

XRF data, which detected the elemental composition for elements heavier than neon, showed that the European asphalt had an approximately 50:50 mixture of silica and calcium carbonate (limestone), with 3% magnesium oxide, 5% iron oxide and 7% alumina. The exact chemical species were not known from the XRF; that is, one could not identify if the alumina and silica were separate species, or if they were an aluminosilicate. The amount of calcium carbonate was calculated from the calcium oxide that was measured by the XRF technique.

### 2.2 Agent.

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

### 2.3 NMR Instrumentation.

<sup>13</sup>C SS MAS (solid state magic angle spinning) NMR spectra were collected at 9.4 Tesla and 22 °C 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 5 times the measured relaxation time, T<sub>1</sub>, and spectra were referenced to external tetramethylsilane (TMS). A standard (<sup>13</sup>C-labeled 2-chloroethyl phenyl sulfide, CEPS\*, plus TMS on sand) was run daily to ensure that the total integrated peak areas were unchanged and unaffected by the instrumentation. The spin-lattice relaxation times, T<sub>1</sub>, were measured using a standard inversion recovery sequence.<sup>6</sup>

### 2.4 Chemical Shifts.

A list of common mustard degradation products and their literature chemical shifts is given in Table 2 below. The chemical shifts may change when the matrix changes, a typical range is ±2 ppm. Many products, and mustard itself, have chemical shifts in the 32 to 35 ppm region of the <sup>13</sup>C spectrum, which makes using this region of the spectrum for product identification difficult.

Table 2. Chemical Shifts for Mustard and its Degradation Products

Abbreviation	Name	Formula	<sup>13</sup> C Chemical Shift, ppm	Toxicity Comment [Ref.]
H, HD	Mustard gas; bis(2- chloroethyl) sulfide	(ClCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S	43, 35	Blister agent, PGI [4]
CH	Chlorohydrin	ClCH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> OH	43, 33, 35, 61	PGI [4]
TDG	Thiodiglycol	(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S	61, 35	Non-toxic [4]
CH-TG	-	HOCH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> S <sup>+</sup> (CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	62, 35, 27, 43, 45, 58	Toxic [2]
H-TG	-	ClCH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> S <sup>+</sup> (CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	43, 33, 29, 44, 46, 59	PGIII [4]; PGI [5]
H-2TG	-	S[CH <sub>2</sub> CH <sub>2</sub> S <sup>+</sup> (CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub> ] <sub>2</sub>	27, 44, 46, 59	PGII [4]
CEVS	2-chloroethyl vinyl sulfide	ClCH <sub>2</sub> CH <sub>2</sub> SCH=CH <sub>2</sub>	110, 132, 34, 43	
HOEVS	2-hydroxyethyl vinyl sulfide	HOCH <sub>2</sub> CH <sub>2</sub> SCH=CH <sub>2</sub>	33, 60, 109, 138	
DVS	Divinyl sulfide	CH <sub>2</sub> =CHSCH=CH <sub>2</sub>	114, 129	

Toxicity ratings from 49CFR 173.133 (a)(1): Oral LD<sub>50</sub>: 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.

### 3. RESULTS

#### 3.1 Sand.

##### 3.1.1 European Foundry Sand.

When placed on dry sand, the mustard was unreactive over a period of 7 months. When HD\* and water were placed on sand, with a H<sub>2</sub>O:HD\* ratio of 17:1, a reaction was detected in six days. The degradation of the mustard was complete in 8 weeks, but too little data had been collected in the interim to determine the order of the reaction or a rate constant. The mustard T<sub>1</sub>s were 2.5 and 3.0 seconds, whereas the sulfonium ion T<sub>1</sub>s ranged from 0.6 to 1.0 seconds. The products were 87% H-2TG and 13% TDG (Figure 1 and Table 3). Comparison of the total integrated peak areas for all of the spectra showed that mass balance was maintained throughout the 8-week period of study.

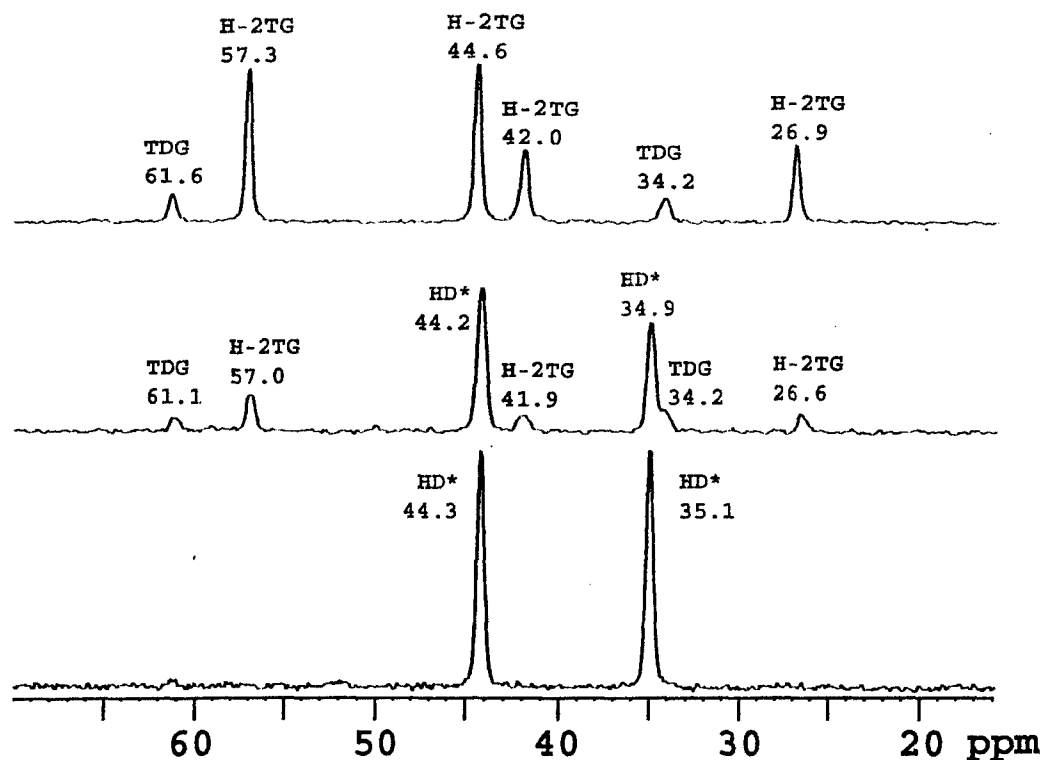


Figure 1. <sup>13</sup>C SSMAS NMR Spectra of the Degradation of Mustard on European foundry sand, showing HD\* (44.3 and 35.1 ppm), TDG (61.6 and 34.2 ppm), and H-2TG Sulfonium Ion (57.3, 44.6, 42.0, 26.9 ppm). Identities from bottom to top are: Initial, 6 days, and 8 weeks.

## 3.1.2

US Southern Products Filter Sand #2.

When HD\* and water were placed on the sand with a H<sub>2</sub>O:HD\* ratio of 17:1, a reaction was detected in two weeks. The degradation of the mustard was complete in 8 weeks, but too little data had been collected in the interim to determine the order of the reaction or a rate constant. The products identified were sulfonium ion H-2TG (90%) and TDG (10%) (Figure 2 and Table 3). The mustard T<sub>1</sub>s ranged from 2.6 to 3 seconds, whereas the sulfonium ion T<sub>1</sub>s were 0.5 seconds. When placed on dry sand, only 5% of the total integrated peak area was in the spinning side bands, and the mustard was unreactive over a period of 5 months. Comparison of the total integrated peak areas for all of the spectra showed that mass balance was maintained throughout the 8-week period of study.

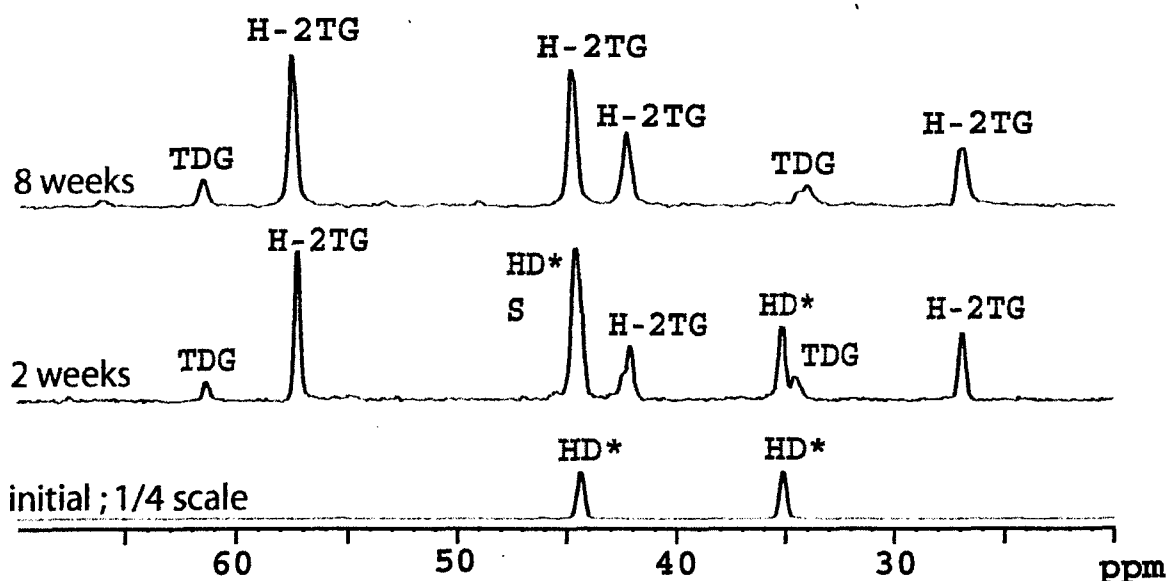


Figure 2. <sup>13</sup>C SSMAS NMR Spectra of the Degradation of Mustard on US Southern Products Filter Sand#2, Showing HD\* (44.3 and 35.1 ppm), TDG (61.7 and 34.4 ppm), and H-2TG Sulfonium Ion (57.2, 44.6, 41.9 and 26.9 ppm). Age of spectra from bottom to top: initial, 2 weeks, and 8 weeks

## 3.1.3

UK ASF-50 Fine Sand.

This sand was moist when supplied; allowing it to dry in a fume hood for 96 hours showed that it contained 6.7% moisture. Three experiments were run with this sand: HD\* on the hood-dried sand, HD\* on the as-received sand, and HD\* plus water on the hood-dried sand. When placed on the hood-dried sand, the mustard was unreactive over a period of 5 months.

The H<sub>2</sub>O:HD\* ratios were 23:1 for the as-is sand and 17:1 for the hood dried sand with added water. A reaction was seen in 6 days for both samples. The degradation of the mustard was complete in 8 and 7 weeks respectively, but too little data had been collected in the interim to determine the order of the reaction or a rate constant. For both samples, the

mustard T<sub>1</sub>s were 2.6 seconds, whereas the sulfonium ion T<sub>1</sub>s ranged from 0.2 to 0.5 seconds. The products for the as-is sand were 81% H-2TG, 11% TDG, and 8% CH. The products for the dried and re-wet sand were 80% H-2TG, 10% TDG and 10% CH (Figure 3 and Table 3). Comparison of the total integrated peak areas for all of the spectra showed that mass balance was maintained throughout the 8-week period of study.

The thiodiglycol formed in the UK sand was seen in six days at 61.4 and 34.5 ppm; after 7 weeks it had shifted to 60 and 33.6 ppm on the as-is sample and to 60.6 and 34.2 ppm after 8 weeks on the re-wet sample. In addition, the peaks became quite broad, and resonances at 31.8 (and 32.5) ppm were observed. The 6-day dried & re-wet UK sand had an additional resonance at 42.3 ppm; this peak was not seen in the 7 week sample. The explanation for the 6-day spectrum is that the products seen are a mixture of H-2TG and CH (61.4, 34.5, 42.3, 33), in which the 33 ppm CH resonance is hidden under the HD\* peak.

Table 3. <sup>13</sup>C NMR Chemical Shifts and Product Distributions for HD\* Degradation on Moist Sand at 22 °C

Calculated	European Foundry Sand	US Southern Products Filter Sand #2	UK ASF-50 Fine Sand As-is	UK ASF-50 Fine Sand Dried & re-wet
H-2TG	H-2TG, 87%	H-2TG, 90%	H-2TG, 81%	H-2TG, 80%
26.8	26.9	26.9	27.4	27.4
59	57.3	57.2	57.4	57.4
46.4	44.6	44.6	45.5	45.2
43.8	42.0	41.9	43.1	42.8
TDG	TDG, 13%	TDG, 10%	TDG, 11%	TDG, 10%
61.3	61.6	61.7	60	60.6
35.4	34.2	34.4	33.6	34.2
CH			CH, 8%	CH, 10%
60.7			60	60.6
35			Hidden	Hidden
43			39	42.3
33			32.5	31.8
Age of final Sample	8 weeks	8 weeks	8 weeks	7 weeks



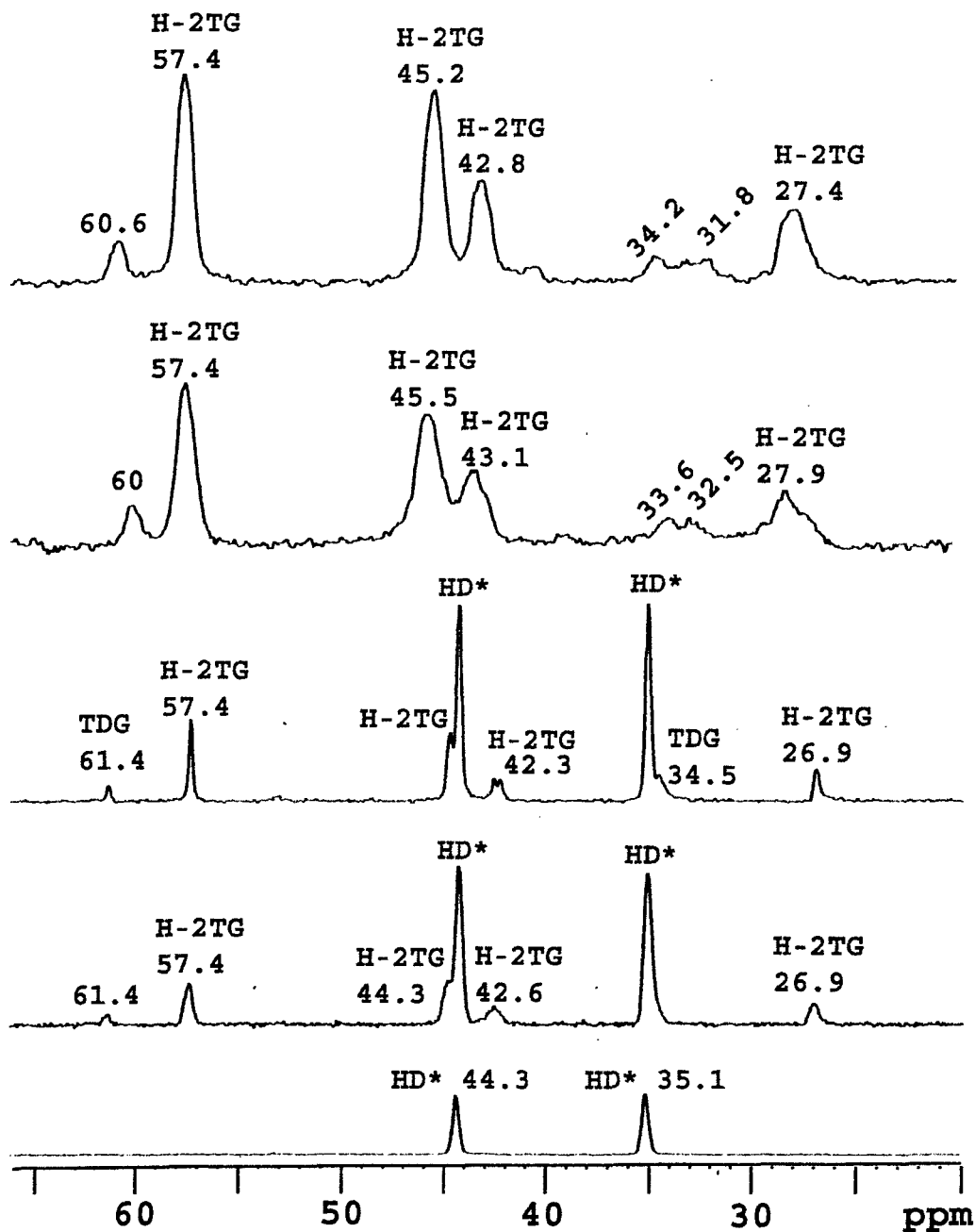


Figure 3.  $^{13}\text{C}$  SSMAS NMR Spectra of the Degradation of Mustard on UK AFS-50 Fine Sand, Showing HD\* (44.3 and 35.1 ppm), TDG (61.4 and 34.5 ppm), and H-2TG Sulfonium Ion (57.4, 45.5, 43.1 and 27.9 ppm). Identities of the spectra from bottom to top are: Initial; HD\* on as-is UK sand, 6 days; HD\* &  $\text{H}_2\text{O}$  on dried UK sand, 6 days; HD\* on as-is UK sand, 8 weeks; HD\* &  $\text{H}_2\text{O}$  on dried UK sand, 7 weeks

## 3.2

Limestone.

When placed on dry limestone, the mustard was unreactive over a period of 7 months. Small spinning side bands, about 4% of the total integrated peak area, were seen.

When HD\* and water were placed on limestone with a H<sub>2</sub>O:HD\* ratio of 18:1, a reaction was detected in six days. The degradation of the mustard was complete in seven weeks, but too little data had been collected in the interim to determine the order of the reaction or a rate constant. Spinning side bands were not visible; the mustard T<sub>1</sub>s were 2 seconds, and the sulfonium ion T<sub>1</sub>s were 0.2 seconds. The products were 72% H-2TG sulfonium ion, 15% chlorohydrin and 13% thiodiglycol (Figure 4 and Table 3). Comparison of the total integrated peak areas for all of the spectra showed that mass balance was maintained throughout the 7-week period of study.

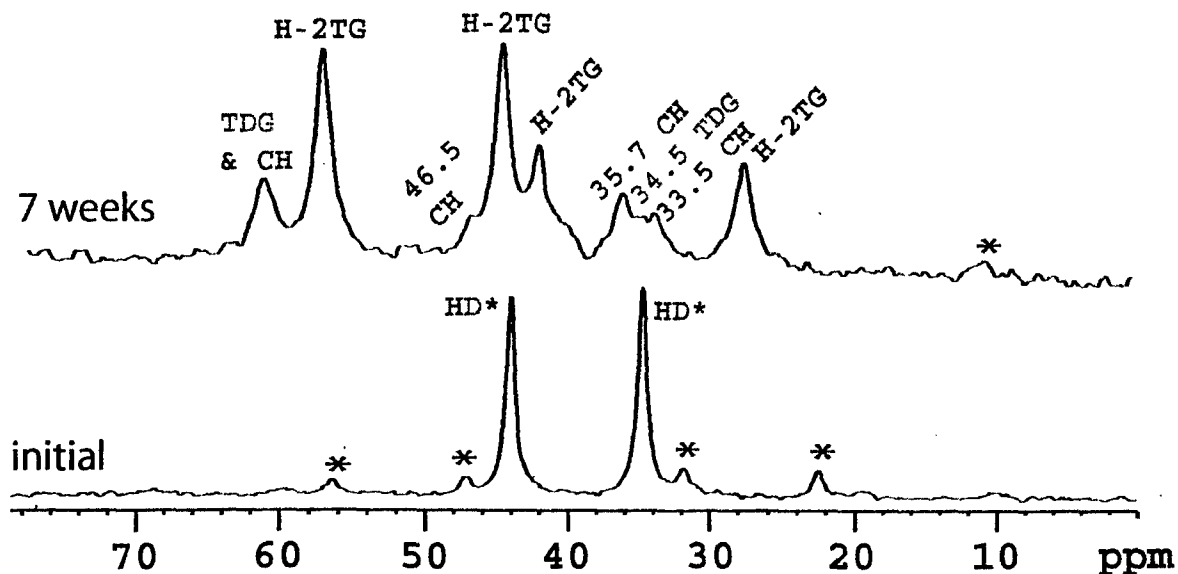


Figure 4. <sup>13</sup>C SSMAS NMR Spectra of the Degradation of Mustard on Caldera Limestone, Showing HD\* (44.3 and 35.1 ppm), TDG (61.2 and 34.5 ppm), CH (35.7, 46.5, 33.5 and ~61 (hidden) ppm), and H-2TG Sulfonium Ion (57.2, 44.4, 41.7 and 27.0 ppm). Age of spectra: initial (bottom) and 7 weeks (top). The \* denote spinning side bands

## 3.3

Asphalt.

## 3.3.1

European Asphalt.

When placed on dry European asphalt, the mustard was unreactive for a period of 5 months. However, on moist European asphalt, with a H<sub>2</sub>O:HD\* ratio of 14:1, no mustard was detected at the end of 10 weeks. The spinning side bands accounted for ~40% of the total integrated peak area, and persisted during the reaction. The products were identified on the basis of their chemical shifts and relative integrated peak areas. It was often

necessary to acquire the data at two different spin rates in order to distinguish between the spinning side bands, whose frequency shifted with the spin rate, and the product and reactant peaks, whose frequency did not shift. The mustard  $T_{1s}$  were 1 second, whereas the sulfonium ion  $T_{1s}$  ranged from 0.2 to 0.6 seconds. Thus, spectra were occasionally acquired with a recycle time of 1 second, in order to enhance the product resonances relative to the reactant resonances, and further aid in product identification. The products seen at 14 weeks were 82% H-2TG, 16% TDG, and 2% of a third product, whereas at 26 weeks the products were 55% H-2TG and 45% TDG (Figures 5 and 6; Table 4). Comparison of the total integrated peak areas for all of the spectra showed that mass balance was maintained throughout the 26-week period of study.

### 3.3.2 ACE Asphalt.

When placed on dry ACE asphalt, the mustard was unreactive for a period of 5 months. However, on moist ACE asphalt, with a  $H_2O:HD^*$  ratio of 13:1, no mustard was detected after the passage of 14 weeks. The spinning side bands accounted for only 10% of the total integrated peak area, and became negligible as the reaction proceeded. The products TDG and H-2TG were identified on the basis of their chemical shifts. CH, which had chemical shifts that were very similar to the sum of TDG and H, was identified as a tentative product. Traces of CEVS were also observed. The products observed at 24 weeks were 71% H-2TG, 29% TDG and a trace of CEVS (Figures 7 and 8, Table 4). The mustard  $T_{1s}$  were 2 seconds, whereas the sulfonium ion  $T_{1s}$  ranged from 0.2 to 0.5 seconds. Comparison of the total integrated peak areas for all of the spectra showed that mass balance was maintained throughout the 24-week period of study.

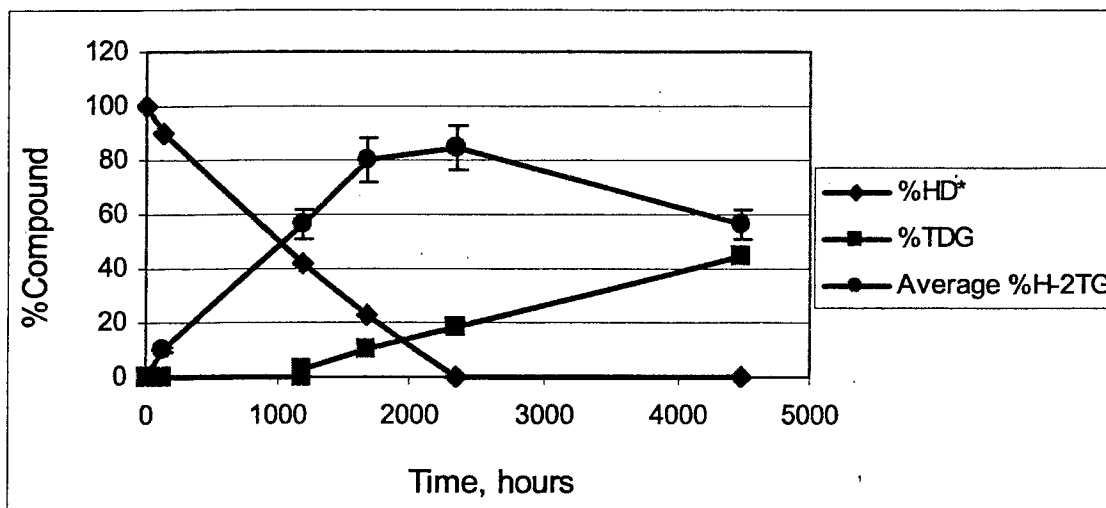


Figure 5. Plot of  $HD^*$  Loss, TDG Gain, and Sulfonium Ion Gain and Loss for Mustard and Water on European Asphalt

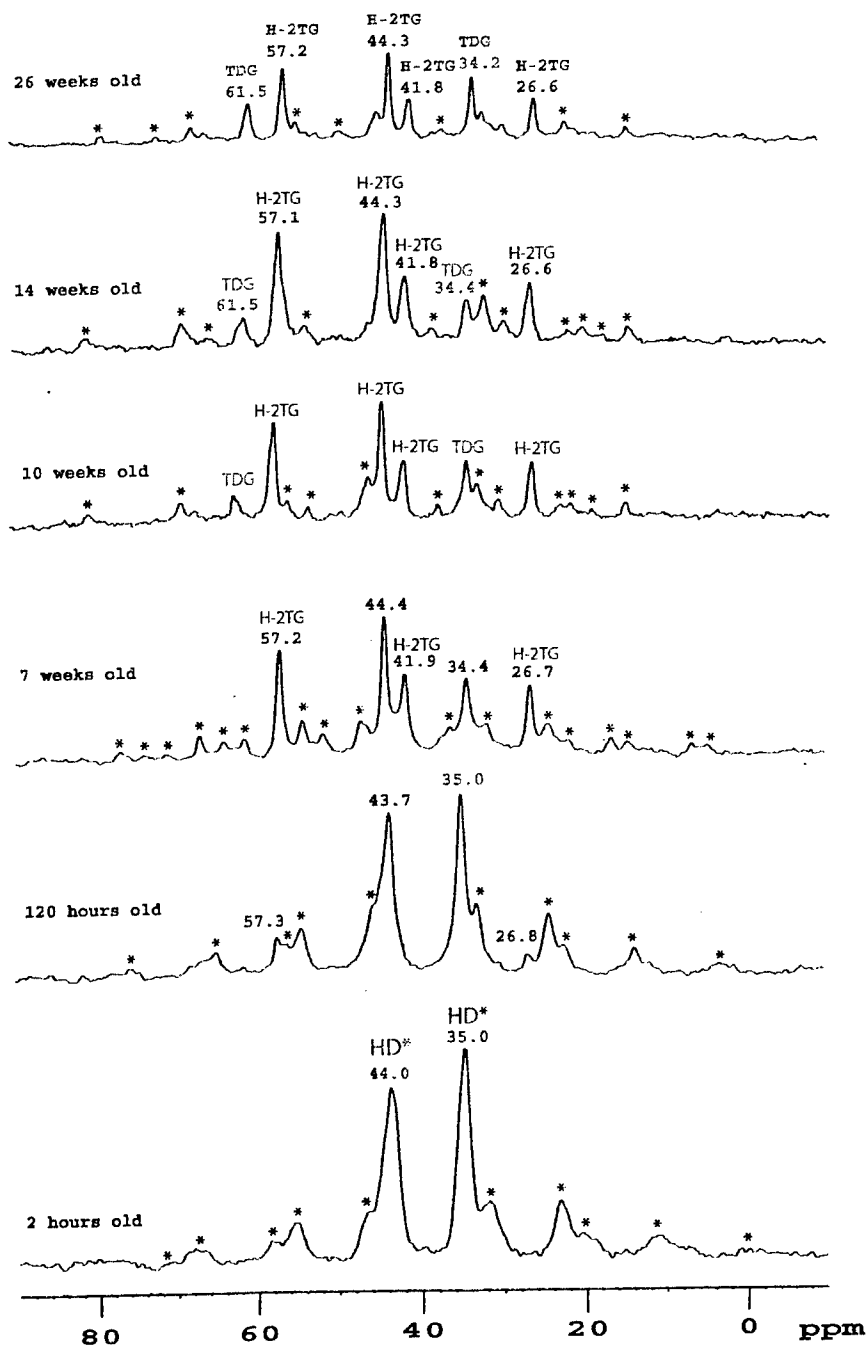


Figure 6.  $^{13}\text{C}$  SSMAS NMR Spectra of the Degradation of Mustard on European Asphalt, Showing Mustard, HD\* (44.0 and 35.0 ppm), TDG (61.5 and 34.4 ppm), and H-2TG Sulfonium Ion, Labeled S (57.1, 44.3, 41.8 and 26.6 ppm). The \* denote spinning side bands.

Table 4.  $^{13}\text{C}$  NMR Chemical Shifts and Product Distributions of the Ultimate Samples for HD\* Degradation on Moist Asphalt and Limestone at 22 °C

Calculated	European Asphalt	ACE Asphalt	Caldera Limestone
H-2TG	H-2TG, 55%	H-2TG, 71%	H-2TG, 72%
26.8	26.6	26.6	27.0
59	57.2	57.2	57.2
46.4	44.3	44.3	44.2
43.8	41.8	41.7	41.7
TDG	TDG, 45%	TDG, 29%	TDG, 13%
61.3	61.5	61.5	61.2
35.4	34.4	34.3	34.3
CH		CH	CH, 15%
60.7		61.5	61.2
35		Hidden	35.7
43		46.5	46.5
33		32.0	33.5
1,4-dithiane	Other, 2%		
29	32.3		
Time at which no HD* was detected	10 weeks	14 weeks	7 weeks
Age of Ultimate Sample	26 weeks	24 weeks	7 weeks

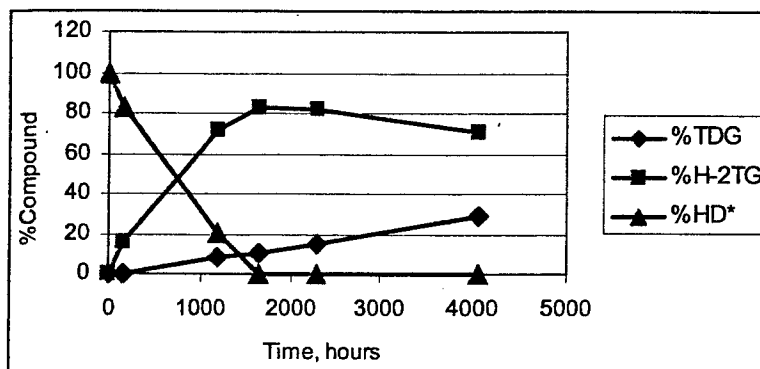


Figure 7. Loss of Mustard (▲, HD\*), Gain of H-2TG (■), and TDG (◆) with Time for HD\* and Water on ACE Asphalt

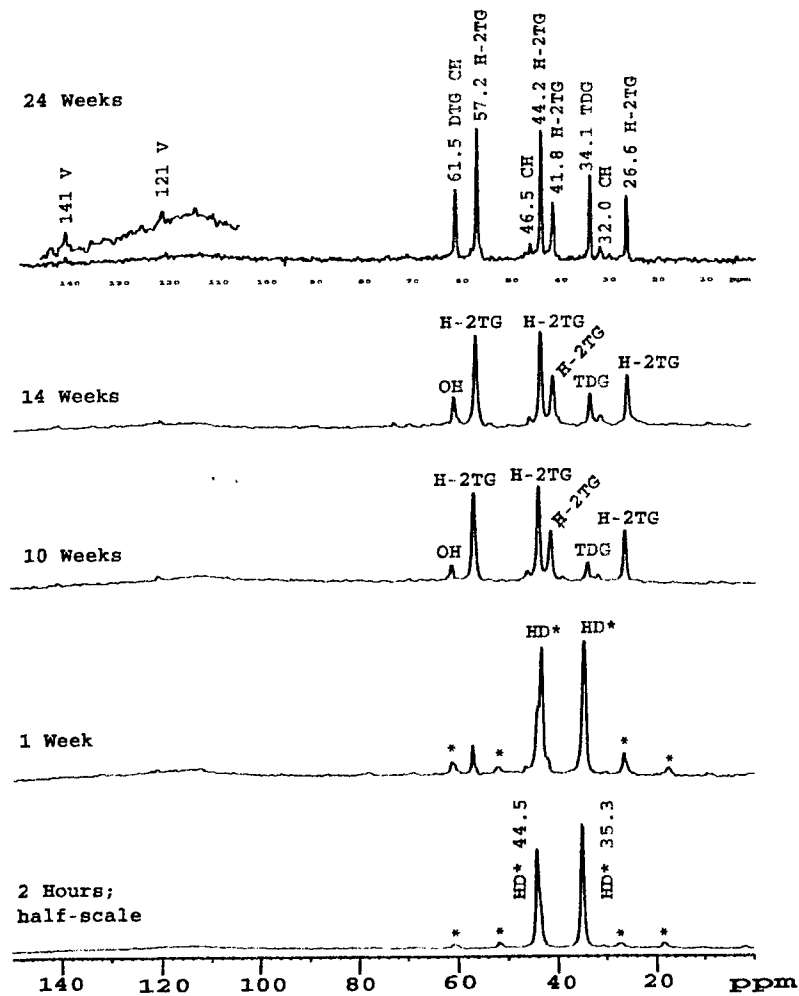


Figure 8.  $^{13}\text{C}$  SSMAS NMR Spectra of the Degradation of Mustard on ACE Asphalt, Showing Mustard, Labeled H (44.5 and 35.3 ppm), TDG (61.5 and 34.3 ppm), H-2TG Sulfonium Ion (57.4, 44.3, 41.7 and 26.6 ppm), CH (61.5, 46.5 and 32.0 ppm), and traces of vinyl species, labeled V (120 and 141 ppm). The peak at 61.5 ppm is for the C next to the OH for both CH and TDG. The \* denote spinning side bands.

#### 4. DISCUSSION

##### 4.1 Spinning Side Bands.

It was noticed that samples that had more iron, a paramagnetic species, had more spinning side bands. The concrete samples exhibited more spinning side bands for a given %iron than the sand, limestone or asphalt samples did. The correspondence between spinning side bands and paramagnetic species has been documented in the literature,<sup>7</sup> and the relationship found in this work is shown in Figure 9.

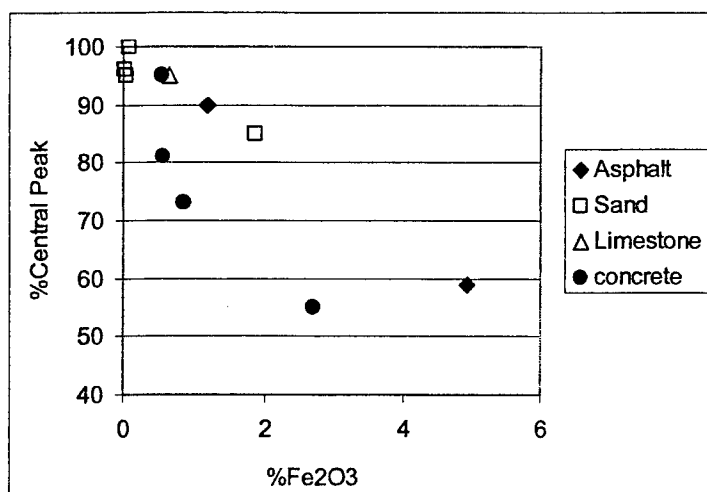


Figure 9. Plot of % Central Peak vs. % Fe<sub>2</sub>O<sub>3</sub> in the Sample

#### 4.2 T<sub>1</sub> Relaxation Times.

The T<sub>1</sub> of the mustard on the substrates was 1 to 3 seconds, compared to 0.1 to 0.6 seconds for the sulfonium ion. The longer T<sub>1</sub> may have indicated that the mustard had more liquid-like properties, whereas the shorter T<sub>1</sub> suggested that the sulfonium ion had more solid-like properties. This trend was observed on all three types of substrates, and may suggest an interaction of the H-2TG hydroxyl moieties with the substrate. It is also possible that the presence of the S<sup>+</sup> cation shortened the T<sub>1</sub>, in a manner similar to paramagnetic metal ions shortening T<sub>1</sub>.

#### 4.3 Products.

##### 4.3.1 Sand and Limestone.

The major products seen on the sand, TDG and H-2TG, were formed in comparable ratios; ~85% H-2TG for all of the substrates. The European Foundry sand, the Southern Products #2 sand, and the European asphalt samples had formed only these two products by the end of the monitoring period (Table 4). Reaction schemes for the formation of the products are shown in Figure 10.<sup>8</sup>

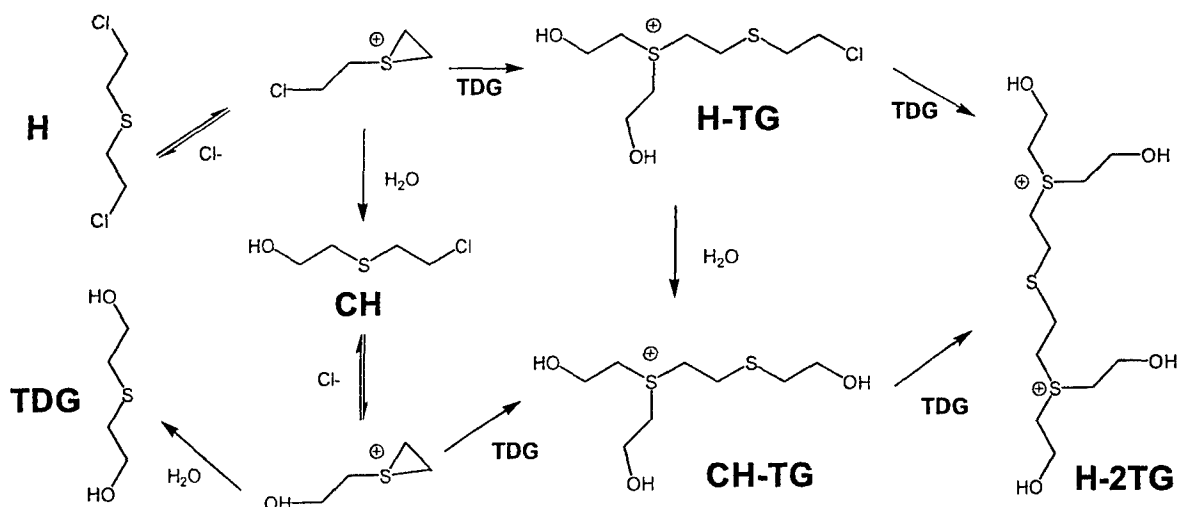


Figure 10. Formation of CH, TDG, and H-2TG from Mustard<sup>8</sup>

Resonances observed in the 32 to 36 ppm range in the UK fine sand and limestone indicated the presence of another minor product. Possibilities were CH, whose calculated chemical shifts were 60.7, 35, 43 and 33 ppm, and 1,4-dithiane, whose calculated chemical shift was 29 ppm. The 60.7 ppm CH resonance was coincident with the TDG resonance at the same chemical shift, but the integrated peak area for the 60.7 ppm TDG peak was higher than that of the ~34 ppm TDG, which was consistent with the presence of a CH species. The 43 ppm peak was also detected, although on the as-is UK fine sand it had shifted greatly to ~39 ppm.

Thus, the third species, which had a peak at ~33 ppm in the moist UK fine sand and limestone samples was assigned to CH, rather than to 1,4-dithiane.

The sand samples were extracted with chloroform or acetonitrile at the end of 8 weeks in order to extract and better identify the products using GC/MSD and 2-D NMR. The extracts were too dilute to give good 2-D NMR spectra. Only trace (<0.1%) amounts of HD\* and TDG were found using the GC/MSD; no sulfonium ion was seen.

#### 4.3.2 European Asphalt.

These data were difficult to analyze quantitatively due to the multiple spinning side bands. The sample was run at two speeds whenever multiple products were present, and the relative peak areas were calculated using both deconvolution and integration. The spin speeds for this sample were relatively low, about 750 to 1400 Hz, and thus the spinning side bands often overlapped the peaks. The peaks were generally broad, 80 to 150 Hz, partially as a result of the low spin speeds. Hence, calculating how much mustard remained was difficult, since the H-2TG peak at 44.3 ppm was close to the mustard resonance at 44.0 ppm, and the TDG peak at ~35 ppm was close to the other mustard peak. Thus, to calculate the amount of thiodiglycol, the relative peak area of the 61.5 ppm peak was doubled. This is



because the 61.5 ppm peak accounted for half of the carbon atoms in the thiodiglycol (Figure 11). Similarly, to calculate the amount of H-2TG, the peak at 26.7 ppm was multiplied by 6, and the peaks at 57.1 and 41.9 ppm were multiplied by 3 (Figure 12). The %H-2TG data thus calculated were averaged and used in Figure 13; the error bars represent one standard deviation of the averages.

It was difficult to determine the order for the loss of HD\*; the data were so sparse that they could be fit to either a zero- or first- order plot with  $r^2=0.98$  in both cases. The loss of H-2TG and the gain of TDG were both extrapolated to an end-point of ~8750 hours using a zero-order kinetic plot. These extrapolations must be interpreted with caution due to the limited data from which they have been generated.

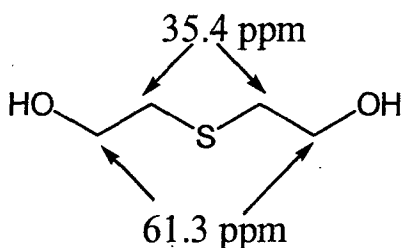


Figure 11. Structure and  $^{13}\text{C}$  NMR Chemical Shifts of Thiodiglycol

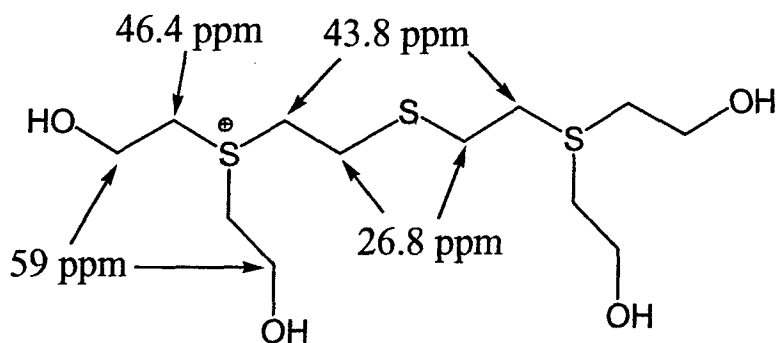


Figure 12. Structure and  $^{13}\text{C}$  NMR Chemical Shifts of H-2TG. Relative ratios of the peaks are  $59:46.4:43.8:26.8 = 2:2:1:1$ .

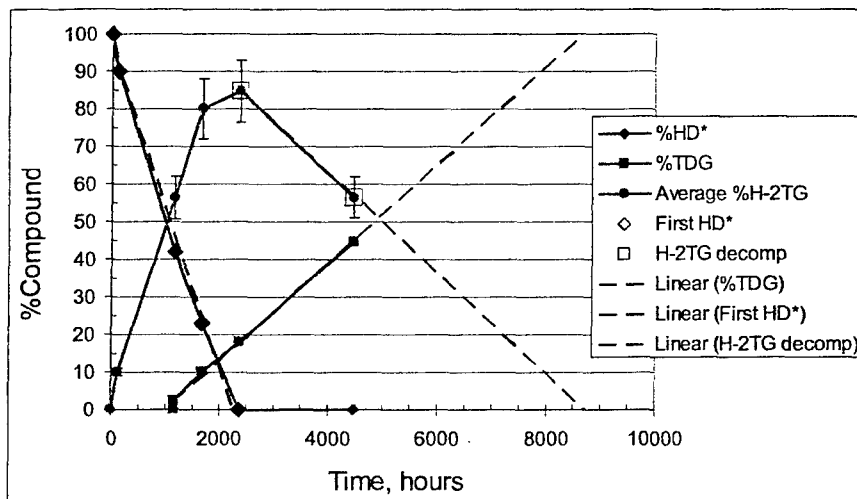


Figure 13. Loss of Mustard (◆, HD\*) and Gain of H-2TG (●) and TDG (■) with Time for HD\* and Water on European Asphalt. Zero-order kinetic plots are also shown.

Zero-order kinetics for the loss of mustard were evident by the plot of mg HD\* vs. time (Figure 13); the plot was a straight line of slope  $k$ , and each half-life was half as long as the previous.

Zero-order kinetics may occur when an enzyme or surface catalyst is present, and manifest when the reactant saturates the catalyst surface [13]. In this case, the presence of zero-order kinetics suggested that the sand surface played a role in facilitating the degradation of the mustard. One possibility is an interaction of the mustard with the sand, and then formation of the  $\text{ClC}_4\text{H}_8\text{S}^+\text{Cl}^-$  sulfonium ion, which would then react with the water to form CH, a process that has a half-life of minutes in aqueous solution [3, 14]. The subsequent steps would be consistent with the previously published reaction scheme (Figure 9) [8]. The interaction of the mustard simulant 2-chloroethyl phenyl sulfide with silica and titania surfaces has been demonstrated, and thus forms a precedent for mustard interacting with the surface\*.

Another possible source of the zero-order kinetics is the dissolution of the mustard at the water-surface interface; that is, the mustard coated the asphalt, and gradually dissolved into the water, and then reacted. Since the dissolution of mustard is slow relative to its reaction rate in water [8], the dissolution of mustard would be the rate-determining step of the reaction. This scenario is consistent with the observed  $T_1$  relaxation time values of 2 seconds that persisted until all of the mustard was used, and is also consistent with the observation of zero-order kinetics [13].

The degradation of H-2TG was also zero-order reaction; the reaction sequences in Figure 14 were postulated. The species CH-TG and H-TG were postulated as

\*Willey, R.J.; Brevett, C.A.S.; MacIver, B.; Wagner, G.W. Reactivity of CEPS (2-chloroethyl phenyl sulfide) on Silica and Titania Surfaces as Detected by  $^{13}\text{C}$  SSMAS NMR, 2006, unpublished data December 2006.

potential intermediates during the formation of H-2TG, and CH-TG was postulated as an intermediate in the decomposition of H-2TG. Neither intermediate was detected in the NMR, thus suggesting that they reacted quickly.

#### 4.3.3 ACE Asphalt.

It was difficult to determine the order for the loss of HD\*; the data was so sparse that it could be fit to either a zero- or first- order plot with  $r^2=0.99$  in both cases. The sample was monitored after the disappearance of the HD\*; TDG continued to form; the gain of TDG was consistent with zero-order kinetics and not with first-order kinetics; the data showed that 25% of the integrated peak area was due to TDG after 3500 hours, and projections indicated that all the material would be TDG after 14000 hours (83 weeks) have elapsed (Figure 14).

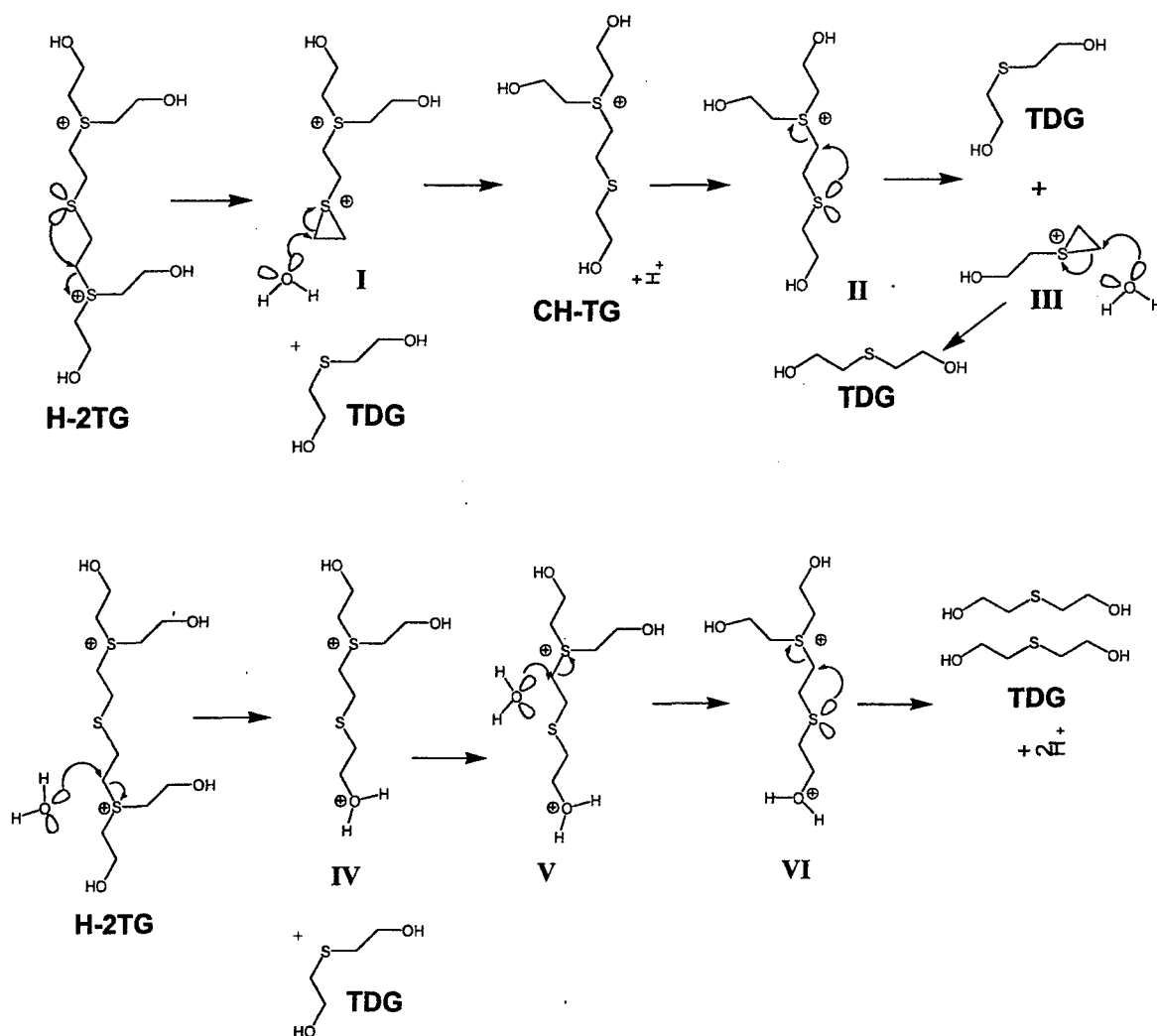


Figure 14. Postulated schemes for the degradation of H-2TG. Top: intermolecular. Bottom: intramolecular.

The 24-week spectrum had 71% H-2TG, 29% TDG, and trace amounts of CEVS, which was most clearly seen at 7 weeks. The CEVS product has previously been observed to form when mustard degraded on a basic metal oxide.<sup>11,12</sup> Continued monitoring showed that the concentration of H-2TG reached a maximum of 83% after an elapsed time of 1700 hours, and then decreased, as the TDG increased. This indicated that the TDG formed from the H-2TG.

Two rates for the H-2TG decomposition were projected assuming zero-order kinetics, using the final three and final two data points collected. These indicated that all of the H-2TG would be gone after an elapsed time of 15000 to 17000 hours, which is consistent with the projection for TDG formation (Figure 15).

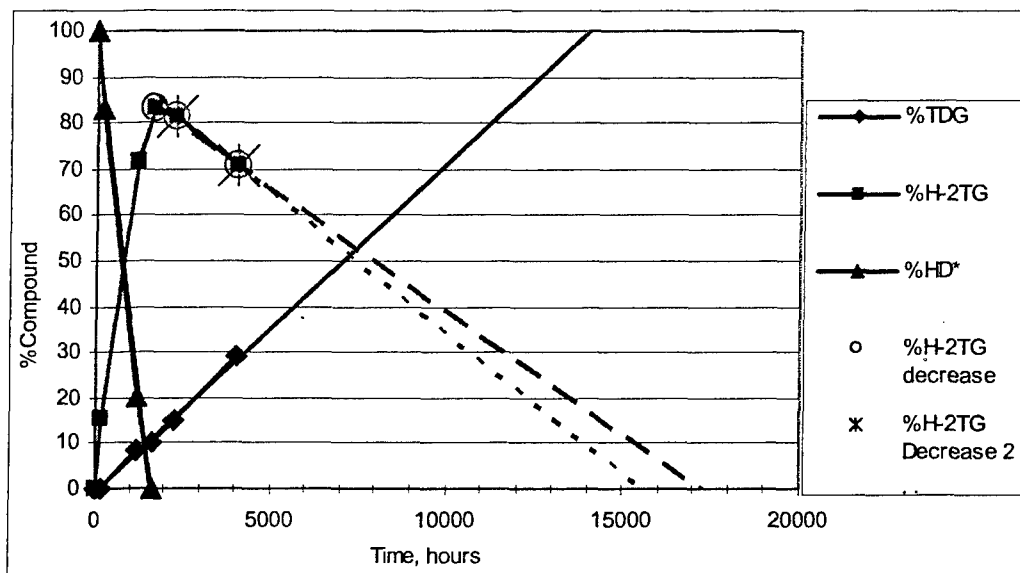


Figure 15. Loss of mustard ( $\blacktriangle$ , HD\*); loss of H-2TG ( $\blacksquare$ ) and gain of TDG ( $\blacklozenge$ ) with time for HD\* and water on ACE asphalt.

## 5. CONCLUSIONS

The lack of reaction on the ambient substrates, plus the formation of the same products that were seen in water and moist soil suggested that the sand, asphalt and limestone functioned as chemically inert surfaces on which the reaction between mustard and water occurred. The degradation of mustard on moist asphalt followed half-order kinetics; too little data was collected on the sand or limestone to determine the order of the reaction. The data indicated that the mustard on a moist substrate initially formed H-2TG, which then decomposed to form TDG.

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