

ENVIRONMENTAL AND SAFETY ASPECTS OF THE USE OF SULFUR  
IN HIGHWAYS PAVEMENTS

PART II - WEATHERING AND IN-SERVICE CONSIDERATIONS

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INTRODUCTION

This paper is the second of a two part series dealing with the environmental and safety aspects of sulfur modified paving materials. PART I deals with the emissions and associated safety considerations involved in mix preparation and during construction. This paper deals primarily with those aspects related to post construction exposure to the elements and problems which could occur while the pavement is in use.

Selective sulfur asphalt and sulfur concrete paving mixtures were subjected to a variety of simulated in-service weathering traffic conditions including hot temperatures, actinic light (U.V. radiation), rainfall, freeze-thaw, biological activity, chemical spills and fires. Pollutants in the form of dusts, fumes and run-off products were collected and analyzed for their safety and environmental impact. The nature of the pollutants ( $H_2S$ ,  $SO_2$ , and particulate sulfur) and their relative toxicities are discussed in PART I and will not be repeated here.

The results of this study were generated when an FHWA sponsored program with the Texas Transportation Institute [1]. Assessments of personnel safety and allowable exposure limits were derived from the literature [2-8]. One of the best references on the impact of sulfur with the environment is the two-volume work edited by Nriagu [9]. Except for standard EPA test techniques [10] virtually all of the test apparatus and experimental methodology were developed specifically for this project.

Mix Designs

The nine mix designs shown in Table 1 were used in the study and included 5-sulfur/asphalt systems, two sulfur concretes and two (2) A/C designs (MD-4 and MD-6) which were used as controls. Of the five (5) - sulfur/asphalt designs, two (2) were sulfur-extended-asphalt (SEA) systems, two (2) were aggregate-asphalt-sulfur (AAS) systems and one (1) was a sulfur-recycled system. Of the two sulfur concretes one utilized Dicyclopentadiene (DCPD) as a plasticizing additive. The mix designs were selected as representative of the types of sulfur modified paving materials currently in use.

Table 1. Mix Designs Used in Weathering and In-Service Studies

Number	System	Weight Sulfur	Percent, w/o* Asphalt	Binder Content, w/o	Aggregate Material	Gradation
MD-1	AAS	1.8	5.1	6.9 (Asphalt)	Crushed Limestone	Dense
MD-2	SEA	25	75	6.9	Crushed Limestone	Dense
MD-3	AAS	70	30	19.5 (Asphalt)	Beach Sand	Uniform
MD-4	Recycled	1.25	0	1.25	Nellis AFB Runway	Dense
MD-5	Recycled	1.25	1.0	2.25	Nellis AFB Runway	Dense
MD-6	A/C	0	100	4.5	Crushed Limestone	Dense
MD-7	SEA	20	80	4.0	Crushed Limestone	Open
MD-8	Sulfur Concrete	24	0	24	Gravel/Sand	Dense
MD-9	Sulfur Concrete w/DCPD**	21	0	21	Gravel/Sand	Dense

\*In SEA systems sulfur and asphalt proportions are given as weight percent of binder. All others are given as percent of total mix.

\*\*Dicyclopentadiene (DCPD) was added at 5 percent by weight of sulfur.

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### WEATHERING

#### Exposure of Large Scale Pavement Slabs

The combined affects of temperature, actinic light, and rainfall conditions on emissions and run off products were achieved by exposing slabs of six (6) selected mix designs to natural daily and seasonal weathering. Slabs, 2 ft. (61 cm) x 3 ft. (91.5 cm) x 2 in. (5 cm) thick, were cast into wooden frames lined with aluminum foil, and placed on the roof of a six-story building (see Figure 1) mix designs used were MD-1, 2, 3, 6, 8, and 9.

A clear plastic box 1 ft. (30.5 cm) x 2 ft. (61 cm) x 0.5 ft. (15.3 cm) deep with a 2 in. (5 cm) diameter vent was constructed to fit over the slabs, and provide a constant volume, controlled environment for emissions monitoring. Two 3/8 in (1 cm) diameter ports were drilled into the side of the box opposite from the vent. The inlet vent was fitted with a 2 in. (5 cm) diameter x 39 in. (1 m) polyethylene stand pipe, to assure that air drawn through the vent was not contaminated by emissions from adjacent slabs.

Surface temperatures were measured using a copper-constantin thermocouple, placed in intimate contact with the slab. The plastic box, fitted with a white card-board, was placed over the slab after which the surface temperature allowed to equilibrate. Outlets were combined then split 3 ways such that one air stream was drawn through an  $H_2S$  meter, one through a  $SO_2$  meter, (Inter-scan Model No.'s 1176 and 1248, respectively) and the other through a series of refrigerated solvent traps. Solvent traps were combined, reduced in volume by vacuum distillation and analyzed by gas chromatography (CG) for organics. Air was drawn with a vacuum pump over the specimen surface, through each meter, and solvent traps at a constant flow rate of 1 liter/min.

Volatilized constituents were measured with respect to each mix design, surface temperature and exposure time. Measurements were made between 2 and 4 pm so as to effect a maximized surface temperature relative to daily and seasonal variability.

Once the box was placed on a slab specimen, it generally required approximately 15 minutes to reach a maximum surface temperature ( $T_{max}$ ) as monitored by continuously recording thermocouple response. At  $T_{max}$  the vacuum pump was turned on to initiate sampling.

A typical pattern for  $H_2S$  evolution continuously monitored with respect to time is shown in Figure 2. The concentration rose quickly to a maximum and then diminished to much lower levels, often that of the background air drawn into the volatilization chamber. The decline in concentration was attributed to a decrease in surface temperature as the cooler air passed over the slab specimen.

$H_2S$  and  $SO_2$  vapor flux with respect to time for an asphalt pavement with no added sulfur is given in Table 2. The data demonstrate a relatively small net flux from virgin asphalt. Corresponding flux values for mix designs with approximately 2% added sulfur are given in Tables 3, 4, and 5 for the MD-1, MD-7, and MD-2 mixes, respectively. All demonstrated initially higher  $H_2S$  vapor flux values over that of the asphalt alone.

The higher sulfur containing AAS-Sand mix (MD-3) produced considerably higher  $H_2S$  and  $SO_2$  vapor flux values (Table 6). However, values were rapidly diminished to those approximating the initial flux of the asphalt along within 12 weeks.

Flux values for sulfur concrete, and sulfur concrete modified with dicyclopentadiene (Tables 7 and 8) were approximately equal in magnitude to those of the lower sulfur-asphalt pavement materials, although they contained more than 10 times the total sulfur of the latter.

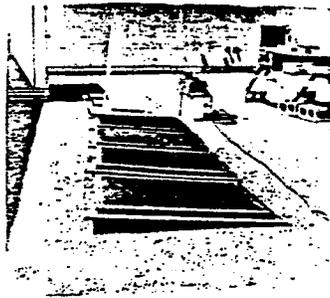


Figure 14. (End View)

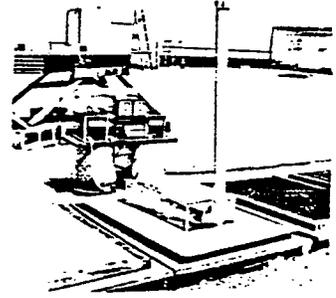


Figure 15. (Side View)

Test Set-up Showing Weathering Studies.

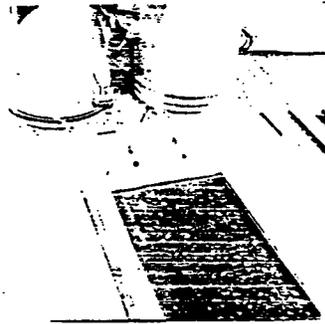


Figure 16. Test Set-up. Showing Suction Lines from Slab Surface to Meters.

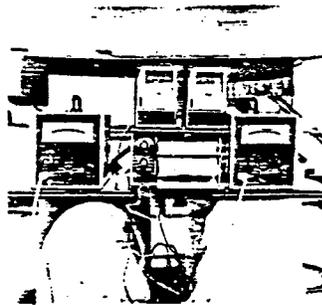


Figure 17. Close up of Emissions and Temperature Monitoring Equipment Used in the Weathering Studies. Showing Suction Lines from Slab Surface to Meters.

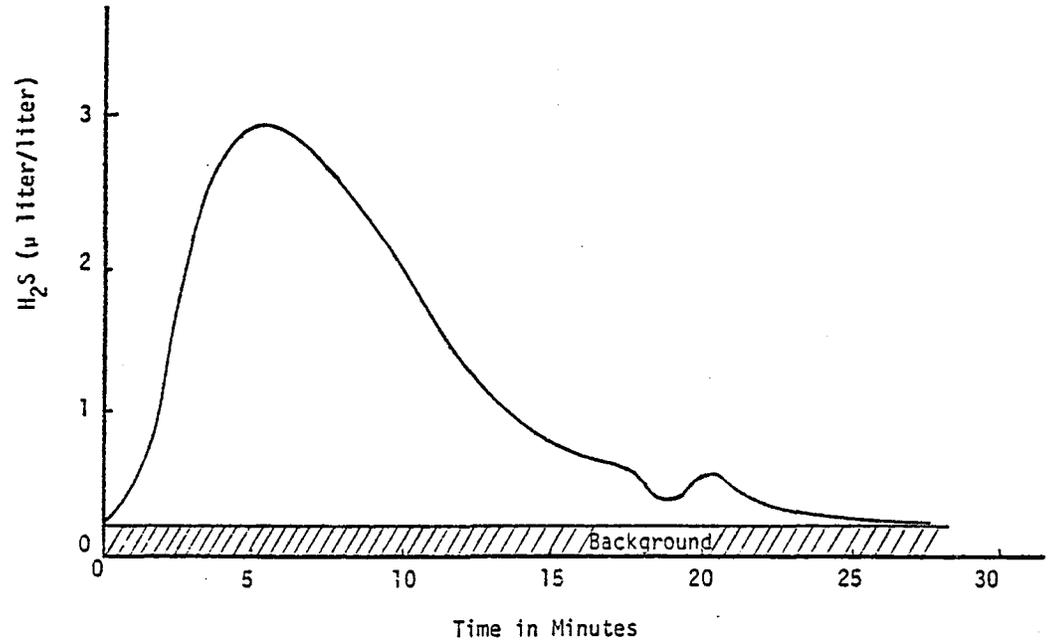


Figure 2. Typical Pattern of H<sub>2</sub>S Evolution as Continuously Recorded with Respect to Time.

Table 2. Variation of H<sub>2</sub>S and SO<sub>2</sub> Vapor Flux with Temperature and Time for MD-6 (See Table 1).

Time	Surface Temperature		Vapor Flux	
	H <sub>2</sub> S	SO <sub>2</sub>		
<u>weeks</u>	<u>°F</u>	<u>(°C)</u>	<u>µg/m<sup>2</sup>/hour</u>	
0	167	(75)	38.7	153
1	176	(80)	37.8	142
2	176	(80)	<37.8	< 74
4	172	(78)	ND	ND
12	169	(76)	ND	ND
24	86	(30)	ND	ND

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Table 3. Variation of H<sub>2</sub>S and SO<sub>2</sub> Vapor Flux with Temperature and Time for MD-1 (See Table 11, page 42).

Time	Surface Temperature		Vapor Flux	
	H <sub>2</sub> S	SO <sub>2</sub>		
<u>weeks</u>	<u>°F</u>	<u>(°C)</u>	<u>µg/m<sup>2</sup>/hour</u>	
0	181	(83)	262	352
1	181	(83)	119	140
2	185	(85)	75	69
4	178	(81)	< 37.7	< 71
12	172	(78)	ND	ND
24	86	(30)	ND	ND

Table 4. Variation of H<sub>2</sub>S and SO<sub>2</sub> Vapor Flux with Temperature and Time for MD-7 (See Table 11).

Time <sup>1/</sup>	Surface Temperature		Vapor Flux	
	H <sub>2</sub> S	SO <sub>2</sub>		
<u>weeks</u>	<u>°F</u>	<u>(°C)</u>	<u>µg/m<sup>2</sup>/hour</u>	
0	181	(83)	165	135
1	189	(87)	147	138
2 (pm)	187	(86)	75	70
(am)	154	(68)	< 39	< 70
4	185	(85)	37.1	69
12 (pm)	181	(83)	< 37.0	< 71
(am)	113	(45)	ND	ND
24	122	(50)	ND	ND

<sup>1/</sup> pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

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Table 5. Variation of H<sub>2</sub>S and SO<sub>2</sub> Vapor Flux with Temperature and Time for MD-2

Time <sup>1/</sup>	Surface Temperature		Vapor Flux	
	°F	(°C)	H <sub>2</sub> S	SO <sub>2</sub>
<u>weeks</u>	<u>°F (°C)</u>		<u>µg/m<sup>2</sup>/hour</u>	
0	172	(78)	183	141
1	181	(83)	119	126
2	172	(78)	114	143
4 (pm)	172	(78)	< 38.2	< 73
(am)	144	(62)	ND	ND
12 (pm)	163	(73)	ND	ND
(am)	115	(46)	ND	ND
24	86	(30)	ND	ND

<sup>1/</sup> pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

Table 6. Variation of H<sub>2</sub>S and SO<sub>2</sub> Vapor Flux with Temperature and Time for MD-3

Time <sup>1/</sup>	Surface Temperature		Vapor Flux	
	°F	(°C)	H <sub>2</sub> S	SO <sub>2</sub>
<u>weeks</u>	<u>°F (°C)</u>		<u>µg/m<sup>2</sup>/hour</u>	
0	181	(83)	955	872
1 (pm)	185	(85)	778	707
(am)	154	(68)	---	75
2 (pm)	189	(87)	637	699
(am)	169	(76)	462	435
4 (pm)	181	(83)	281	284
12 (pm)	181	(83)	150	141
(am)	158	(70)	< 39	< 74
24 (pm)	113	(45)	ND	ND

<sup>1/</sup> pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

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Table 7. Variation of H<sub>2</sub>S and SO<sub>2</sub> Vapor Flux with Temperature and Time for Sulfur Concrete - MD-8

Time <sup>1/</sup> weeks	Surface Temperature		Vapor Flux	
	°F	(°C)	H <sub>2</sub> S	SO <sub>2</sub>
			μg/m <sup>2</sup> /hour	
0	154	(68)	159	201
1	163	(73)	156	231
2	163	(73)	78	136
4	158	(70)	39	77
12 (pm)	163	(73)	39	73
(am)	140	(60)	ND	ND
24	79	(26)	ND	ND

<sup>1/</sup> pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

Table 8. Variation of H<sub>2</sub>S and SO<sub>2</sub> Vapor Flux with Temperature and Time for Sulfur Concrete Modified with Dicyclopentadiene - MD-9

Time weeks	Surface Temperature		Vapor Flux	
	°F	(°C)	H <sub>2</sub> S	SO <sub>2</sub>
			μg/m <sup>2</sup> /hour	
0	142	(61)	164	232
1	154	(68)	199	300
2	153	(67)	120	150
4	144	(62)	82	115
12	140	(60)	41	77
24	79	(26)	ND	ND

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Although vapor flux values were still measurable up to 12 weeks following placement of the slab specimen on the roof, the impact of volatilization from these sulfur-asphalt test units was small relative to the magnitude of the flux term. To put the magnitude of the flux values in perspective, consider that the 995 g/m<sup>2</sup>/hour reported for the initial H<sub>2</sub>S concentration from the high sulfur-asphalt blend corresponds to a volume concentration in air of 2.6 ppm (Table 5). This is 50 percent of the MAC. It should also be noted that the samples were subjected to abnormally high temperatures, releasing fumes into a closed environment, during the temperature equilibration period and prior to air withdrawal.

At no time during the course of the volatilization study did vapors or fumes emanating from the pavement slabs exceed that of the background air quality with respect to organic or organic sulfur compounds.

### SIMULATED IN-SERVICE CONDITIONS

#### Temperature, Actinic Light and Run-off Effects

Compacted specimens of the nine mix designs were prepared for exposure to temperature, and actinic light. Asphalt and sulfur-asphalt were formed into 4 inch (10 cm) dia. x 3/2 inch (9 cm) thick disc. The two sulfur concrete materials were shaped into rectangular bricks. Each formulation was made in quadruplicate. Two samples from each mix design were selected at random and wrapped in aluminum foil to eliminate the impact of ultraviolet light.

Following a 6 month exposure the outer edges were chipped away then ground in a ore crusher for subsequent total sulfur analysis. Total sulfur values obtained were utilized as test statistics to determine the potential weathering affect of a combination of high temperature and UV-light with potential loss as run off from rain. In addition, the ground materials were subjected to both acid (pH2 water) and base (pH10 water) hydrolysis at 187°F (86°C) reaction temperature to determine weathering resulted in subtle differences in emissions or hydrolysis products compared to laboratory control specimens.

Total sulfur relative to a particular mix design and exposure level to UV radiation from full sunlight is summarized in Table 9. An Analysis of Variance (ANOVA) was used to aid interpreting the results. Initially, the variability between reps for sulfur concrete materials (MD-8 and MD-9) dominated as the greatest source of variation apart from mix design. A second ANOVA excluding sulfur concrete data was determined, and results from this test presented in Table 10. Results of this test show reps were not significant, making definitive statements about the experiment relative to sulfur-asphalt possible.

UV radiation from full sunlight had no affect on the total sulfur measured. The greatest source of variation, as would be expected, was that of mix design, due principally to the high sulfur content of AAS-Sand (MD-3) and low sulfur level of the control asphalt (MD-6). Surprisingly, the ANOVA revealed a UV-light by mix design interaction which was statistically significant at a 5% level. There was no distinct pattern in the data, and the only explanation for the interaction suggests that the samples randomly selected for exposure to sunlight had a slightly higher total sulfur content when processed. Conservation of the sulfur suggests no loss from a rainfall run-off mechanism.

Ground materials subjected to both acid and base hydrolysis reacted the same as the laboratory control samples, suggesting that actinic light in combination with high surface temperature gives no added inducement towards hydrolysis, or the effects are too subtle for the technique employed. The assessment was made relative to H<sub>2</sub>S emission levels. No organics were detected in emissions trapped in refrigerated solvents, or dichloromethane extracts of filtered hydrolysates.

Table 9. Total Sulfur of The Various Mix Designs Following Exposure to Full Sunlight at Normal High Surface Temperatures.

Exposure	Rep No.	Mix Design Number								
		1	2	3	4	5	6	7	8	9
		% Sulfur								
No UV-Light	1	3.1	2.0	15.1	2.4	2.8	0.4	1.6	21.0	36.3
	2	3.0	2.2	15.4	2.0	2.8	0.5	2.0	27.3	27.6
	Avg.	3.1	2.1	15.3	2.2	2.8	0.5	1.8	24.2	32.0
UV-Light	1	2.3	2.8	17.1	2.4	2.5	0.4	2.5	22.0	32.7
	2	2.6	2.3	15.8	2.9	2.4	0.4	1.5	28.4	28.8
	Avg	2.5	2.6	16.5	2.7	2.5	0.4	2.0	25.2	31.3

Table 10. Results of Analysis of Variance (ANOVA) For Mix Designs MD-1 Through MD-7.

Source	Df	Sum of Squares	Mean Square	Fexp	F.01	F.05
Reps	1	0.481	0.481	4.45	9.07	4.67
Light (L)	1	0.241	0.241	2.23	9.07	4.67
Mix Design (No)	6	665.359	110.893	1026.78	4.62	2.92
LxMD	6	2.129	0.355	3.28	4.62	2.92
Error	14	1.398	0.108			
Total	27	670.144				

Freeze-Thaw

Compacted specimens for the nine mix designs were subjected to the weathering impact of freeze-thaw cycling (ASTM C-666). Following the final thaw, the water used as the surrounding matrix was filtered and extracted by separatory funnel partitioning into 15% diethyl ether in dichloromethane. Extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, reduced in volume to approximately 0.2 ml then taken up to 2 ml with benzene. Aliquots were analyzed by GC using both FID and FPD detector systems.

The outer edges of the sample beam was chipped away from the bulk sample, ground to pass a 1 mm sieve, and subsequently subsampled for total sulfur analysis. Subsamples were also subjected to acid and base hydrolysis in pH2 and pH10 water, respectively, to determine if freeze-thaw weathering results in enhanced chemical weatherability.

FID and FPD scans of freeze-thaw leachates partitioned finally into benzene are given in Figures 3 to 11, for MD-1 through MD-9, respectively. Detector response to hydrocarbons (FID scan) suggests at first glance that there are significant quantities solubilized by freeze-thaw weathering. However, contamination appears to be a more logical explanation, due to the fact that even the sulfur concrete materials with no asphalt added reflect a significant FID detector response. FPD scans revealed that they hydrocarbons were not sulfur containing.

Samples chipped from the freeze-thaw beams and subjected to acid and base hydrolysis reactions did not show any FID response, further supporting the conclusion that the leachate organics were actually freeze-thaw sample container contaminants and not solubilized sample constituents.

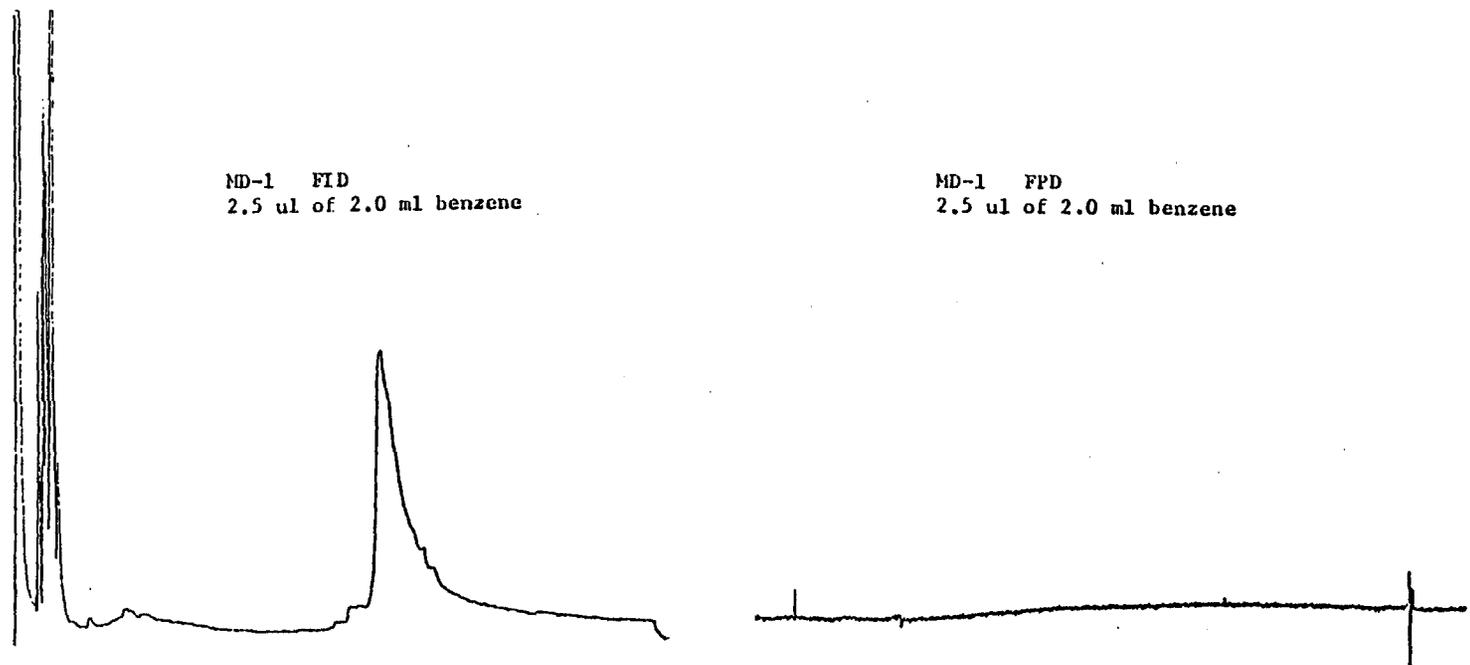
A total sulfur analysis (Table 11) suggested that there was no loss of sulfur from the sample following the multiple freeze-thaw weathering sequence. The difference between total sulfur values reported for MD-9 in Table 9 and Table 11, resulted from sample preparations. Although materials from both tests were ground to pass a 1 mm mesh sieve, the freeze-thaw samples were further ground to fine powder prior to subsampling for total sulfur analysis. Rock fragments may have been excluded in the previous study (Table 9) biasing the matrix toward an indication of the presence of sulfur particles.

Table 11. Total Sulfur Content of Compacted Specimens Following Freeze-Thaw Weathering.

	Mix Design								
	1	2	3	4	5	6	7	8	9
	% Sulfur								
Rep 1	3.12	2.90	17.0	1.87	3.02	0.42	2.02	25.44	18.62
Rep 2	2.68	1.56	1.57	1.98	2.42	0.57	1.93	22.50	18.93
Avg.	2.90	2.23	16.4	1.93	2.72	0.50	1.98	24.0	18.8

Chemical Weathering

Analysis of hydrolysates by gas chromatographic techniques performed on both weathered specimens and laboratory control materials revealed that no organics were solubilized by hydrolysis reactions in either pH2 or pH10 water at a reaction temperature equivalent to the maximum surface temperature. Much more acidic or basic reactions, at the pavement surface, than what could occur naturally would be required to induce chemical hydrolysis of sulfur asphalt pavements. While a specific study revealed H<sub>2</sub>S emissions during hydrolysis were functions of both mix design and pH of the hydrolyzing



MD-1 FID  
2.5 ul of 2.0 ml benzene

MD-1 FPD  
2.5 ul of 2.0 ml benzene

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Figure 3. FID and FPD Scans for MD-1 Freeze-Thaw Leachates.

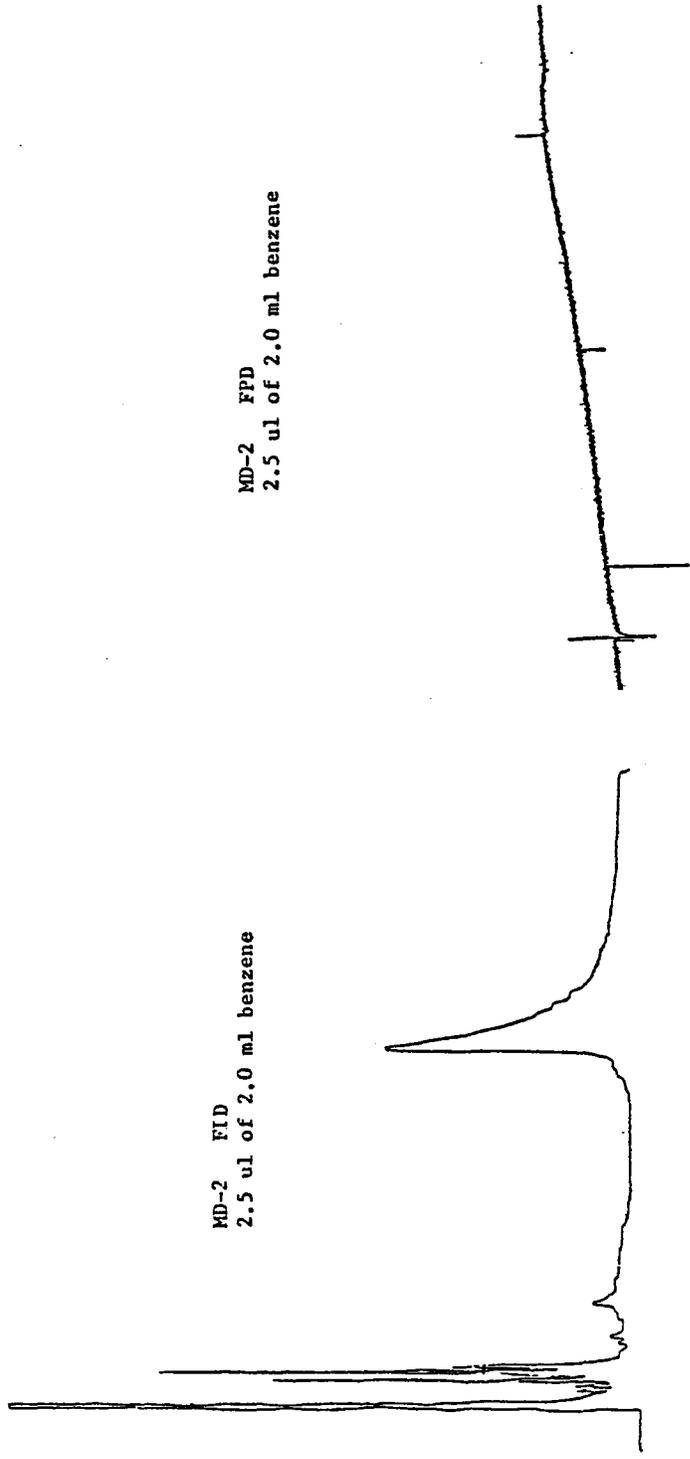
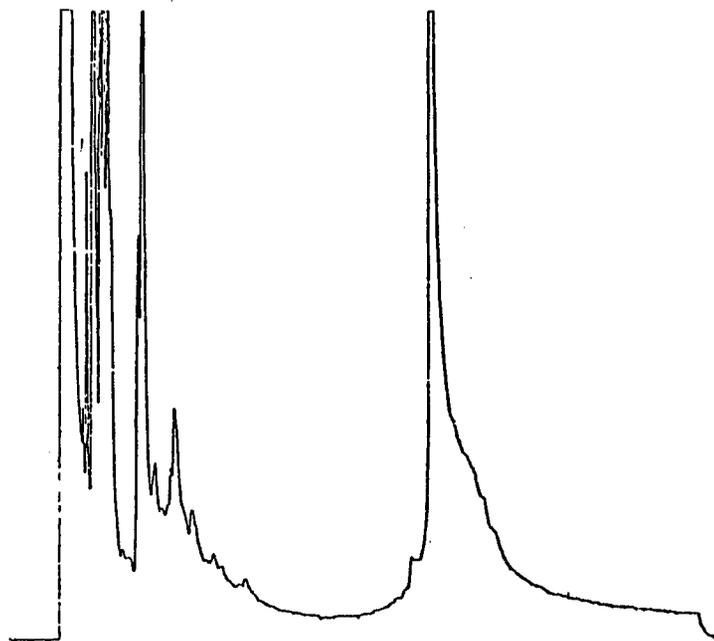
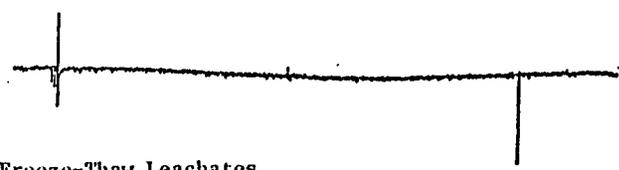


Figure 4. FID and FPD Scans for MD-2 Freeze-Thaw Leachates.

MD-3 FID  
2.5 ul of 2.0 ml benzene



MD-3 FPD  
2.5 ul of 2.0 ml benzene



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Figure 5. FID and FPD Scans for MD-3 Freeze-Thaw Leachates.

MD-4 FID  
2.5 ul of 2.0 ml benzene

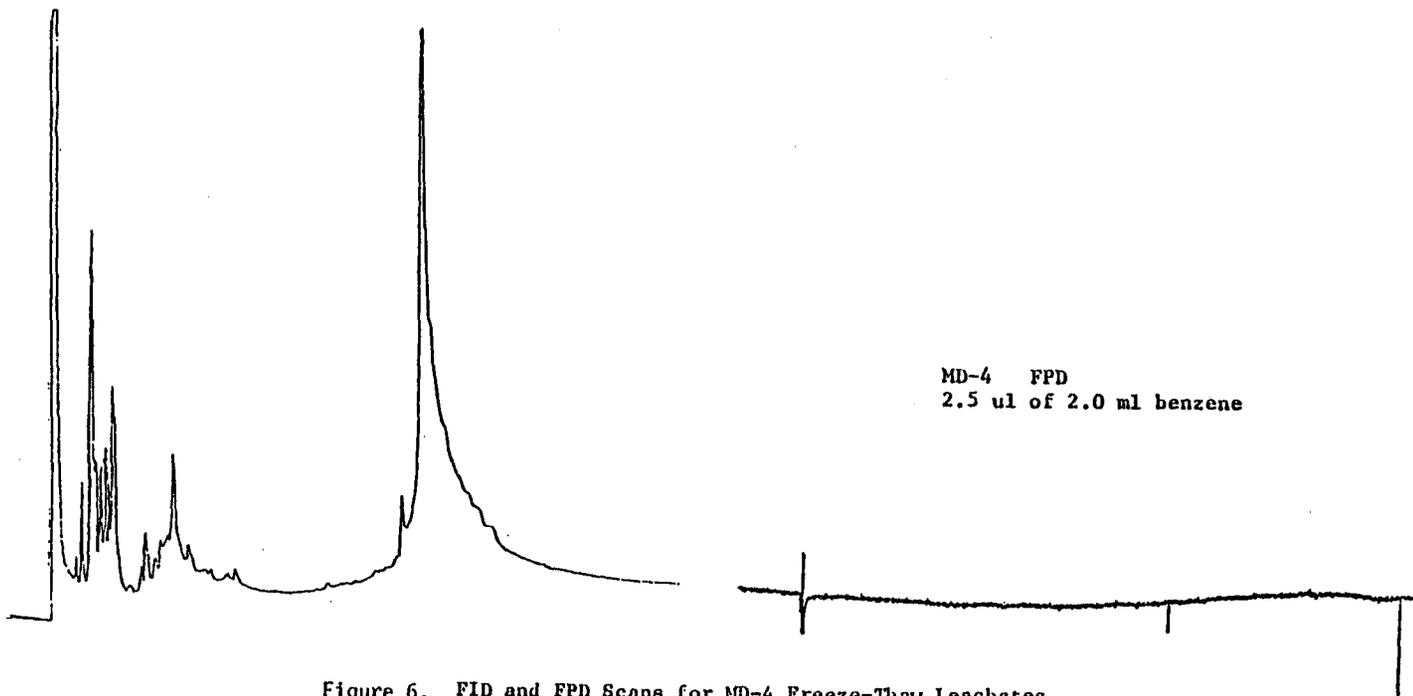
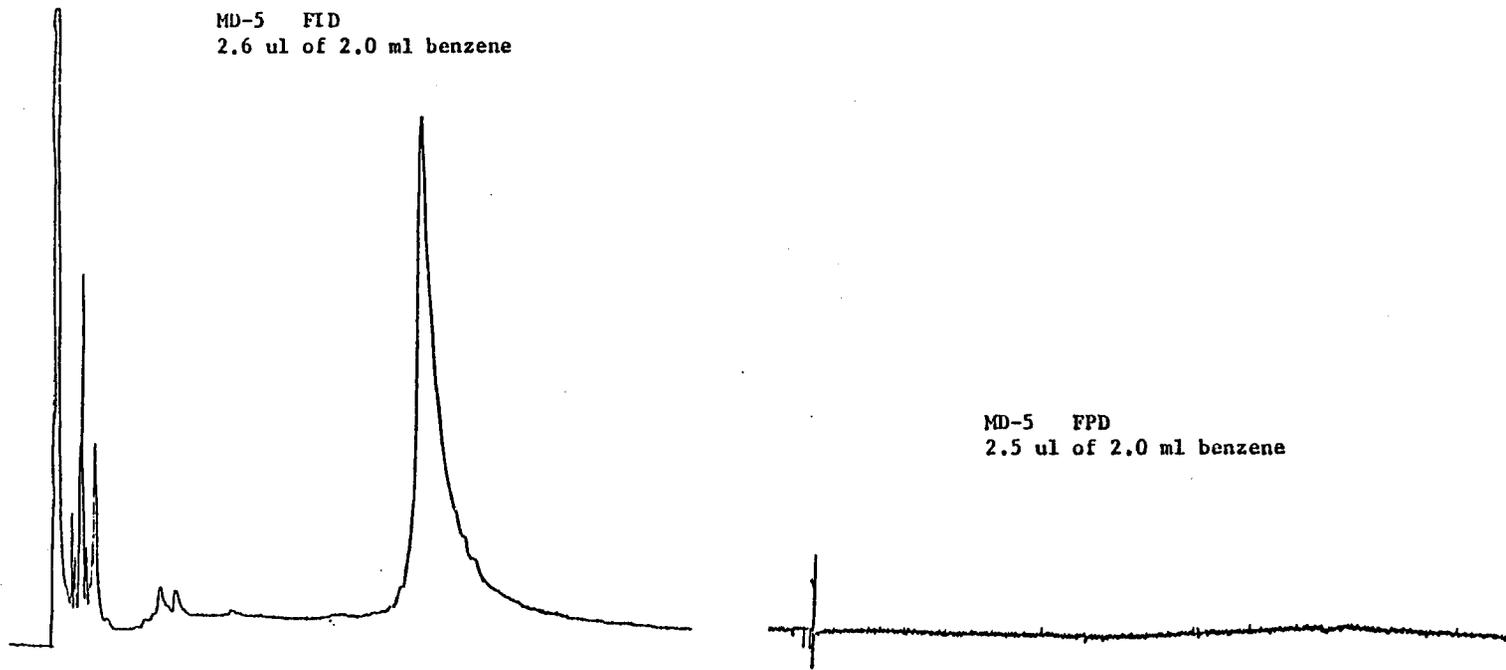
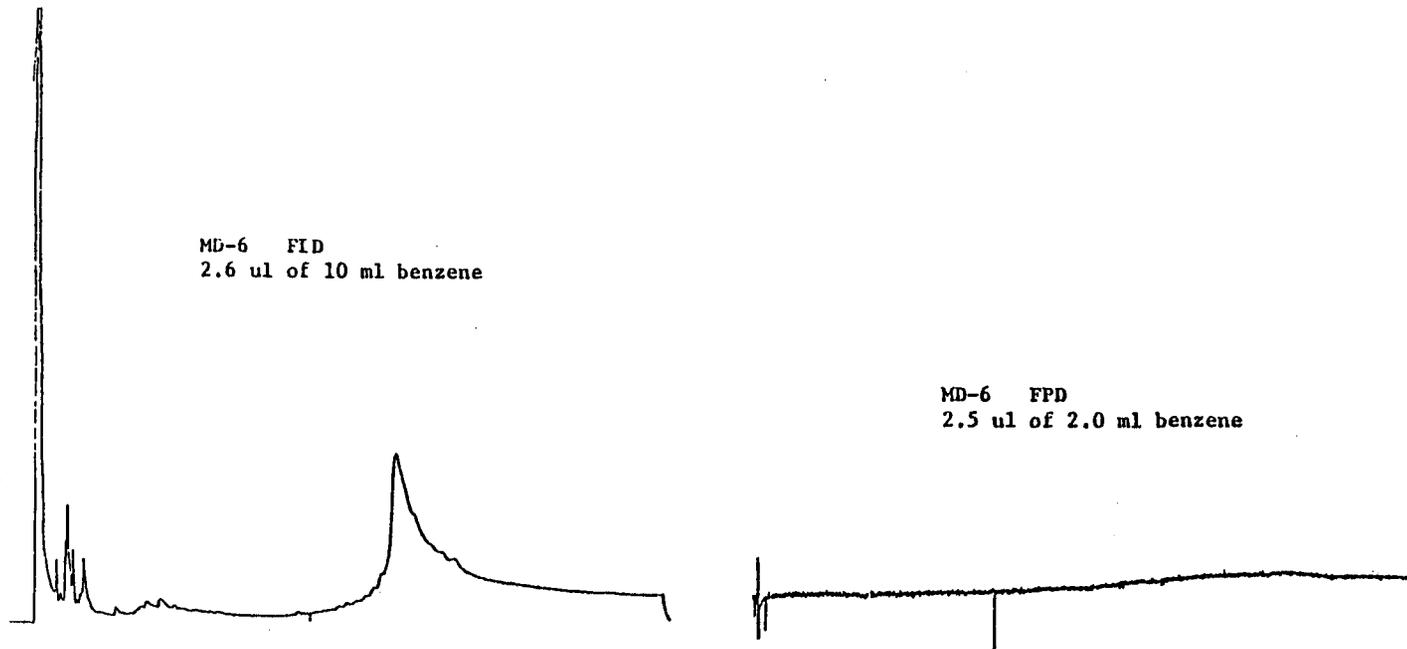


Figure 6. FID and FPD Scans for MD-4 Freeze-Thaw Leachates.



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Figure 7. FID and FPD Scans for MD-5 Freeze-Thaw Leachates.

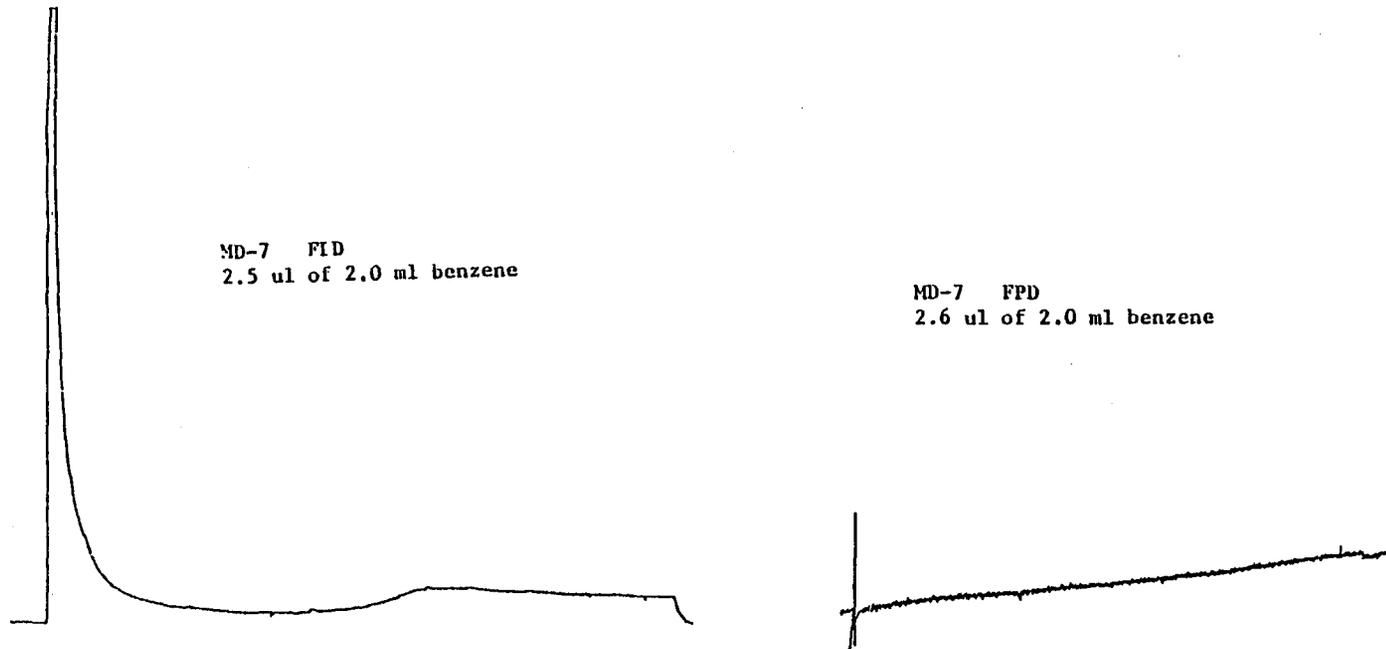


MD-6 FID  
2.6 ul of 10 ml benzene

MD-6 FPD  
2.5 ul of 2.0 ml benzene

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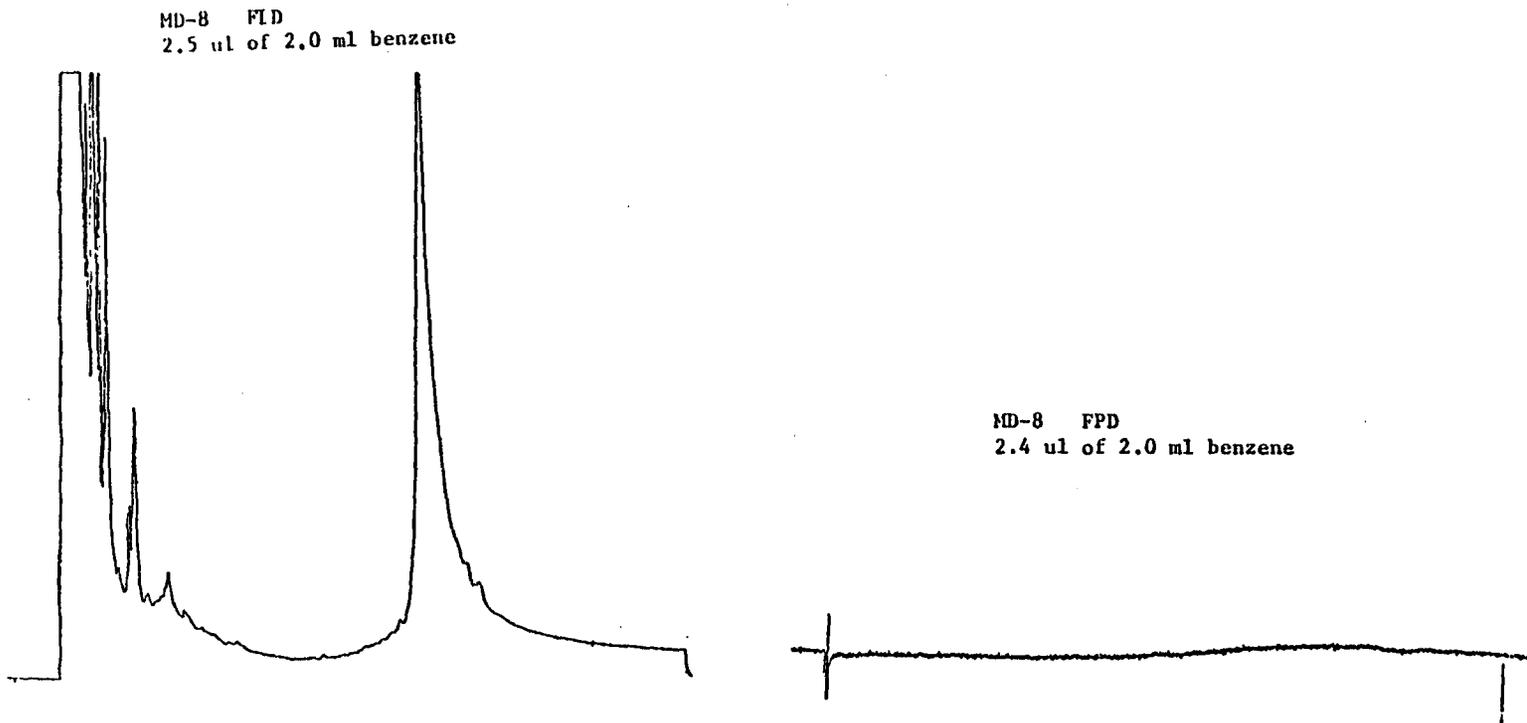
Figure 8. FID and FPD Scans for MD-6 Freeze-Thaw Leachates.



MD-7 FID  
2.5 ul of 2.0 ml benzene

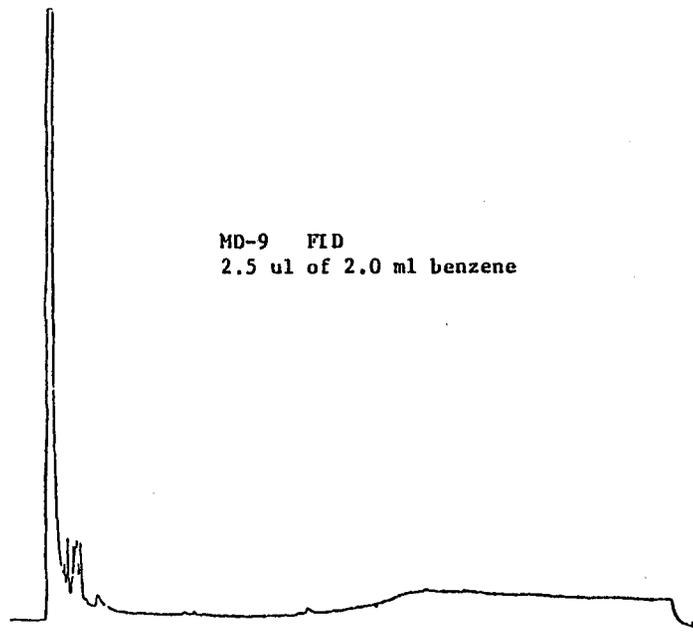
MD-7 FPD  
2.6 ul of 2.0 ml benzene

Figure 9. FID and FPD Scans for MD-7 Freeze-Thaw Leachates.

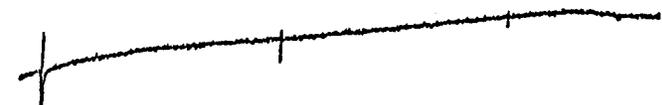


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Figure 10. FID and FPD Scans for MD-8 Freeze-Thaw Leachates.



MD-9 FID  
2.5 ul of 2.0 ml benzene



MD-9 FPD  
2.5 ul of 2.0 ml benzene

Figure 11. FID and FPD Scans for MD-9 Freeze-Thaw Leachates.

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solution (Tables 12 and 13), the total sulfur lost as  $H_2S$  was small in magnitude suggesting that hydrolysis reactions would at best be significant in weathering of sulfur-asphalt pavements over a long term. An alkaline surface reaction may be more favorable for chemical hydrolysis but would tend to buffer the acidifying potential of any elemental sulfur oxidized. Chemical oxidation of sulfur is an exceedingly slow reaction at ambient temperatures of natural environment.

### Biological Weathering

The various mix designs were ground to pass a 1 mm mesh sieve and 10g samples were incorporated into 100g fresh soil matrix to determine potential biological degradation. Degradation was followed by  $CO_2$  evolution over a 90 day incubation period. Soil was maintained at a field capacity moisture level throughout the experiment. The soil employed for this test was a sand loam, with a high native fertility, although low in nitrogen. No nitrogen was added in this study to better simulate natural conditions.

Biological degradation estimated as cumulative  $CO_2$  evolved is given for the various mix designs in Table 14. The data suggests that sulfur tends to increase the biological activity of the soil. Although the experimental design tends to maximize the effects of biological activity, the trend of the data suggested it was a plausible mechanism for sulfur-asphalt weathering and will need further study at a field level. There are micro-organisms common to all soils which can utilize sulfur as an energy source.

Whereas no significant levels of sulfur were lost from compacted specimens exposed to a natural weathering environment over a relatively short time interval, it is suggested from these data that soil-borne microbes may be important in the overall long term weathering of sulfur-asphalt paving materials. All soils contain micro-organisms which can utilize sulfur as an energy source, with potential for deposition on in-service pavements.

### Simulated Traffic Effects

The factors resulting from traffic which could impact the environment include skidding, snow low friction, tire-pavement interactions, and exhaust fumes. With the exception of exhaust fumes, the above conditions would manifest themselves in the creation of fine dust sized particulates through erosion or friction. This dust would eventually be blown by wind or carried by rainfall from the pavement to adjacent soils or streams.

A sulfur-asphalt riding surface is needed to better evaluate the potential impact of this weathering mode. Elemental sulfur was detected in dusts created by grinding the test samples of the various mix designs in the laboratory, but it was felt the test exaggerated the potential as a loss mechanism.

### Simulated Fire Tests

Compacted specimens put in direct contact with a natural gas flame using the apparatus shown in Figure 12, resulted in significant sulfur losses as  $H_2S$  and  $SO_2$  (Table 15). Sulfur losses were proportionate to the total sulfur incorporated in the mix. Except for the DCPD modified sulfur concrete (MD-9), none of the systems tested sustained a burn once the burner flame was removed.

Sulfur-asphalts materials with the exception of MD-3 resulted in surprisingly low gaseous sulfur values, but with proportionately higher  $H_2S$  levels than anticipated. The asphalt matrix definitely reduced sulfur emissions.

Attempts to recover particulate sulfur were completely frustrated due to immediate deposition on cooler surfaces not associated with filter devices and traps employed. A material sulfur balance was not attempted due to the nature of the test.

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Table 12. H<sub>2</sub>S Emissions as a Function of Mix Designs and pH.

Solution pH	Mix Design*					
	1	2	3	4	5	6
			H <sub>2</sub> S ppm			
2.45	0.3	1.7	0.4	0.4	1.4	0.1
5.98	1.4	1.4	2.6	0.6	3.3	0.2
10.70	4.0	3.1	10.6	1.1	7.5	0.6

\*Average of two determinations.

Table 13. ANOVA for H<sub>2</sub>S as a Function of Mix Design and pH.

Source of Variation	Degree of Freedom	Sum of Squares	Mean Square	Exponent F
Between pH	2	110.44	55.22	448**
Between Mix Design	5	93.76	18.75	152**
Interaction	10	82.69	8.27	67**
Error	18	2.22	0.12	
Total	35	289.12		

\*\* Significant at the 1% level

Table 14. CO<sub>2</sub> Evolved from Asphalt, Sulfur Asphalt, and Sulfur Concrete Materials Incorporated into a Soil Matrix.

Mix Design	Cumulative CO <sub>2</sub> Evolved
	Mg
MD-1	194
MD-2	171
MD-3	149
MD-4	311
MD-5	373
MD-6	105
MD-7	136
MD-9	366
Soil Blank	183

Table 15. H<sub>2</sub>S and SO<sub>2</sub> Concentrations Emitted During a Simulated Burn.

Sulfur Specie	Mix Design								
	1	2	3	4	5	6	7	8	9
	Concentration, ppm								
H <sub>2</sub> S	25	18	350	75	25	0	20	0	25
SO <sub>2</sub>	100	47	750	65	25	0	30	2800	3400

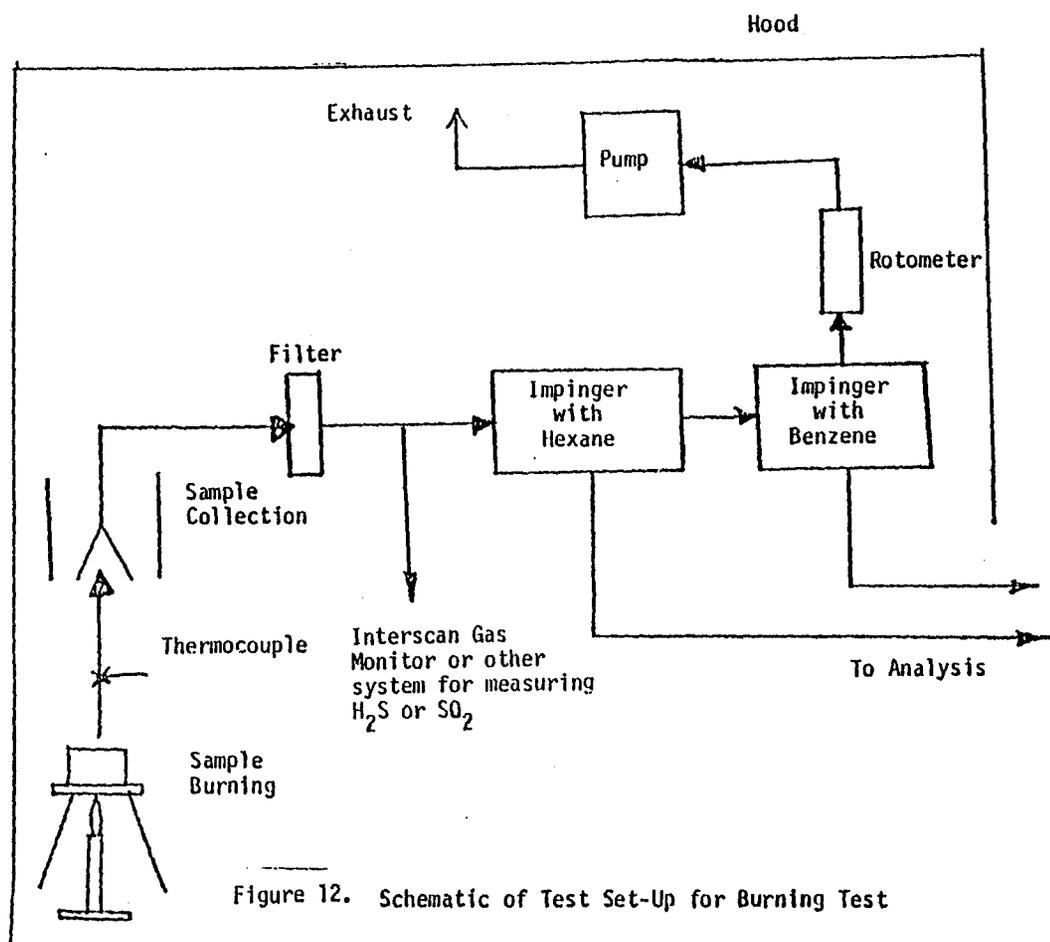


Figure 12. Schematic of Test Set-Up for Burning Test

MD-3 FID  
2.8 ul of 4 ml hexane

MD-6 FID  
2.7 ul of 4 ml hexane

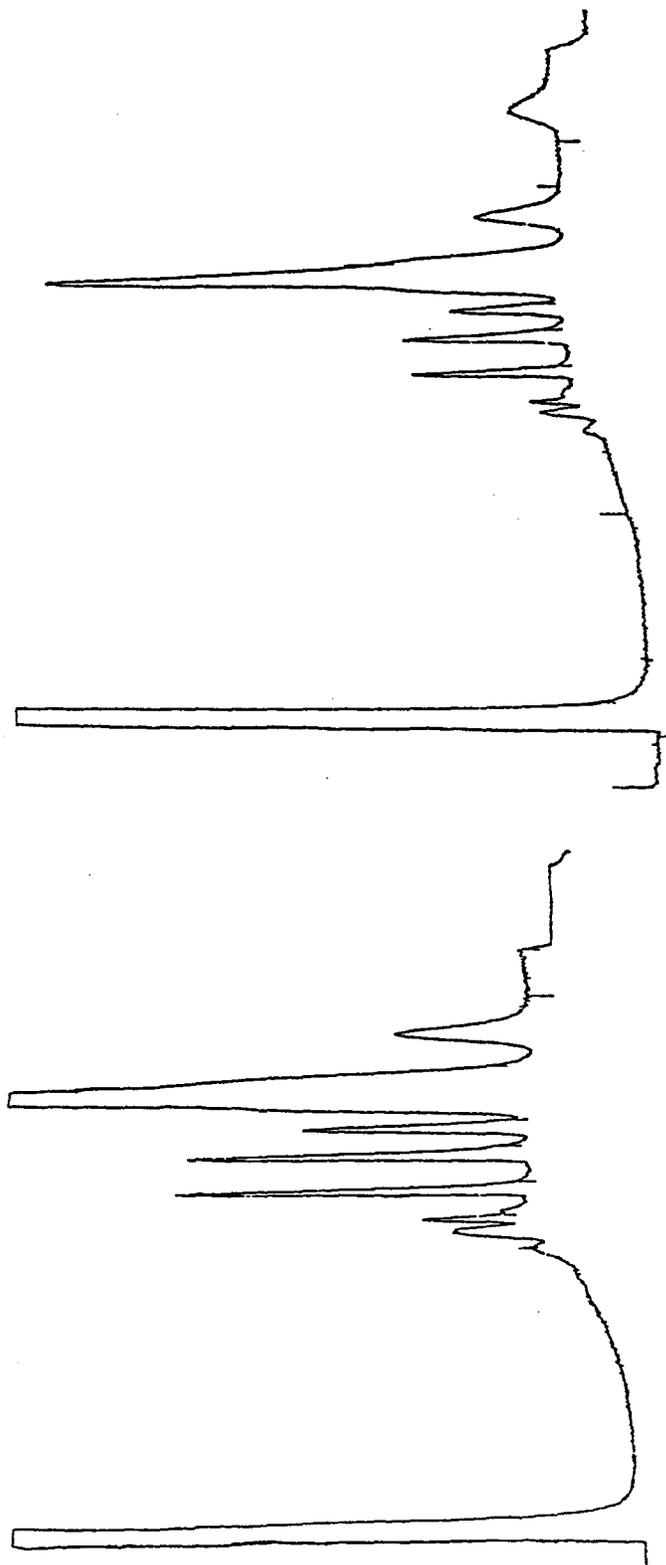


Figure 13. FID Scans of Emissions Generated on Burning Compacted Specimens of MD-3 and MD-6.

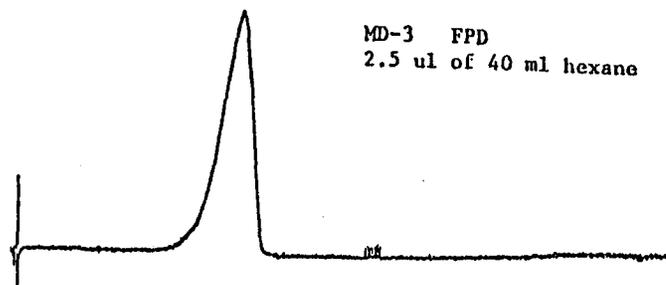


Figure 14. FPD Scan of Emissions Generated on Burning a Compacted Specimens of MD-3.

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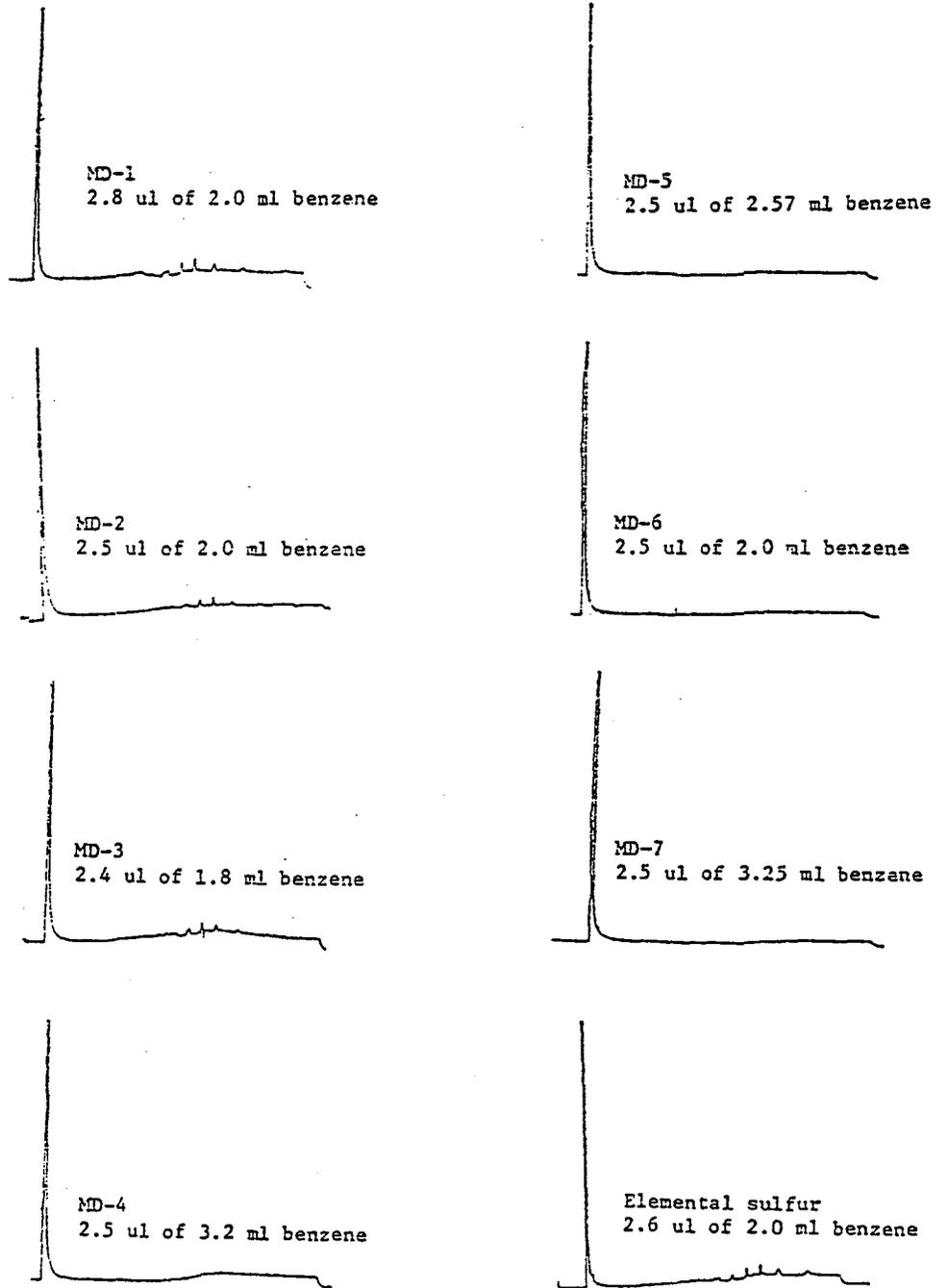


Figure 15. FID Scans of Fragmented Paving Materials Leached with Saturated NaCl.

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Although dense fumes were noticeable throughout the tests, low levels of organics actually trapped in refrigerated solvent indicated an inadequate design of the test procedure. However, attempts to modify the system were completely thwarted by the physical nature of the fumes. Apparently the organics emitted were occluded with or onto sulfur particulates.

While no attempt was made to quantite organic emissions FID scans of solvents assayed by GC technique revealed significant hydrocarbon emissions for the sulfur-asphalt pavements. Comparison of organic emissions for MD-3 and MD-6 suggested that elemental sulfur mixed with asphalt does not materially affect the nature of the organics released on burning (Figure 13). Sulfur alone dominated the FPD scans, and is demonstrated in Figure 14, for MD-3 emissions.

### Simulated Road Spills

Compacted specimens of the asphalt and asphalt paving materials were fragmented into particles retained on a 2 mm sieve. Ten grams of each material were then placed in glass columns and leached with 100 ml saturated NaCl at an elution rate of 4 ml per minute. Leachates were acidified to pH6 and partitioned into benzene using 2, 50 ml volumes of the latter. Benzene extracts were combined, reduced in volume and subsequently analyzed by GC using both FID and FPD detector systems.

Separate 10g samples were leached with 100 ml volumes of nano-grade quality iso-octane to simulate the affect of gasoline spills. Iso-octane extracts were analyzed directly by GC using FID and FPD detector systems.

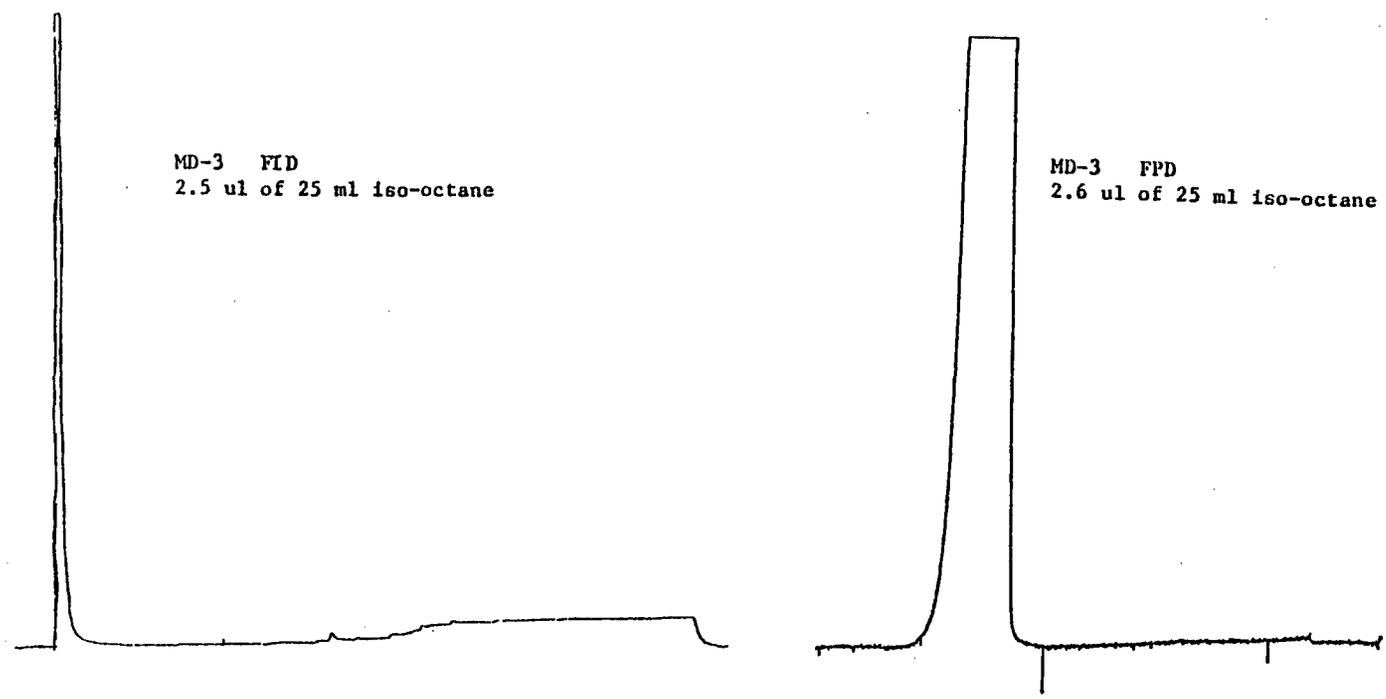
Saturated NaCl leach solution was used to simulate the affect of potential brines from deicing salts on sulfur-asphalt paving materials. FID scans of the salt leachates (Figure 15) showed no organics were stripped from either asphalt or sulfur-asphalt paving materials. The peaks showing up in several of scans were found to be contaminates of a new bottle  $\text{Na}_2\text{SO}_4$  used to dry the benzene extracts. The elemental sulfur blank is designated as such. Straight line chromatograms were obtained in the FPD analyses of the brine leach. The use of fractured pavement specimens in the test gave a much larger surface area than intact pavement materials, and would tend maximize the effect of a brine leach on a comparative basis. One can only conclude that brines from saturated deicing salts would have a minimal impact on run off waters emanating from sulfur-asphalt or asphalt pavements.

Simulated gasoline spills, using iso-octane as a leach solvent revealed that elemental sulfur could be leached from contacted surface materials as typified in the FID and FPD scans for MD-3 (Figure 16). This is based on the fact that sulfur shows up on FPD detection with no commensurate peak in the FID mode. The impact of gasoline spills will of course be lessened with an intact compacted pavement surface. However, the fact remains that organic solvents or naptha mixture will solubilize free sulfur.

The data suggests that a much longer contact time than that afforded by the column leach technique employed will be required to solubilize significant asphalt borne organics.

### CONCLUSIONS

Nine mix designs were examined under a variety of weathering and in-service oriented conditions. Dusts, fumes and run-off created as a result of exposure to the elements and traffic wear were analyzed for potential safety hazards and environmental impact. It was found that exposure to the elements had negligible effect on the paving materials studied and run-off either by wind or rain produced little or no effect on the immediate environment. It should be noted that in both mix preparation and simulated weathering experiments were designed to maximize the test conditions and thus the results generated may be considered conservative.



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Figure 16. FID and FPD Scans of Fragmented MD-3 Paving Material Leached with Iso-Octane.

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The possibility of accidental events such as fires and chemical spills were investigated and revealed some possible short term undesirable effects. These effects were essentially obnoxious fumes and/or short-term pollution. Virtually all of the sulfur paving materials were difficult to ignite and were self-extinguishing.

The effect of simulated brine and gasoline spills on sulfur pavements were studied. Whereas salt-based deicers would have minimal effect, organic solvents or naphtha mixtures can solubilize elemental sulfur. There was nothing revealed in this study which would prohibit the use of sulfur modified paving materials on the nations highways.

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