ENVIRONMENTAL AND SAFETY ASPECTS OF THE USE OF SULFUR IN HIGHWAY PAVEMENTS:

PART I - MIX PREPARATION AND CONSTRUCTION

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INTRODUCTION

Throughout the development of the sulfur/asphalt concept one of the major concerns of the industry has been the potential hazards created at the construction site due to the evolution of toxic gasses (H_2S and SO_2) and particulate sulfur. Over the past nine years the Texas Transportation Institute (TTI) has monitored the pollutants both in the laboratory as well as in conjunction with their full scale experimental field trials. An FHWA sponsored research program at TTI [1] whose objective is to assess the environmental and safety implications of using sulfur as a highway paving material has concluded that as long as the temperature of the mix is maintained below 300°F, concentrations of these pollutants remain below the maximum allowable concentrations (MAC) suggested by the American Conference of Governmental Industrial Hygienists (ACGIH) [2]. Similar studies at the Bureau of Mines [3], Gulf [4], Shell [5] and SUDIC [6] also support this claim.

Paving materials prepared using modified sulfur binders require that the mix temperatures be maintained in the range of 240 to 300°F during construction. Under these conditions elemental sulfur, S_8, can be oxidized to SO_2, which, in turn, can be converted to SO_3 by:

$$\frac{1}{8}S_8 \xrightarrow{\text{air}} SO_2 \xrightarrow{\text{air}} SO_3 \qquad (1)$$

The oxidation of sulfur dioxide to sulfur trioxide is rather slow in the absence of catalysts. In the presence of moisture these two oxides of sulfur will dissolve in any water droplets present. Sulfur dioxide, which is quite soluble in water, will be physically dissolved in the droplets with an exceedingly small part reacting with the water to form sulfurous acid.

$$SO_2 \xrightarrow{H_2O} SO_2 \ \text{dissolved} \xrightarrow{H_2O} H_2SO_3 \qquad (2)$$

Aqueous solutions of sulfur dioxide possess acidic properties with a dissociation constant of 1.3×10^{-2} ascribed to the medium-strong sulfurous acid [7].

Sulfur trioxide will form the strong and corrosive sulfuric acid.

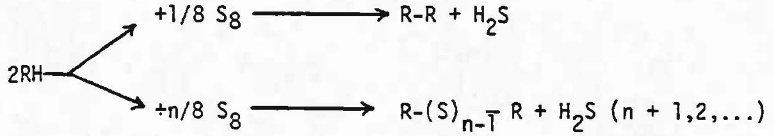
$$SO_3 \xrightarrow{H_2O} H_2SO_4 \qquad (3)$$

During the various operations carried out at elevated temperatures sulfur will be dispersed into the air in particulate form. This particulate sulfur can be deposited or be slowly oxidized.

Sulfur reacts with many organic compounds: saturated hydrocarbons are dehydrogenated with formation of hydrogen sulfide. The thus generated olefins can

$$RCH_2\text{-}CH_2R' \xrightarrow[\text{heat}]{S} RCH = CHR' + H_2S \qquad (4)$$

add sulfur across the double bond forming organic sulfur derivatives, or can polymerize to hydrocarbons of higher molecular mass. Instead of olefine formation, sulfur may couple two hydrocarbon molecules (Eq. 5) or yield an organic sulfide (Eq. 6). Both of these reactions produce hydrogen sulfide.



$$2RH \rightarrow +1/8\ S_8 \longrightarrow R\text{-}R + H_2S \qquad (5)$$

$$2RH \rightarrow +n/8\ S_8 \longrightarrow R\text{-}(S)_{n\text{-}1}\text{-}R + H_2S\ (n + 1,2,...) \qquad (6)$$

The reactions of sulfur with organic compounds are very complex and have not yet been elucidated in detail. The organic products formed in these reactions are expected to be non-volatile at the temperatures prevalent during preparation, paving and normal in-service use of the sulfur-asphalt mixture. Hydrogen sulfide is the most important gaseous product of these reactions. The extremely poisonous gas, hydrogen sulfide, which can be detected at concentrations as low as 0.02 ppm by its revolting order but tends to dull the sense of smell at higher concentrations and during longer exposure, is thermally very stable. Only 75% of a sample is decomposed at 3000°F. In air, hydrogen sulfide is oxidized to sulfur dioxide (Eq. 7). The lifetime of hydrogen sulfide under normal atmospheric conditions was estimated to be approximately four days [8]. Hydrogen sulfide and sulfur dioxide can then react to form elemental sulfur (Eq. 8) which would appear in the air as particulate matter.

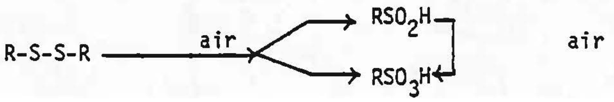
$$H_2S \xrightarrow{\text{air}} H_2O + SO_2 \qquad (7)$$

$$2H_2S = SO_2 \longrightarrow 3/8\ S_8 + 2H_2O \qquad (8)$$

The reactions of sulfur with air or the hydrocarbons in the asphalt will produce large quantities of noxious gasses only at temperatures above 200°F. One can, therefore, expect to find sulfur dioxide, hydrogen sulfide trioxide and their reactions products with water in the air in the vicinity of locations where hot sulfur-asphalt mixes are handled, when the air is humid.

Under normal use of the sulfur-asphalt pavements, (i.e. temperature below 200°F) hydrogen sulfide and sulfur dioxide will very likely not be generated in amounts to exceed their respective maximum allowable concentrations (MAC). Slow oxidation of some of the sulfur will occur as described by Eq. 1.

Sulfur-asphalt pavements are naturally exposed to the influence of atmospheric agents. The oxygen of the air will very slowly oxidize the sulfur dioxide. This reaction is too slow to cause any pollution problems. It could also happen, that the organic sulfides in the mix are oxidized to sulfinic or sulfonic acids by oxygen. (Eq. 9).



$$R\text{-}S\text{-}S\text{-}R \xrightarrow{\text{air}} RSO_2H,\ RSO_3H; \quad RSO_2H \xrightarrow{\text{air}} RSO_3H \qquad (9)$$

These acidic substances are more soluble in water than, for instance, the disulfides. They could be leached out by rain and enter surface and ground water streams. These compounds are related to synthetic surfactants, which are constituents of detergents, and should be biodegradable. Highly polar solvents such as water de-icing liquids, aqueous acids and alkalies are not expected to dissolve much more from the sulfur-asphalt pavement than from a pure asphalt mix. Depending on the strength of an alkaline solution part of the elemental sulfur can be converted to alkali polysulfides (Eq. 10), which are soluble in aqueous medium. In water containing dissolved oxygen these sulfides

$$\frac{n}{8} S_8 \xrightarrow[N_2O]{NaOH} Na_2S_n \qquad (10)$$

will be oxidized to sulfuric acid as the final product. Non-oxidizing acids, such as hydrochloric acid, do not dissolve sulfur. Oxidizing acids convert sulfur to sulfuric acid.

Sulfur will not be dissolved to an appreciable extent by engine oil, grease and gasoline. The organic sulfur compounds are more likely to be extracted from the pavement by these materials. Through the mechanical action of the atmospheric agents, sulfur particles can be torn loose from the pavement and enter the run-off.

This paper is the first of two part series which deals with evolution of fumes, dusts and gasses associated with sulfur-asphalt mixtures. The results of evolved gas analyses conducted during mix preparation and actual construction is also presented. Part II of this series deals with post-construction in-service aspects such as weathering, fires, chemical spills, biological activity, etc. Six mix designs representing four types of sulfur-asphalt pavement materials are treated and include: (a) Sand-Asphalt-Sulfur (SAS), (b) Sulfur Extended Asphalt (SEA), (c) Sulfur-recycled systems and (d) Sulfur concrete. Results are compared with a conventional asphaltic concrete used as a control.

TOXICITY OF SULFUR INITIATED POLLUTANTS

The three most common sulfur initiated pollutants are H_2S, SO_2 and particulate sulfur. The safety problems of each of these contaminates will now be discussed.

Relative Toxicity of H_2S

Hydrogen Sulfide is known for its characteristic "rotten egg" odor. Although this odor is noticeable at concentrations as low as 0.02 ppm [7], odor is not a good indicator of concentration level. Hydrogen sulfide can have a paralyzing effect on the sense of smell [9]. Therefore, high concentrations of H_2S can escape recognition.

The basis used for establishing the relative toxicity of emissions data generated during this project were the relationships between H_2S concentrations and human effects as specified by ACGIH [10]. These relationships are shown below:

H_2S Concentration, ppm	Effect
0.02	Odor Threshold
0.10	Eye Irritation
5-10	Suggested Maximum Allowable Concentration (MAC) for Prolonged exposure

H_2S Concentrations, ppm	Effect
70-150	Slight Symptoms after Exposure of Several Hours
170-300	Maximum Concentration which can be inhaled for one hour without serious consequences
400-700	Dangerous after exposure for 1/2 to one hour
600	Fatal with 1/2 hours exposure

On the basis of these effects a MAC value of 5 ppm is normally specified as the upper threshold limit for continuous exposure to H_2S emissions in areas normally expected to be occupied by construction or plant personnel.

Relative Toxicity of Sulfur Dioxide

Sulfur Dioxide (SO_2) us a colorless gas with a pungent odor which unlike H_2S gives ample warning of its presence. The principle health hazard from SO_2 comes from inhalation of excessive quantities above its MAC. The basis for establishing the relative toxicity of emissions data generated during construction would be the relationships between SO_2 concentrations and human effects as specified by the National Institute for Occupational Safety by Health and the Manufacturing Chemists Association (11, 12) are shown in the following table.

SO_2 Concentration, ppm	Effect
0.3 - 1	Detected by taste
1	Injurious to plant foliage
3	Noticeable odor
5	MAC (ACGIH)
6-12	Immediate irritation of nose and throat
20	Irritation to eyes
50-100	MAC for 30-60 min. exposures
400-500	Immediately dangerous to life

The present Federal standard for SO_2 in an 8-hour time weighted average is 5 ppm (see 29CFR, 1910, 93 published in the Federal Register, Volume 37, p. 22139 (October 18, 1972). This is the MAC specified as the upper threshold limit concentration for SO_2 emissions in areas normally expected to be occupied by construction of plant personnel.

Relative Toxicity of Particulate Sulfur

Vapor given off during mixing and dumping operations contain a certain amount of undissolved and unreacted sulfur. As the vapors come in contact with air and cool, the sulfur crystallizes into small particles which are carried by the wind in a manner similar to dust and fine sands. Since there is no practical way to eliminate this pollutant its effects on both environment and personnel need to be considered. A detailed discussion of the relative hazards associated with sulfur dust may be found in Reference [13].

The principal problems associated with sulfur dust lie in its contact with eyes. Sulfur is virtually nontoxic and there is no evidence that systemic poisoning results from the inhalation of sulfur dust. However, sulfur is capable of irritating the inner surfaces of the eye lids. Sulfur dust may rarely irritate the skin. This problem is minimized by the requirement that goggles be worn in areas subject to this pollutant such as at the hot mix plant and in the vicinity of the paver.

The primary hazard in handling solid sulfur results from the fact that sulfur dust suspended in air may be ignited. This problem is almost always limited to enclosures and unventilated areas such as storage silos and hoppers.

To minimize possible irritation, unnecessary contact with skin and eyes should be avoided. Following the work period, sulfur dust should be removed with mild soap and water. For relief of eye irritation, eyes should be thoroughly flushed with large quantities of plain water or physiological saline. Inadequate amounts of water may actually increase eye irritation.

EMISSIONS ASSOCIATED WITH MIX PREPARATION IN THE LABORATORY

Test Conditions

Emissions generated during mix preparation were investigated as functions of mix design, mixing temperature and atmospheric conditions (i.e. moisture content of the air, ambient air and nitrogen environments). Emissions produced by mixing in both open and controlled test conditions were studied. The primary objective of this series of test was to determine the concentrations, if any, of H_2S, SO_2, SO_3, elemental sulfur and organics released due directly to the incorporation of sulfur into paving materials.

The seven mix designs (MD-1 to MD-7) evaluated are given in Table 1. Environmental parameters controlled during the test are given below.

Temperatures, °F	250	300	350
Moisture Content of Air,		Dry	Wet
Ambient Air, %		<5	>95
Nitrogen, %		<5	-

Inorganic Sulfur Contaminants

The apparatus used to measured H_2S and SO_2 emissions in a closed or controlled environment is shown in Figure 1. Materials used in the study were prepared in bulk by mixing in a 1 gallon beacon mixer at 250°F for 30 seconds. The materials were immediately cooled and ground to pass a 1 mm mesk sieve. Sample preparation in this manner was necessary to minimize material surface area variability due to the difference in the mix design ingredients and quantities.

A 3 g sample of each mix design was placed in a flask and heated at a rate of 7°F per minute. Air was drawn over the sample at a measured rate of 1 to 3 liters per minute and subsequently mixed with a measured volume of dilution air. Sampling times were established by emission levels so as not to induce a variable associated with the amount of sulfur in the sample. For example, emissions would be erroneously diminished if air was drawn once sulfur was materially reduced. Sampling time for the 250°F measurements averaged about 20 minutes. The interval was reduced to approximately 10 minutes for the 350°F measurements. A suitable fraction of the air mixture was drawn and continuously monitored for H_2S and SO_2 using Interscan gas analysers Models 1176 and 1248, respectively.

Table 1. Selected Mix Designs and Materials for Laboratory Samples of Asphaltic Concretes.

Mix Number	Mixing System	Binder Proportions	Binder Content	AGGREGATE	
				Material	Gradation
1	Aggregate -Asphalt -Sulfur	25% Sulfur 75% Asphalt	6.9 w/o	Crushed Limestone	Dense*
3	(AAS)	70% Sulfur 30% Asphalt	19.5 w/o	Beach Sand	Uniform
4		1.25% Sulfur 0% Asphalt	1.25 w/o	Nellis Runway Recycled Material	Dense
5		1.25% Sulfur 1.0% Asphalt	2.25%		
2	Aggregate -Emulsion	25% Sulfur 75% Asphalt	6.9% w/o	Crushed Limestone	Dense
7	(AE)	20% Sulfur 80% Asphalt	$\sim$4 w/o		Open**
6	Asphaltic Concrete (AC) (Control)	0% Sulfur 100% Asphalt	4.5%	Crushed Limestone	Dense

*Asphalt Institute Gradation IVb.

**Texas Highway Department Grade 4.

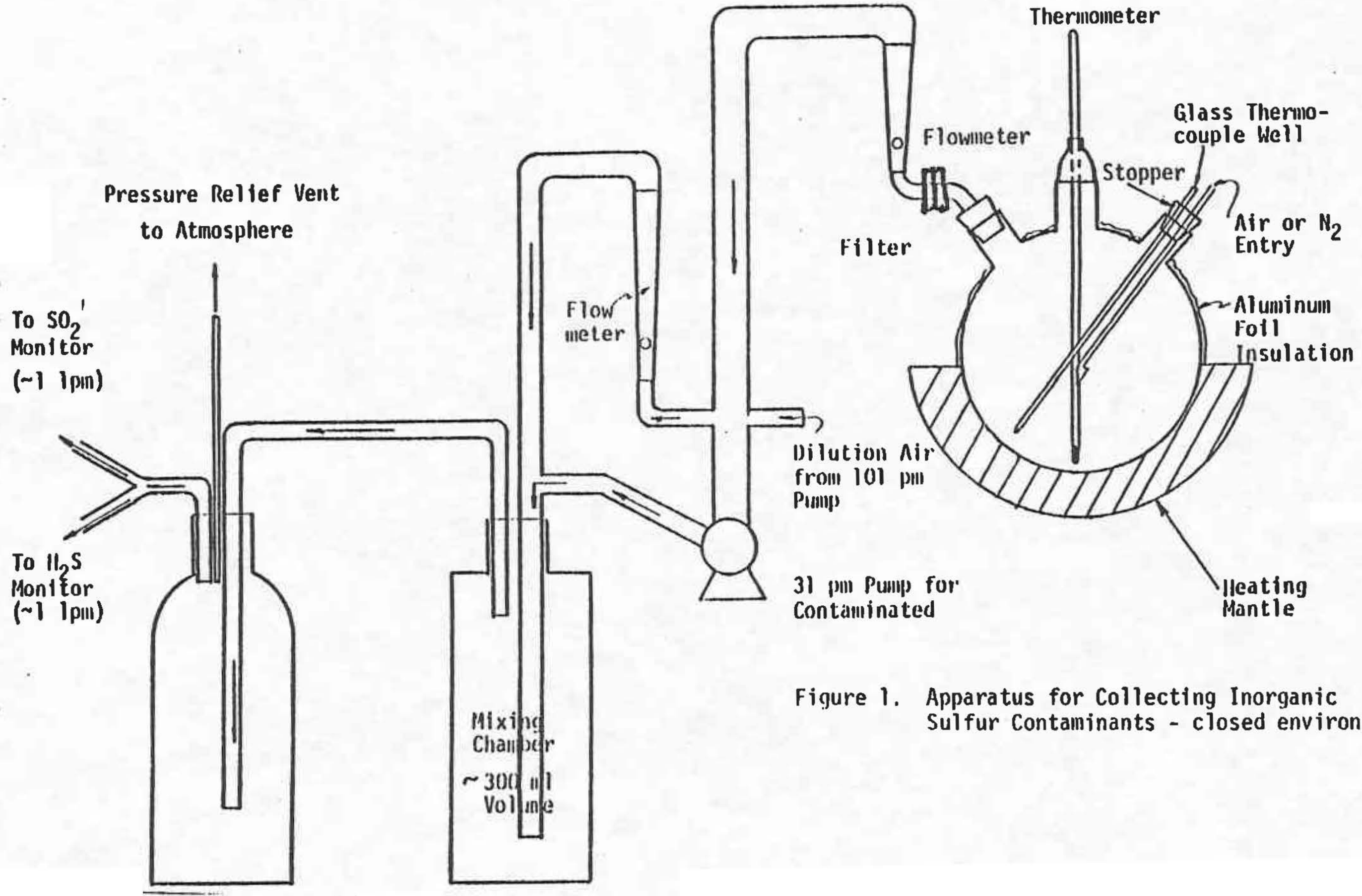


Figure 1. Apparatus for Collecting Inorganic Sulfur Contaminants - closed environment.

Relative humidities of <5% and >95% for nitrogen and air drawn through the reaction vessel were achieved by either drying the sweep gas with anhydrous $CaSO_4$, or saturating with water vapor. Vapor flux values were calculated by converting concentrations expressed in microliter/liter to total mg H_2S or SO_2 evolved, then dividing by sample weight in Kg and the sampling time interval in minutes.

Particulates generated were trapped onto a pre-weighed 0.1 μm filter disc. The stainless steel filter housing was heated at a slightly higher temperature than the reaction vessel to circumvent the problem of clogging the filter with condensed vapors, which would hamper the ability to maintain calibrated flow rates. The reaction vessel was cooled prior to dismantling the filter holder and removal of the filter disc. Filters were placed in a vacuum dessicator for additional cooling prior to gravemetric analysis.

SO_3 emissions were determined or separate subsamples by selective absorption into 80% isopropanol, followed by titrametric analysis as sulfate in accordance with EPA Method No. 6 [14].

In contrast to the closed or controlled environment, another series of emission measurements were made for mixes prepared in an "open", laboratory environment. To better simulate normal operating conditions the above measurements were made at approximately 18 inches from the surface of the mix.

Concentrations of H_2S and SO_2 emitted during the preparation of the seven mix designs are shown in Table 2. Table 2a shows the concentrations generated using a closed system (Figure 1) and Table 2b reflect the concentrations generated under the open atmospheric conditions of the laboratory. Emissions collected in the closed environment were significantly higher than those taken under the more job-simulative conditions of the laboratory. Both H_2S and SO_2 increase with temperature and with the rate of evolution once the temperature exceeds 300°F. Emissions from mixes prepared in the closed system exceeded the MAC values for both H_2S and SO_2 at temperatures above 300°F (149°C). Emissions, where detectable, relative to the seven sulfur-asphalt designs appeared to be in the same proportion for both the closed and open laboratory test environments.

In order to make comparisons between mix designs the total H_2S and SO_2 emitted was normalized to a flux term. Flux values in mg/kg/min are given in Table 3. These data suggest that similar masses of H_2S and SO_2 are emitted at corresponding formulation temperatures for a given mix design. At the highest formulation temperature the high-sulfur content mix (MD-3) and the control (i.e. 0% sulfur) (MD-6) differed markedly in H_2S and SO_2 flux values. Although the peak concentrations of MD-3 were equivalent to or lower than the other mix designs as indicated in Table 2a, the concentrations were sustained for a longer time interval, due to the fact that MD-3 (a typical sand-asphalt-sulfur system) contained from 5 to 8 times more sulfur in the mix initially. This resulted in larger H_2S and SO_2 flux values for the MD-3 material.

Comparisons of vapor flux values for MD-3 under different atmospheric conditions are presented in Table 4. The increase in vapor flux with a corresponding increase in temperature was statistically significant at the 1% level. Although there were not staticsally significant difference between vapor flux values with respect to atmospheric condition, moist air (>95% relative humidity) resulted in numerically higher H_2S and SO_2 emissions at lower temperatures. No attempt was made to study atmospheric conditions on vapor flux values of the other mix designs due to negative results obtained on the high sulfur mix design.

A more thorough study of the high sulfur MD-3 material was made in an effort to mathematically model probable emission levels relative to the mix temperature. Both H_2S and SO_2 gaseous emissions were described by an

Table 2. Variations of Gaseous Emissions with Mix Temperature Generated During Mix Formulation.

Controlled Environment - Table 2a

Gaseous Vapor	Temperature °F	Mix Design Number*						
		1	2	3	4	5	6	7
		Concentration, ppm						
H_2S	250	3.5	15	12	10	9	0.5	2.0
	300	8.0	280	305	110	90	2.0	78.0
	350	173.0	620	595	1100	500	2.5	385.0
SO_2	250	4.0	8.0	6.0	10	0.4	0.5	1.0
	300	9.0	140.0	160.0	39	83.0	2.0	17.0
	350	87.0	361.0	245.0	550	250	2.0	187.0

Laboratory Environment - Table 2b

Gaseous Vapor	Temperature °F	Mix Design Number*						
		1	2	3	4	5	6	7
		Concentration, ppm						
H_2S	250	Tr	Tr	1.1	Tr	>0.1	0.5	Tr
	300	2.5	1.5	3.0	1.7	2.0	1.0	3.0
	350	50	5	65	20	25	1.5	22
SO_2	250	←			(Tr) (0)			→
	300	1.5	1.0	1.0	.5	1.7	1.2	0.4
	350	23	2.8	33	8	13	1.5	7

*Mix designs and numbers are given in Table 1.

Note: All concentrations were measured within 5 sec. after mixing had begun.

Table 3. Variation of Vapor Fluxes of H_2S and SO_2 with Respect to Mix Temperatures Generated During Mix Formulation.

						Mix Design*			
Vapor	Temperature		1	2	3	4	5	6	7
	°F	(°C)				mg/kg/min			
H_2S	250	(121)	4	18	9	12	1	1	3
	300	(149)	9	260	114	26	42	2	90
	350	(176)	120	294	552	255	232	3	356
SO_2	250	(121)	9	14	5	22	1	1	3
	300	(149)	114	176	92	47	40	4	38
	350	(176)	240	267	610	240	218	4	326

*Mix designs and numbers are given in Table 1.

Table 4. Variation of Vapor Flux Values for MD-3 As Affected by Atmosphere.

			Vapor Flux (mg/kg/min)	
	Temperature °F	(°C)	H_2S	SO_2
Air Dry	240	(121)	9.3	5.4
	300	(149)	114	92
	350	(176)	552	610
Air Wet	250	(121)	63	30
	300	(149)	320	531
	350	(176)	440	526
N_2 Dry	250	(121)	7.6	1.3
	300	(149)	417	234
	350	(176)	648	610

exponential function of the mix temperature (Figure 2). Regression coefficients approaching unity strongly suggest that temperature alone, if free sulfur is present in the mix, control H_2S and SO_2 emission levels.

SO_3 was measured for all samples prepared at each of the respective mix temperatures. Only the high sulfur mix MD-3 at 350°F (176°C) resulted in any measurable SO_3. The vapor flux value was 2.8 mg/kg/min.

Organic Contaminants

The apparatus used to collect organic emissions is shown in Figure 3. Collection of organic emissions entailed heating the sample to a desired temperature, followed by a sweep gas purge into refrigerated solvent (benzene, hexane, petroleum-ether, etc.) traps. A sweep gas was drawn over the sample at a rate of 2 liters per minute for 15 minutes.

Contents of a 2-trap series were combined, passed through anhydrous Na_2SO_4, and reduced in volume by vacuum distillation for subsequent gas chromatographic (GC) analyses. Mercaptans were screened separately by a selective trapping technique [15, 16]. A bubble containing 25 ml of a 5% $HgCl_2$ solution with 0.3 ml of 5% NaOH which was added to adjust the pH was placed in-line with the sweep gas in lieu of refrigerated solvents. Two-glass fiber filters impregnated with $KHCO_3$ and $ZnCl_2 + H_3BO_3$ immediately preceeded the bubbles to scrub SO_2 and H_2S gases, respectively. Mercaptans and disulfides were purged with H_2 gas from the Hg complex into refrigerated pentane following acidification of the bubbles contents with 20% HCl. Pentane traps were combined, dried over anhydrous Na_2SO_4 and reduced to a suitable volume for gas chromatographic analysis.

The instruments used for analyses were a Tracor Model 550 equipped with both flame ionization (FID) and flame photometric (FPD) detectors, and a Tracor Model 560 GC equipped with dual FID detectors. An in-line 394 mμ filter was used for operation of the FPD in a sulfur specific mode. A standardization study was initiated to evaluate the detector response. Responses were measured in integration units (IU) relative to the moles of carbon and moles of sulfur injected in a complex array of structurally dissimilar materials. Materials used in the standardization study are shown in Table 5.

Trapped emissions were first screened for hydrocarbons using the FID detector system, followed by a second chromatographic analysis using the FPD in the sulfur mode. Compounds containing carbon and sulfur will show up in both GC scans. However, some organo-sulfur compounds of minute concentration may not be detected by FID, but show up by FPD, due to the latter's greater sensitivity.

Hydrocarbons emissions from mix designs formulated at 350°F are given in Figure 4. Two principles were used to determine which organic emissions, if any were present, would be considered significant. All emissions that could be attributed to normal asphalt were eliminated from consideration. This is not to imply that there is no hazard associated with these emissions, only that the scope of this work was limited to emissions induced by the use of sulfur. Also, organic emissions are not considered significant unless they exceed 1 ppm under the test conditions. Interpretation of the data based on these principles show no organic compound present in emissions at the 1 ppm level. At the temperatures in the study no significant amount of organic emissions, sulfur containing or otherwise, were detected above that normal to asphalt. FID scans of MD-2, MD-3, MD-4, MD-5, and MD-7 were developed following concentration to volumes suitable to detect 1 ppm of a $C_{11}H_{22}$ hydrocarbon relative to the total volume of sweep gas trapped. FID scans for MD-1 and MD-6 were concentrated even more than required to demonstrate the similarities between characteristic GC profiles developed for a sulfur-asphalt mix and virgin asphalt.

Sulfur containing emissions were found to increase significantly with

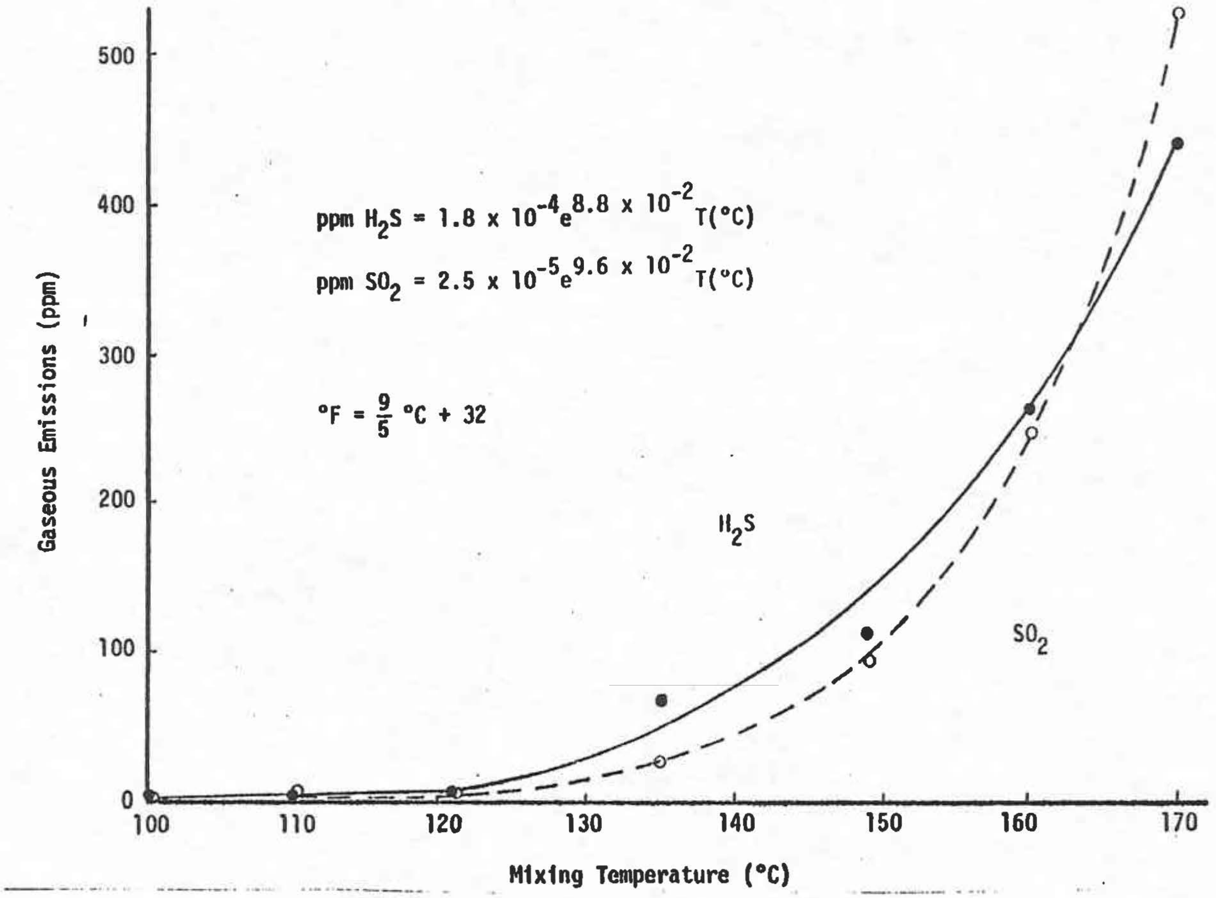


Figure 2. H_2S and SO_2 Emissions from MD-3 as Influenced by Mix Temperature-Controlled Environment.

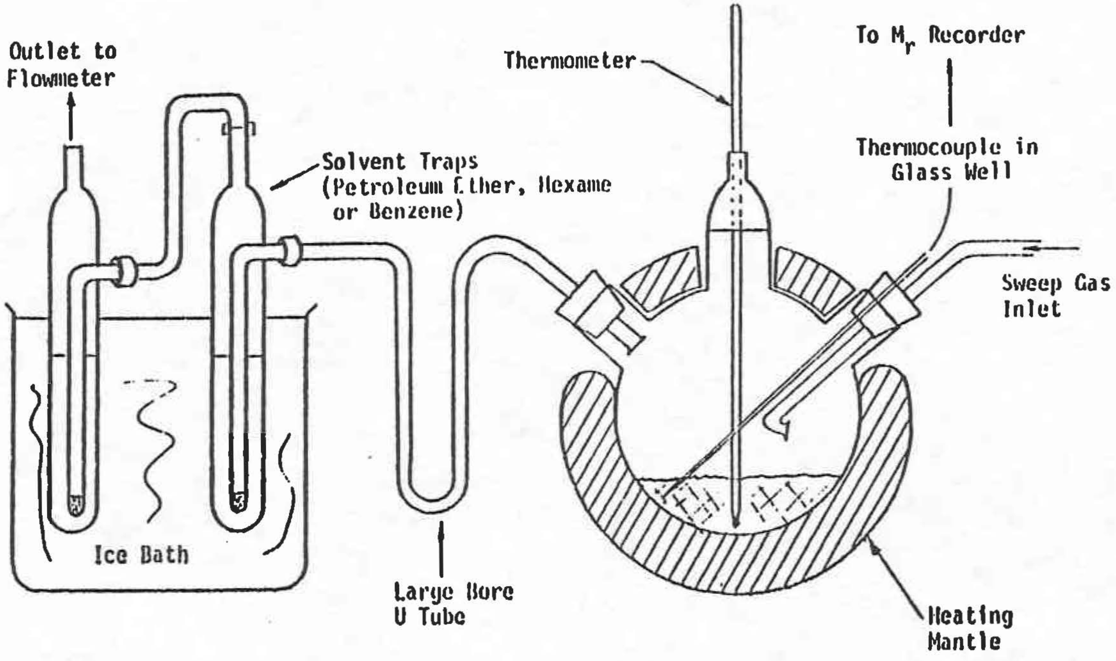


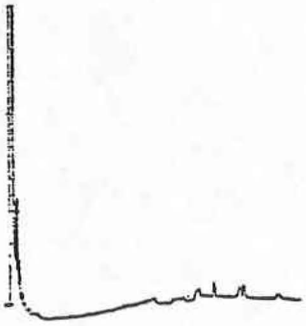
Figure 3. Apparatus Used to Collect Organic Emissions.

Table 5. Sulfur Compounds and Hydrocarbons Employed in Detector Response Study.

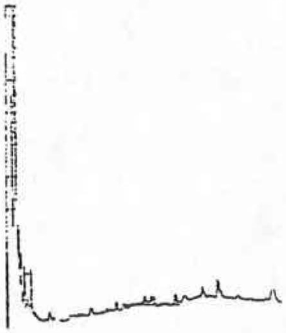
	DETECTOR RESPONSE	
	Flame Ionization	Flame Photometric
Hydrocarbon	IU*/mole of Carbon x 10^{12}	IU*/mole of Sulfur x 10^{13}
Anthracene	1.3	
Biphenyl	1.3	
Dibenzothiophene	1.4	3.8
Fluoranthene	1.5	
n-Hexadecane	1.4	
n-Hexacosane	1.5	
Napthalene	1.4	
n-Phenyls Carbazole	1.3	
o-Terphenyl	1.4	
Tetraphenylethylene	1.3	
1, 3, 5-Triphenylbenzene	1.3	
Triphenyl methane	1.4	
Xanthene	0.9	
-Butyl mercaptan		3.2
n-Hexyl mercaptan		4.3
n-Heptyl Mercaptan		4.4
Diethyl Sulfide		6.4
Diallyl Sulfide		6.1
Di-n-butyl Sulfide		5.2
Carbon Disulfide		3.8

*IU = Integration units.

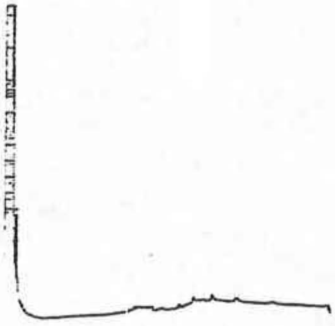
MD-1
2.7 ul
0.3 ml benzene
FID



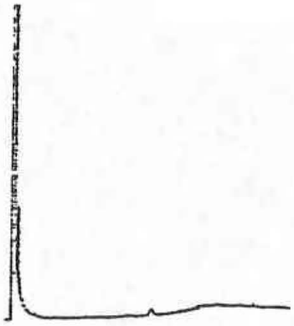
MD-2
2.7 ul
1.4 ml benzene
FID



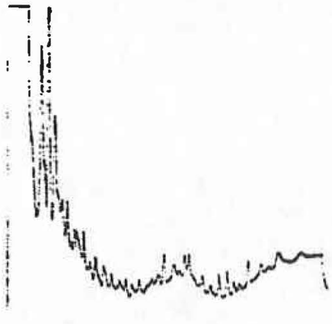
MD-3
2.5 ul
1.1 ml benzene
FID



MD-4
2.6 ul
2.6 ml benzene
FID



MD-5
2.5 ul
1.6 ml benzene
FID



MD-6
2.5 ul
0.3 ml benzene
FID

MD-7
2.6 ul
3.3 ml benzene
FID

Figure 4. Hydrocarbon Emissions from Mix Designs Formulated at 350°F (176°C).

increased mix temperature for all but MD-6. The temperature effect is demonstrated for the high sulfur mix MD-3 in Figure 5. A comparison of the FPD scans at the high mix temperature of 350°F (Figure 6) clearly demonstrates that the sulfur containing peak is independent of the asphalt used in mix. Only the large peak is of significant magnitude, although numerous other sulfur compounds were detected. The one sulfur containing compound present in significant amounts was identified as elemental sulfur using mass spectroscopy.

Mass Balance

Based on the fact that no significant organo sulfur compounds were generated at the high mix temperature, a mass balance was utilized to quantitate elemental sulfur emission levels. Elemental sulfur emissions were estimated by difference between total sulfur lost and the sum of that accounted for as H_2S, SO_2 and SO_3. Organic sulfur was too minute in quantity to have any effect on the material balance. Sulfur lost was measured by subtracting the difference between initial sulfur levels and those measured on residues retained in the reaction vessel. Total sulfur was analyzed by the LECO Combustion Method whereby sulfur is oxidized in an induction furnace to SO_2, transferred to the LECO 532 Automatic Titrator and measured by idometric titration. Several NBS sulfur standards were used to calibrate the buret against known quantities of sulfur.

The sulfur balance developed for the various formulations mixed at 250, 300 and 350°F (121, 149 and 176°C) are given in Tables 6, 7, and 8, respectively. It can be seen from this data that the bulk of sulfur lost during formulation will be as elemental sulfur, particularly at the lower mix temperature. Although total sulfur lost by the sulfur asphalt mix designs increased with increased temperature, that lost as elemental sulfur was diminished, corresponding to increased H_2S and SO_2 emissions.

A much lower percentage of sulfur incorporated in MD-7 was lost compared to the other sulfur-asphalt materials, and all emissions were conserved at 350°F (176°C).

EMISSIONS GENERATED DURING CONSTRUCTION

Field Trials

An assessment of the typical concentration levels of H_2S, SO_2 and sulfur particulates which may be anticipated during the construction of a sulfur-asphalt pavement can be made using emissions data which were collected during the experimental field trials in Lufkin-1975 [17], Kenedy County-1977 [18] and Brazos County-1978 [19], Texas. Of the three, the most extensive was conducted at the SAS trials in Kenedy County which involved personnel and equipment from TTI, the Bureau of Mines and the Texas Air Control Board (TACB). The Lufkin and Brazos County projects dealt with SEA mixtures.

TACB data was obtained using their mobile sampling van which was equipped with a Meloy SA1655 total sulfur analyzer, Houston Atlas H_2S tape sampler and an Interscan Model 1176 H_2S analyzer. An Omniscible Model 5213-15 dual pen chart recorder was used to record signals from the Meloy and Interscan instruments and a Weather Measure Corporation electronic polyrecorder Model EPR - 200A was used to record signals from the Houston Atlas unit.

The mobile van moved about the various sampling sites at the discretion of TACB personnel. Specifically, measurements were taken at the following locations: sulfur storage tank, hot-mix plant mixing chamber and the paver hopper and auger. Additional measurements were

Table 6. Sulfur Balance for Materials Mixed at 250°F (121°C).

	Mix Design Number*						
	1	2	3	4	5	6	7
	Weight of Sulfur, mg						
Total S	84.3	74.1	467.0	61.2	78.3	13.8	55.2
Residual	59.5	41.3	345.3	27.1	32.9	14.1	46.6
Total Emission	24.8	32.8	122.7	34.1	45.4	--	9.6
H_2S-S	0.1	0.5	0.4	0.4	0.2	--	--
SO_2-S	0.1	0.3	0.2	0.3	0.1	--	0.1
Total	0.2	0.8	0.6	0.7	0.3		
Elementals	24.6	32.0	122.1	33.4	45.1	--	9.5

Table 7. Sulfur Balance for Materials Mixed at 300°F (149°C).

	Mix Design Number*						
	1	2	3	4	5	6	7
	Weight of Sulfur, mg						
Total	84.3	74.1	467	61.2	78.3	13.8	55.2
Residual	25.7	23.4	314.3	22.9	29.4	12.4	45.7
Total Emission	58.6	50.7	152.7	38.3	48.9	1.4	9.5
H_2S	0.4	8.3	12.5	1.1	1.3	.1	2.7
SO_2-S	0.4	3.9	2.8	0.6	0.6	.1	0.6
Total	0.8	12.2	15.0	1.7	1.9	0.2	3.3
Elementals	57.8	38.5	137.7	36.6	47.0	--	6.2

*Mix designs are given in Table 1.

Table 8. Sulfur Balance for Materials Mixed at 350°F (176°C).

	Mix Design Number*						
	1	2	3	4	5	6	7
	Weight of Sulfur, mg						
Total S	84.3	74.1	467	61.2	78.3	13.8	55.2
Residual	18	24	207.5	18.7	26.1	13.6	40
Total Emission	66.3	50.1	259.5	42.2	43.3	0.2	15.2
H_2S-S	4.0	14.8	19.4	8.9	8.3	0.1	10.7
SO_2-S	2.1	7.5	9.2	4.2	3.9	0.1	4.9
SO_3-S	--	--	2.8	--	--	--	--
Total	6.1	22.3	31.4	13.1	12.2	0.2	15.6
Elemental Sulfur	60.2	27.8	230.9	29.1	31.1	0.0	0.0

*Mix designs are given in Table 1.

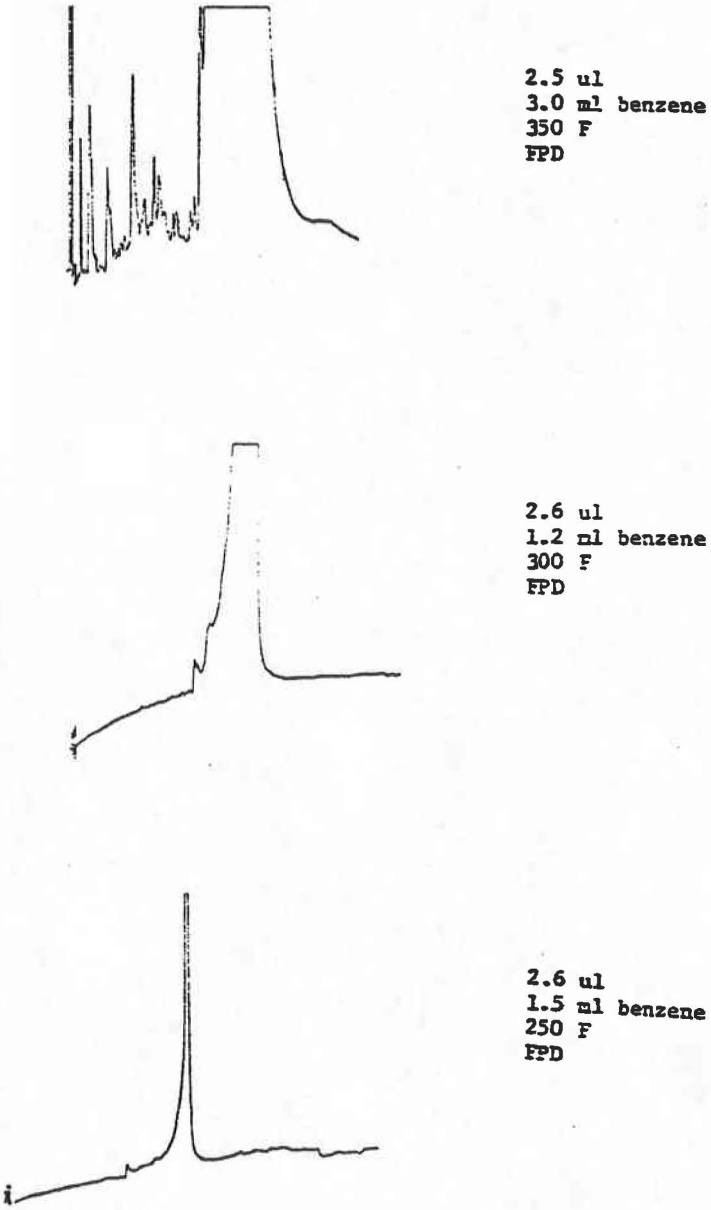
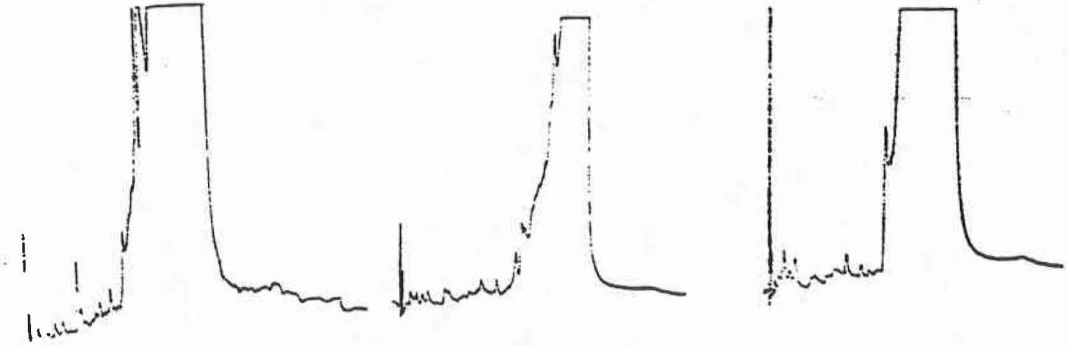


Figure 5. Sulfur Containing Emissions at 250, 300, and 350°F (121, 149, and 176°C) for MD-3.



MD-1
2.4 ul
1.4 ml benzene
FPD

MD-2
2.6 ul
2.0 ml benzene
FPD

MD-4
2.5 ul
1.8 ml benzene
FPD

MD-5
2.6 ul
3.3 ml benzene
FPD

MD-6
2.6 ul
3.0 ml benzene
FPD

MD-7
2.4 ul
2.5 ml benzene
FPD

Figure 6. Sulfur Containing Emissions at 350°F (176°C) for MD-1, MD-2, MD-4, MD-5, MD-6, and MD-7.

taken downwind of the plant and paver so as to establish dissipation factors.

Except for downwind samplings, most of the emissions readings generated by TACB were considered to be source type data; that is measurements were taken directly over the mixture. This was accomplished using a Midget Impinger Gaseous Air Sampling Train (MIGAST). MIGAST samples were taken using Bendix Telematic 150A automatic air samplers with a cadmium hydroxide absorbing solution. Samples were collected with 5-ft. length probe of 3/8 in O.D. stainless steel tubing. Gases were sucked back to the analyzer through a 1/4 in. polythylene tube by a Metal Bellows Company, Model MB-41 pump. Samples were collected by placing the probe tip at distances which ranged from 1 to 12 inches from the suface of the material from which the gases were being evolved. These distances are much less than that normally occupied by personnel (normally 3 to 6 ft.) hence the designation "source data" were assigned to these samplings. As a backup to the source data collected by TACB, both TTI and The Bureau of Mines samplings were obtained at locations more representative of those which might be expected to be occupied by personnel.

One such area was on the platform of the hot-mix plant where the various mix ingredients were introduced into the pug mill. Continuous samplings over a 24-hour period were taken in the vicinity of the manually operated feed controls at a height equal to nose level of the operator. Additional 24-hour continuous samplings were taken at a point under the pug mill and just over the dump bodies of the trucks. Both of these points were monitored using a Houston Atlas Sampler of the type mentioned above. This unit was furnished by The Bureau of Mines Metallurgy Research Laboratory of Boulder City, Nevada.

TTI personnel took samplings for both H_2S and SO_2 using two types of portable sensing instruments. A Metronics Model 721 "Rotorod" Gas Sampler which is designed for monitoring only H_2S emissions was used to collect data in the vicinity of the plant, within the quality control testing laboratory, inside the cab of hauling trucks, at the paver operator's seat, alongside the paver at the hopper and at the auger and in the vicinity of the sulfur storage tanks.

The Rotorod Gas Sampler spins a disc on which is mounted a lead acetate treated pad. Upon exposure to H_2S the pad changes color which can be compared with 5 standards located around the perimeter of the treated pad. The color grade number of the stain produced on the pad and the duration of the sampling time are then converted to H_2S concentrations using a manufacturer's monograph. Colortek cards were also mounted on walls and other locations where sampling duration times were greater than 30 minutes.

The other portable sampler employed was a Drager Tube Sampler with a manually operated bellows. Appropriate callibrated tubes for monitoring both H_2S and SO_2 were used with this device.

Samplings were taken at essentially the same locations monitored by the Metronics Rotorod Sampler. Drager tube measurements of H_2S concentrations thus provided a back up to those taken with the Rotorod Sampler.

Discussion of Results of Evolved Gas Analysis

Hydrogen Sulfide

The results of the measurements taken of H_2S concentrations at various locations of the construction site and plant given in Tables 9 to 11. Table 9 includes data taken at and in the vicinity of the hot mix plant and sulfur storage area. Table 10 contains emissions monitored in the

Table 9. H_2S Emissions At and In the Vicinity of the Hot Mix Plant.

Location	Sampling Agency	Sampling Equipment	Average Concentration (ppm)	Remarks NPA - non personnel area PA - Personnel area
Sulfur Storage Tank Area				
a) Tank Inlet Port	TACB	Telematic	2939	NPA
b) 5 ft. from Tank Inlet Port	TACB	Telematic	23	NPA
c) On the ground at the base of the sulfur storage tank	TTI	Rotorod	0.9	PA (moderate)
d) Ground level between sulfur tank and Hot Mix Plant Kiln	TACB	Telematic	0.02	PA (moderate to dense)
Hot Mix Plant Area				
a) Operator Platform	TACB	Telematic	>0.007	PA (1-2 people)
	BOM	Houston-Atlas	0.5 to 2.0	PA (1-2 people)
	TTI	Rotorod	Trace	PA (1-2 people)
	TTI	Drager Tube	Trace	PA (1-2 people)
b) Base of Platform	TTI	Rotorod	Trace	PA (light)
Stairwell	TTI	Drager Tube	Trace	PA (light)
c) At Pugmill Discharge and Over Dump Body	BOM	Houston-Atlas	0.5 to 0.6	NPA
d) 125 ft. downwind of Hot Mix Plant	TACB	Telematic	0.01	PA (light)
	TTI	Rotorod	Trace	PA (light)

Table 10. H_2S Emissions At and In the Vicinity of the Paver.

Location	Sampling Agency	Sampling Equipment	Average Concentration (ppm)	Remarks NPA - non personnel area PA - personnel area
Paver				
a) Floor at Paver Operator's Feet	TACB	Telematic	1.4	PA (1 person)
b) In Paver Operator's Chair	TTI	Rotorod	Trace	PA (1 person)
	TTI	Drager Tube	Trace	PA (1 person)
c) Paver Hopper	TACB	Telematic	4.3	NPA
	BOM/TTI	Drager Tube	2-5	NPA
d) Alongside Paver (at Auger) Downwind	BOM/TTI	Drager Tube	0-20*	PA (1-2 people)
e) Over Paver Auger	BOM/TTI	Drager Tube	20-80*	NPA
Paver Vicinity				
a) 300 ft. Upwind	TACB	Telematic	0	PA (light)
b) 25 ft. Downwind	BOM/TTI	Drager Tube	0	PA (light)
c) 100 ft. Downwind	TACB	Telematic	0.2	PA (light)
d) 200 ft. Downwind	TACB	Telematic	0	NPA
Over Pavement Behind Paver				
a) 6 in. over surface	TACB	Telematic	1.3	NPA
b) 2 ft. over surface	BOM/TTI	Drager Tube	Trace	NPA

* Highest concentrations were encountered during a period when temperature control of the screed was lost causing mix temperature to exceed 320°F. When temperature was reduced below 300°F concentrations were reduced to near minimum values.

vicinity of the paving operation. Table 11 includes all other areas monitored. Data are presented in a manner to reflect location, sampling agency (TACB, TTI or both), sampling equipment, average concentration and supporting remarks.

As has been reported earlier as long as the temperature of sulfur/asphalt systems was maintained below a maximum of 300°F H_2S emissions were found to be well below suggested MAC values. Except for several occassions when screed temperature was purposely allowed to exceed 300°F, H_2S concentrations as measured in locations normally frequented by construction personnel were found to be significally less than 5 ppm. The fact that no complaints were registered during the entire sulfur/asphalt construction period supports this conclusion. In some cases "source type" emissions; that is samplings taken directly over the mix material, appeared to be excessively high. However in an open-air environment these concentrations are rapidly reduced with distance.

The highest concentrations encountered were at or near the loading port of the sulfur storage tank and inside the pug mill. Since these are not considered to be personnel areas their impact on worker safety is considered to be minimal.

Sulfur Dioxide

All measurements of SO_2 concentrations were monitored by TTI using the Drager Tube. The data given below show the ranges of SO_2 concentrations measured at various locations at the paving site.

Location	Range
Above paving hopper	0 - 0.5
Alongside paver (downwind)	0.5 - 20
Behind paver	0
Paver operator seat	0
Hot mix plant platform	Trace
Inside truck cab	Trace
Vicinity of sulfur storage tank	3 - 12
Alongside paver (over the auger)	3 - 50
Directly over paved surface	0

As indicated, the values varied considerably with some concentration levels exceeding the MAC value recommended by the ACGIH. These values were obtained primarily in areas of minimal worker exposure such as the vicinity of the sulfur storage tank and very close to the material in the paver. The latter were attributed to the temporary overheating of the paver screed. After these readings were taken the screed temperature was reduced and the concentrations subsequently were reduced to the lower values indicated above.

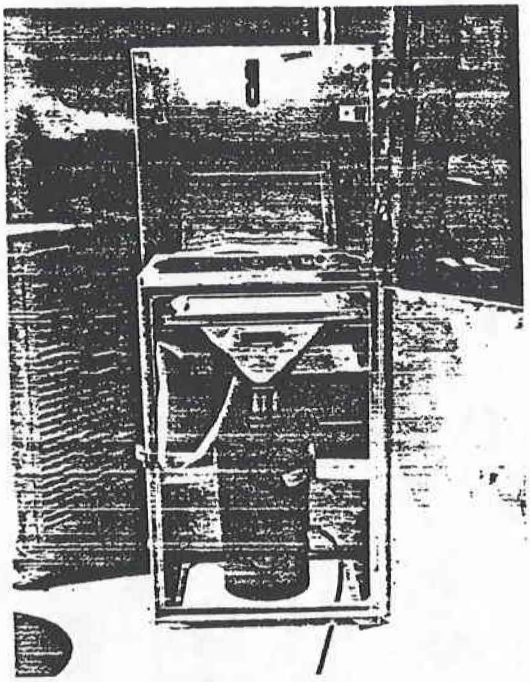
The paver screed without suitable temperature controls, would appear to be the main source of potentially high H_2S and SO_2 emissions. At the operator and workmen levels on the paver and at the hot mix plant platform gas toxicity were negligible. As in the case with H_2S, gas evolution stayed well below established MAC limits when mix and paving temperatures were maintained under 300°F.

Particulate Sulfur

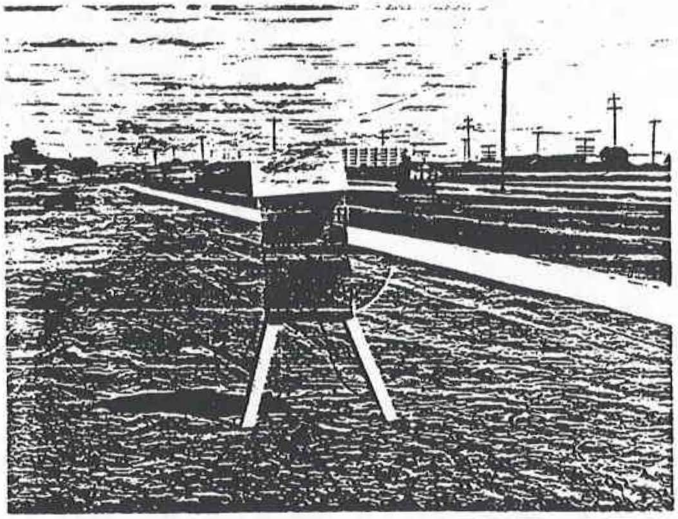
Measurements of particulate sulfur evolved at various locations of the construction site were made using a Hi-Vol Dust Collector manufactured by General Metal Works, Inc. of Cleaves, Ohio. (See Figure 7). During operation air is drawn into a covered housing and through a filter by means of a high flow rate blower at flow rates of 40 to 60 cfm (1.13 to 1.70 m^3/min

Table 11. H_2S Emissions at Miscellaneous Locations.

Location	Sampling Agency	Sampling Equipment	Average Concentration (ppm)	Remarks
Dump Trucks				
a) Inside Cab at Hot Mix Plant	TTI	Rotorod	>0.1	PA (1 person)
b) Inside Cab at Paver During Dump	TTI	Rotorod	0	PA (1 person)
c) Over Inlet to Dump Body	TTI	Rotorod	0.2	NPA
d) Inside Dump Body During Cleaning Operation	TTI	Rotorod	0.3	PA (1-2 persons)
Hot Mix Plant Quality Central Test Laboratory	TTI	Rotorod	Trace	PA (2-3 persons)
Hot Mix Plant Parking Area	TTI	Rotorod	0	PA (light)
At Sulfur Truck During Transfer to Storage Tank	TTI	Rotorod	0.4	PA (1-2 persons)



a. Internal View.



b. On location at the paving site.

Figure 7. Hi-Vol Dust Collector Used for Sampling Sulfur Particulates.

that allows suspended particles having diameters of less than 100 microns to pass to the filter surface. Particles with size range of 100 to 0.1 micron diameter are ordinarily collected in glass fiber filters. The mass concentration of the suspended particulates in the ambient air is computed by measuring the mass of collected particulates and the volume of air sampled.

The high volume air samplers were set up at four locations, two along the roadside at the paving site and two at the hot mix plant. Table 12 shows the details of the particulate sulfur measurements. Although standards vary from state to state, the allowable particulate density for an 8 hour day is in the order of 100 $\mu g/m^3$ [20].

CONCLUSIONS

A number of typical sulfur-asphalt and sulfur-concrete paving systems were evaluated to assess their potential environmental impact and established safety considerations. The evolution of sulfur based pollutants, primarily H_2S, SO_2 and particulate sulfur was investigated from the mix preparation stages through construction.

In the formulation phase the influence of sulfur in seven mix designs was examined against mix temperature,humidity and oxygen content of the air. The results generated in this study tend to support the data generated by others in the laboratory as well as the field that, as long as the mix temperature is kept below 300°F, evolved gases and pollutants can be maintained within safe limits. The conclusions do not apply when sulfur-asphalt mixture are processed or stored in closed environments such as silos and hoppers for prolonged periods of time. Effects of humidity and oxygen were found to be negligible.

As part of the FHWA study [1] a Field Evaluation Document (Volume II) was produced for use by contractors and state agencies to establish worker safety and for the identification of potential hazards at the various locations on a sulfur-asphalt construction site. Recommended clothing and first aid procedures were also included in this document. Handling practices already established in the sulfur industry as well as those common to the asphaltic concrete community are considered to be sufficient to assure adequate personnel safety.

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TABLE 12. Particulate Sulfur Measurements - Brazos County, Texas [19]

Location	Particulate Material, mg	Total Sulfur, mg	Total Particle Concentration $\mu g/m^3$	Sulfur* Concentration $\mu g/m^3$
Paving Site, 35 ft east of paver Engineer Station 57/10	120	0.65	206	1.12
same	140	0.63	250	1.13
Hot-Mix Plant, on Ground Between Colloid Mill and Pug-Mill	1275	1.63	2300	4.10
same	1010	0.60	1126	2.94
Hot-Mix Plant, Downwind Northerly	200	0.01	500	0.06

* Not exclusively particulate sulfur

Note: Measurements were conducted over an 8 hour sampling period

The total particulate matter collected by the High Volume units were analyzed by following ASTM Standard E 30-47.

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