PB83-156687

Field Environmental Evaluation Plan For Sulfur Use In Pavements

Offices of Research
and Development
Washington, D.C. 20590

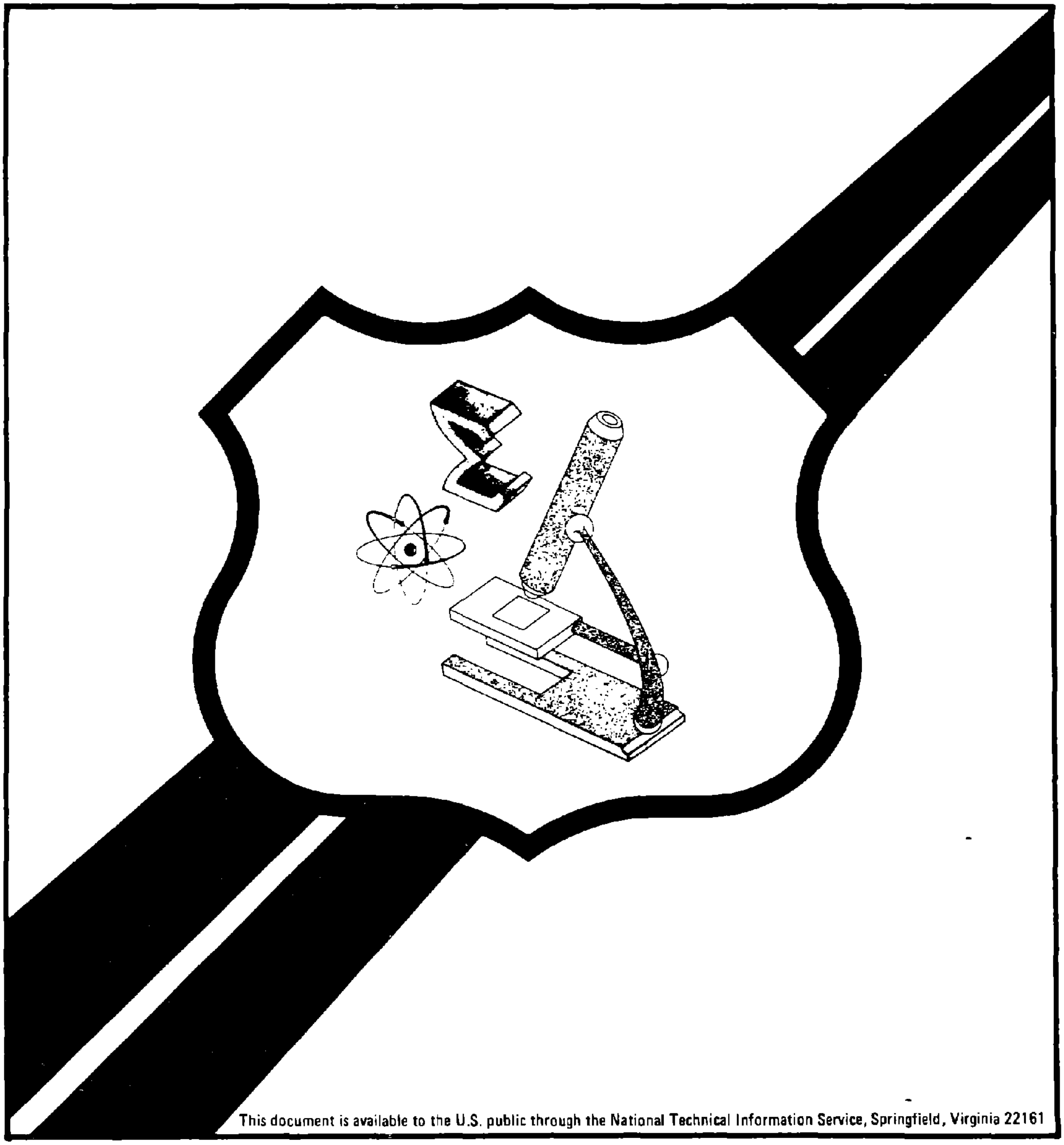
Report No.
FHWA/RD-80/192

Vol. II

Final Report
July 1982

U.S. Department
of Transportation

Federal Highway
Administration



FOREWORD

This report presents field environmental evaluation procedures for the use of sulfur in highway pavements. It is based on the results of a detailed investigation of pollutants generated, their environmental impact and the safety aspects associated with mix preparation and placement.

The evaluation procedures deal with the safety and environmental aspects of storage and handling, formulation, construction, operation and maintenance of highway pavements containing sulfur, including the possible generation of noxious and obnoxious fumes, dust, and gases. This report discusses methods and equipment for monitoring potential emissions and pollutants and recommends safety practices for the handling of sulfur in sulfur-modified asphalt pavements. It will be of interest to research and operations personnel responsible for highway construction and maintenance.

This report is being distributed in sufficient numbers to provide a minimum of two copies to each regional and division office and five copies to each State highway agency. Additional copies of the reports for the public are available from the National Technical Information Service (NTIS), Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.

Charles F. Scheffey
Director, Office of Research

NOTICE

Technical Report Documentation Page

1. Report No. FHWA/RD-80/192	2. Government Accession No.	3. Recipient's Catalog No. PB83 156687

4. Title and Subtitle
Environmental and Safety Aspects of the Use of
Sulfur in Highway Pavements - Volume II
Field Evaluation Procedures

5. Report Date
July 1982

6. Performing Organization Code

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8. Performing Organization Report No.

9. Performing Organization Name and Address
Texas Transportation Institute
The Texas A&M University System
College Station, Texas 77843

10. Work Unit No. (TRAIS)
FCP 34G1-103

11. Contract or Grant No.
DOT-FH-11-9457

12. Sponsoring Agency Name and Address
Offices of Research and Development
Federal Highway Administration
U. S. Department of Transportation
Washington, D. C. 20590

13. Type of Report and Period Covered
June 1978 - Feb. 1982
Final Report

14. Sponsoring Agency Code
MTC/0014

15. Supplementary Notes
FHWA Contract Manager, Brian Chollar (HNR-40)

16. Abstract

The use of sulfur in highway paving mixtures has introduced questions regarding the pollutants generated, their environmental impact and the safety aspects associated with mix preparation and placement. This report presents the Field Evaluation Procedures based on the results of a more detailed investigation in which these factors were assessed.

The evaluation procedures deal with the safety and environmental aspects of storage and handling, formulation, construction, operation and maintenance of highway pavements containing sulfur, including the possible generation of noxious and abnoxious fumes, dust and gases. This report discusses methods and equipment for monitoring potential emissions and pollutants and recommends safety practices for the handling of sulfur and sulfur-modified asphalt mixtures and pavements.

The final report was prepared in three volumes of which the Field Evaluation Procedures is Volume II. The other two volumes are: Volume I - Evaluation of Environmental and Safety Hazards and Volume III -Annotated Bibliography.

17. Key Words
Sulfur, asphalt, concrete, emissions, pollutants, toxicity, fumes, dust,Hydrogen sulfide, sulfur dioxide, soils, organic sulfur, safety, hazard, environmental imput, vegetation, structures.

18. Distribution Statement
No restriction. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	58	

Form DOT F 1700.7 (8-72) Reproduction of completed page authorized

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1 OVERALL PROGRAM PURPOSE, SCOPE, AND OBJECTIVES

1.1 Purpose.

The purpose of this investigation was to evaluate the environmental and safety hazards along with the development of safety guidelines associated with the use of sulfur in highway pavements. This was accomplished by virtue of a series of laboratory and simulated field tests in which the safety and environmental aspects of materials storage and handling, formulation, construction, operation and maintenance of highway pavements containing sulfur were evaluated. The structuring of these tests and the evaluation of the results were complemented by the preparation of a field evaluation plan in which the sources, relative toxicity, safety and methods of monitoring and analyzing pollutants were identified. An annotated bibliography specifically oriented to the safety and environmental effects associated with sulfur-modified paving materials preparation and construction was also prepared.

1.2 Scope and Objectives.

The long range objectives of the study were to evaluate the environmental and safety hazards and define some safety guidelines for the use of sulfur in highway pavements. Consideration was given to the possible evaluation and identification of toxic and obnoxious fumes, dusts and runoffs which might be produced during formulation, storage, construction and maintenance of sulfur modified paving materials. This scope also considered effects on humans, animals, soils, highway structural materials, ground waters and vegetation. The investigation was carried out in four tasks:

Task A - Laboratory Identification and Evaluation of Hazardous
Materials and Conditions

Task B - Human Safety and Environmental Aspects

Task C - Field Evaluation Plan

Task D - Annotated Bibliography

and the final report was prepared in the following three volumes to provide a basis for selective and more cost effected distribution.

Volume I - Evaluation of Environmental and Safety Hazards

Volume II - Field Evaluation Plan

Volume III - Annotated Bibliography

Volume I contains primarily the results of the effort in Task A - Laboratory Identification and Evaluation of Hazardous Materials and Conditions; Task B - Human Safety and Environmental Aspects, the conclusions and recommendations generated in Task C - Field Evaluation Plan, and a discussion of the scope of the annotated bibliography - Task D. Volume II provides a more detailed treatment of the field evaluation plan and Volume III the individually synopsized list of references. The latter have been codified, cross referenced and set up to permit easy updating.

2 FIELD EVALUATION PLAN - TASK C

2.1 General.

The purpose of the field evaluation plan is to describe those operations and situations in the construction, maintenance, and salvage of sulfur-modified pavements where a hazard may arise, to convey a judgment of the acceptability/unacceptability of the risk, and to recommend practices for personnel and the prevention of accidents.

A distinction is made between exposure, hazard, and risk as follows:

1) Exposure is defined as the situation of being subjected to an environmental condition.
2) Hazard is an interrelationship among workers and environmental characteristics such that an accident becomes possible or such that the worker is exposed to toxic substances or dangerous fumes, dusts, and gases [1].
3) Risk is defined as the degree or likelihood of the hazard.

In general, the current standards for job safety as set forth by the Occupational Safety and Health Administration (OSHA) or by OSHA approved state or local programs are used as guidelines [2, 3]. A distinction is made between the workplace and non-personnel areas, the latter being described as areas of obvious hazard normally shielded from worker access (i.e., worker exposure is unlikely).

A further objective of this report is to describe those operations and situations in the construction, maintenance, and salvage of sulfur-modified pavements where air pollution may arise, to convey a judgment of the acceptability/unacceptability of the air contaminant, and to recommend practices for air pollution control. In general, the Environmental Protection Agency (EPA) rules and regulations, as administered by state and local authorities, are used as guidelines [4, 5].

The Field Evaluation Plan begins with the description of hazards generally encountered in handling liquid sulfur. Symptoms of exposure to these hazards are described and first aid treatment is presented. Sulfur has been used in the paving industry to replace a portion of the asphalt binder, or used as a structuring agent by playing the role of an aggregate in upgrading marginal aggregates, or used to completely replace asphalt or cement as a binder when suitably plasticized with additives. These types of pavements are described and the evaluation of risks and safety recommendations associated with operations and situations of sulfur-modified asphalt paving are enumerated. Types of exposures, sources of the exposures, factors affecting the exposure levels, risk evaluation, and recommendations are given.

The last section of the Field Evaluation plan describes the types of monitoring systems that may be necessary in order to comply with existing environmental laws and a description of the operational principles of some currently available instrumentation for monitoring emissions that may be applicable to the sulfur-modified asphalt paving operations and situations.

2.2 Hazards Associated with Handling Liquid Sulfur .

Liquid sulfur is normally handled at a temperature range of 270°F to 290°F (132°C-143°C) [6]. Within this range, it is not corrosive to steel or aluminum unless trapped water or acid is present [6, 7, 8]. Above 320°F (160°C), toxic gases form and increase as temperature continues to rise. The primary hazards due to the presence of sulfur in the pavement operations and handling situations are gaseous emissions of hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) as well as airborne particulate sulfur. These hazards can usually be gauged in terms of temperature, time duration of temperature, and dispersion factors.

Hydrogen sulfide gas, which may be released from liquid sulfur, is extremely toxic to humans. The relative toxicity of H_2S has been documented with corresponding physiological responses to various concentrations and presented in Tables 1 and 2. On the basis of these effects, a maximum allowable concentration (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 [9].

It is dangerous to rely on odor as a measure of concentration because in higher concentrations or long exposures, hydrogen sulfide paralyzes the sense of smell. The chief effects of H_2S are on the eyes, nose, throat, and lungs. An exposure sufficient to cause unconsciousness may lead to an injurious fall, may be fatal in itself, may be followed by bronchial pneumonia, or by temporary blindness [9, 10, 11, 12, 13].

Sulfur dioxide (SO_2) is highly irritating to the eyes, nose, throat, and lungs in concentrations greater than 6 to 20 ppm (by volume). At 150 ppm, the irritation is almost unbearable. Concentrations in excess of 500 ppm result in suffocation [6]. The basis for establishing the relative toxicity of emissions data generated during construction is the relationship between SO_2 concentrations (ppm) and human effects as specified by the National Institute for Occupational Safety and Health

Table 1. Physiological Symptoms at Various Levels of Exposure to H_2S [19, 29, 30, 31, 32].

Concentration, ppm	Physiological Symptoms
0.02	odor threshold
0.1	beginning eye irritation
5-10	suggested maximum allowable concentration (MAC)
50-100	slight conjunctivities and respiratory tract irritation after 1 hour of exposure
100	coughing, eye irritation, loss of sense of smell after 2 to 15 minutes
	altered respiration, pain in the eyes, drowsiness after 15 to 30 minutes, followed by irritation after 1 hour
	several hours exposure results in gradual increase in severity of these symptoms and death may occur within the next 48 hours
200-300	marked conjunctivities and respiratory tract irritation after 1 hour of exposure
500-700	loss of consciousness and possibility of death in 1/2 to 1 hour
700-1000	rapid unconciousness, cessation of respiration and death
1000-2000	unconsciousness at once, with early cessation of respiration and death in a few minutes (death may occur even if the individual is removed to fresh air at once).

Table 2. Olfactory Responses to Various Concentrations of H_2S [19, 32].

Concentration, ppm	Olfactory Response
<0.02	No odor
0.13	Minimal perceptible odor
0.77	Faint but readily perceptible odor
4.6	Easily detectable, moderate odor
27.0	Strong, unpleasant odor, but not intolerable
<90.0	Can no longer smell H_2S; paralysis of olfactory nerves

(NIOSH) from the Manufacturing Chemists Association [14, 15]. This relationship is given in Table 3. The MAC specified as the upper threshold limit concentration for SO_2 emissions is 5 ppm in areas normally expected to be occupied by construction and plant personnel [9, 16]. Exposure to this concentration of SO_2 has no systemic effect [9, 10, 14]. The higher the temperature of sulfur gets above 320°F (160°C), the higher the concentration of H_2S and SO_2 gases generated.

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 of sulfur dust and is carried by the wind. The principal problem of sulfur dust is associated with its contact with eyes. Inhalation of sulfur dust has shown no evidence of systemic poisoning; however, it is capable of irritating the inner surface of the eyelids. Goggles worn by personnel subject to this pollutant will minimize the problem.

Further hazards due to the presence of sulfur are most likely to be the same as those associated with asphalt pavement materials, such as fires, explosions, and burns. Liquid sulfur can be handled safely with the realization that it is hot, it can burn, and the vapor is irritating to the eyes. Liquid sulfur splashed onto the skin in small amounts does not penetrate, it quickly freezes into a thin layer. The resulting first degree burn is less severe than that resulting from momentary contact with a hot sulfur pipe or steam pipe at the same temperature (270-290°F). If the amount of liquid sulfur encountered is greater and the time of contact long, deep third-degree burns will

Table 3. Toxicity of Sulfur Dioxide [14, 15].

Concentration, ppm	Effects
0.3-1	detected by taste
1	injurious to plant foliage
3	noticeable odor
5	maximum allowable concentration (MAC)
6-12	immediate irritation of nose and throat
20	irritation to eyes
50-100	MAC for 30-60 minutes exposure
400-500	immediately dangerous to life

result. This most commonly happens when someone gets a safety boot or shoe full of sulfur [6].

2.2.1 Symptoms of Poisoning.

Sulfur is a mild irritant. It has no immediate adverse effect other than irritation of the eyes, and no long term effect [17, 18, 19].

On the other hand, toxic reactions resulting from exposure to hydrogen sulfide gas are usually acute. Inhalation of a high concentration will produce a dramatically swift poisoning with complete arrest of respiration. The individual falls, apparently unconscious, and may die without moving again [13]. In less acute poisoning, the signs may be nausea, stomach distress, belching, cough, headache, irritation of the eyes, nose, throat, and blistering of the lips. Skin contact with hydrogen sulfide, also, may result in irritation [13].

Exposure to sulfur dioxide gas results in immediate and severe irritation to eyes, nose, and throat. Neither systemic effects nor chronic effects are known [10, 14].

2.2.2 First Aid.

A worker who has been overcome with H_2S or SO_2 gas must be carried at once to fresh air. Artificial respiration must be started immediately if breathing has stopped. If available, oxygen should be administered by a trained operator. With proper equipment and training, breathing can be restored even in a contaminated atmosphere [12, 13, 14, 20, 21].

Inhaled H_2S often acts so quickly on the lungs that there is not time to call a doctor before an attempt must be made to revive the victim. The following steps, therefore, should be taken in the order given:

a) Protect yourself.
b) Summon aid, then proceed with the rescue.
c) Move the victim at once to fresh, pure air.
d) Send for a doctor and an ambulance.
e) If the victim is unconscious and not breathing, immediately apply an approved method of artificial respiration and continue it until natural breathing is restored (or until the victim is pronounced dead by a physician).
f) Keep the patient warm.
g) If it is available, give oxygen mixed with 5% carbon dioxide through a resuscitator [13]. In the initial treatment of the victim, if oxygen mixed with 5% carbon dioxide is not available, it is better to give straight oxygen than none at all.

When a worker is burned by contact with liquid sulfur, clothing and exposed skin is covered with a thin, hard coating of solidified sulfur. Liquid sulfur burns over a small area should be covered with clean, dry dressing. The victim should be treated for shock and removed to a hospital as quickly as possible. Do not remove the sulfur. Where greater areas are burned, no attempt should be made to remove clothing or sulfur from the affected parts because of the danger of tearing the flesh. Instead, cover the affected area with a clean cotton sheet or similar material. Normally, application of burn ointment complicates the removal of foreign matter from the burned area when treatment begins in the hospital [12].

2.3 Sulfur in the Paving Industry.

Sulfur paving operations can be related directly to the practices for construction, maintenance, and salvage of conventional asphalt hot-mix pavements. The sulfur paving mixes, not unlike asphalt hot-mixes, are designed and tested in the laboratory, prepared in asphalt hot-mix plants which have been modified to accommodate the sulfur, and hauled, spread, and consolidated on the roadway using asphalt hot-mix paving equipment modified in some instances to handle the mixes. Asphalt equipment and practices, also with some modifications, will likely be used for maintenance and salvage of sulfur pavements. In fact, sulfur pavements may appear at random with asphalt pavements and machines and practices may be essentially the same.

It follows that a hazard is most likely to arise due to the presence of sulfur in an operation and situation otherwise common to asphalt pavement practices:

1) in the workroom (laboratory) during the design and testing of sulfur-modified pavement mixes,
2) at the stationary source (hot-mix plant) where the materials are stored and paving mixes are prepared,
3) at mobile sources during the hauling and placing of the paving mixes,
4) on the roadway during the maintenance and salvage of the pavement, and
5) on the roadway and at the stationary source (hot-mix plant) where the pavement material is recycled.

2.3.1 Sulfur-Modified Pavement Types.

Research and development have shown that sulfur can be used safely and economically as a paving material. Depending on the manner in which it is introduced, sulfur can be used to replace a portion of the asphalt binder in the Sulfur-Extended-Asphalt (SEA) pavement, or it can be used as a structuring agent by playing the role of an aggregate in upgrading marginal aggregates in the Sand-Asphalt-Sulfur (SAS) pavements. Sulfur can further be added, when suitably flexibilized with additives, to aggregate to replace asphalt as a binder. This sulfur concrete is in the experimental stage, whereas SEA and SAS are considered to be in the demonstration stage of development.

SAND-ASPHALT-SULFUR PAVEMENT (SAS)

SAS pavements are those in which the sulfur is used primarily as a structuring agent for the upgrading or beneficiation of marginal aggregates (sands) and in which, by weight, the amount of sulfur is equal to or more than that of the asphalt. The sulfur content of the pavement will usually be from 10 to 20 weight percent and the asphalt content from 4 to 8 weight percent of the total mix.

The SAS pavement concept was first pioneered by Shell Canada Ltd. [22, 23, 24, 25] and resulted in a patented SAS mix called Thermopave^{R} [26]. In this mixture liquid sulfur is added to asphalt and marginal (open-graded) aggregate. Sulfur fills the interstitial voids around the aggregate particles which, upon cooling, creates a mechanical interlock from which the material derives its strength. Developed primarily for use in areas where quality aggregates are scarce, SAS mixtures prepared with locally available dune sands and beach sands have been shown to have performance characteristics equal to and, in some cases, superior to quality asphaltic concrete mixtures [27, 28].

SULFUR EXTENDED ASPHALT PAVEMENTS (SEA)

SEA pavements are those in which a part of the asphalt is replaced with sulfur and in which, by weight, the amount of sulfur is equal to or less than that of the asphalt. The sulfur content of the pavement will usually be from 1 to 4 weight percent and the asphalt content from 4 to 8 weight percent of the total mix.

Because of the uncertainty of the future availability and cost of asphalt cement, a flurry of research activity in the United States [29, 30, 31, 32], Europe [33], and Canada [34] has been directed to the partial or total replacement of asphalt as the binder in asphaltic concrete. Processes using sulfur as a substitute for up to 50 percent of the asphalt in asphaltic concrete mixtures have been demonstrated in field trials in the United States, Europe, and Canada, each using their own equipment and techniques. As of this writing, SEA pavement performance has shown it to be comparable to conventional asphaltic pavement mixtures.

SULFUR CONCRETE

Sulfur and aggregate mixes prepared without the use of asphalt or portland cement are called sulfur concretes in which sulfur, either in a modified (plasticized) or unmodified state is used as the binder.

Unmodified sulfur concrete has been shown to be very susceptible to freeze-thaw degradation and crystallized sulfur is extremely brittle.

Therefore, unmodified sulfur is an unsatisfactory pavement material.

Modification of sulfur concrete with additives has tremendously increased the durability (resistance to weathering and temperature fluctuations), flexural strength, compressive strength, early rapid strength gain, and other physical properties of sulfur concrete as a pavement material. Plasticizers are still in the experimental stage and the environmental impact of these materials are only beginning to come under surveillance. Some work has been done to determine the typical concentrations of H_2S evolved during the modifying reaction of sulfur with several different additives. Table 4 summarizes the findings of Currell who has measured the H_2S emissions associated with a number of different additives [35]. The modifiers were added (25 weight percent) to elemental sulfur, the mixture was heated at 284°F (140°C) for three hours, and the amounts of H_2S evolved during heating were measured. It is necessary to study further the hazards associated with the modifying reactions as no field data exists. It would be logical, however, to assume that good ventilation of the work area and short duration exposures to the emissions would be justifiable safety practices.

2.4 Evaluation of Risks and Safety Recommendations.

The equipment, operations, and safety practices for asphalt hot-mix pavement are well established in the industry [36, 37, 38, 39]. In general, the equipment used for the preparation and placement of the sulfur-modified pavement mixtures have been the same as those used for asphalt hot-mix. Operations have been modified where necessary to accommodate the sulfur. In considering maintenance and salvage techniques, both types of pavements, sulfur and asphalt, may be encountered

Table 4. Hydrogen Sulfide Emissions from Plasticization of Sulfur with Several Additives.

Additive	H_2S (mg)	Nature of Product
Thiokol LP-31	1.7	flexible
Thiokol LP-32	12.7	flexible
Thiokol LP-33	22.1	flexible
Alloocimene	1.7	brittle
Cyclododeca-1,5,9-triene	1.9	brittle
Cycloocta-1,3-diene	trace	flexible
Dicyclopentadiene	trace	flexible
Limonene	1.3	flexible
Myreene	1.4	elastomeric
Octene (1 and 2)	trace	no reaction
Styrene	trace	brittle

on the roadway at random.

For the purposes of this report, the basic operations and situations regarding sulfur pavements have been described in view of current asphalt pavement practices. Normal operating conditions are assumed in rating the risks encountered of each known and potential sulfur pavement operation and situation. Normal operating conditions consider the standard practice of the temperature of the mix, location of personnel, time of exposure to gases, fumes, and dust, and distance from the source of the contaminants. A slight breeze is also assumed to exist under the definition of "normal operating conditions"; however, since wind conditions are variable, dispersion plays an important role in the rating of the risks involved with sulfur. An in-depth study has been done by the Asphalt Institute relating emission concentration to down-wind distance from source, meteorological conditions, and height of emission source [40]. The distance from the pollution source was considered on the basis of the following two categories:

a) Near Source - This is considered the closest distance from the source of pollution that a worker might be expected to function in the routine performance of his duties. This was based on measurements taken between 18 - 24 inches (0.5 - 0.6 m) from the contaminant.
b) General Area - This is the area in the immediate locale of the source of pollution in which passing personnel might be exposed. This was based on measurements taken at 5 - 50 feet (1.5 - 15.2 m) from the contaminant.

The risks have been rated on the basis of the following terms:

a) Acceptable - Under the worst case, such as no wind or zero dispersion, it is not anticipated that the MAC for the exposure described will be exceeded.

b) Conditional - Under the worst case, the MAC for the exposure may be exceeded, but under normal operating conditions it is not anticipated that the MAC for the exposure will be exceeded.

c) Unacceptable - Under normal operating conditions the MAC for the exposure will be exceeded. (Also, there is reason to expect that levels of concentration may be immediately dangerous to life.) These areas may need continuous monitoring of concentration levels and alarms or other safety devices.

In the absence of positive measurement for sulfur pavements, the operation and situation is rated using the best applicable knowledge and judgments at hand.

Rating the degree of risk associated with exposure to H_2S is based on field data, laboratory measurements, and the previous experience of industries producing H_2S under similar circumstances (specifically the liquid sulfur and the oil production industries) [41, 42, 43, 44, 45].

Rating the degree of risk associated with exposure to SO_2 is based on measurements taken of SO_2 in laboratory situations and during field trials [41, 42, 43, 44, 45]. The current MAC of 5 ppm has been used as the criteria for this evaluation. If the current efforts to reduce the MAC to 2 ppm succeed [46] the results of the evaluation will change such that areas rated "conditional" will become unacceptable, and possibly some areas rated "acceptable" will be deemed conditional.

Rating the degree of risk associated with exposure to sulfur dust is based solely on the data collected by the liquid sulfur industry and field measurements for particulate sulfur taken from Hi-Volume Air Samplers [43]. Relatively little data is available regarding particulate sulfur and efforts to establish amounts of sulfur dust may be interfered with by asphalt fumes showing a misleadingly high amount of particulates.

Laboratory measurements of organic emissions under conditions intended to maximize emissions have shown that the amounts are negligible (See Vol. I). For this reason it appears highly unlikely that exposures to any organic materials in excess of the MAC will occur under any circumstance that may be encountered under normal preparation, hauling, placing a maintenance of sulfur-modified pavement materials, and therefore, the degree of risk is "acceptable" for all operations and situations.

2.4.1 Stationary Sources.

A primary hazard is presumed to exist when sulfur is heated to temperatures over 300°F (149°C) whether or not is is in contact with mineral aggregates. Further hazards may arise due to the nature of sulfur.

Sulfur must be liquid, at a temperature above its melting point, for intimate and thorough mixing with mineral aggregates to form the sulfur pavement mixture. This is true whether the sulfur is applied hot or whether it is received cold and pre-blended with mineral aggregate before heating or added directly to the hot aggregates.

A hazard may arise from the following operations and locations at the hot-mix plant.

QUALITY CONTROL LABORATORY

When samples of sulfur-asphalt pavement mixes are made and/or tested in the quality control laboratory it is essential, as previously stated, that the temperature of the mixture be kept below 300°F (149°C). A hazard is likely to arise when reheating sulfur-asphalt samples in the oven for workability in testing procedures.

Exposures: H_2S, SO_2, S

Sources: Hot sulfur-asphalt samples

Factors Affecting Exposures:

Temperature - mix temperatures in excess of 300°F cause a sharp increase in H_2S and SO_2 emissions.

Dispersion - concentrations vary inversely with distances from source.

Degree of Ventilation

Risk Evaluation	Near Source
H_2S	Acceptable
SO_2	Acceptable
S	Acceptable

Comments: Measurements taken during preparation of sulfur asphalt samples under laboratory conditions showed very low levels of H_2S and SO_2. Short term samples taken in the breathing zone of the laboratory worker during sample preparation showed peak levels of about 0.2 ppm H_2S and 0.1 ppm SO_2. Ample ventilation in the laboratory will control these exposures adequately.

Recommendations:

Under all conditions in the laboratory, safety procedures normally observed in the handling of asphalt pavement mixtures should be followed for sulfur asphalt mixtures.

SULFUR STORAGE TANK

Toxic and explosive quantities of H_2S can collect in the domes of transports and in the domes of tanks containing liquid sulfur. A hot sulfur tank when emptied may contain combustible or otherwise dangerous concentrations of gases [61]. Sulfur spills or sumps filled with waste sulfur harden quickly on the surface while liquid beneath forms a trap for pedestrians. Hardened sulfur may also clog the discharge valves at the bottom of the tank.

Exposures: H_2S, SO_2, S

Sources: Tank dome, inspection ports, vents, valves

Factors Affecting Exposure Levels:

H_2S - Temperatures in excess of 300°F and/or the presence of organic contaminants (e.g., old asphalt) in the tank or in the sulfur itself produce significant increases in H_2S generation.

SO_2 - Formation of SO_2 requires oxygen; storage tank conditions will tend to limit its formation.

Risk Evaluation	Near Source	General Area
H_2S	Unacceptable (>25 ppm)	Acceptable
SO_2	Conditional (2-5 ppm)	Acceptable
S	Acceptable	Acceptable

Fire - There is potential for H_2S and sulfur vapor to build to concentrations exceeding the lower explosive limit within the tank.

Comments: H_2S levels inside the tank dome are known to exceed 600 ppm, the level at which H_2S is immediately dangerous to life. Persons working near tank openings may be exposed to these H_2S concentrations.

Recommendations:

No sparks, smoking, open flames, or welding should be permitted near any opening to a liquid sulfur container. Any person handling liquid sulfur should wear a hat, safety glasses with side shields, and a face shield; also, he should wear long sleeved shirts and pants, heat-resistant gloves without gauntlets, and laced, high-top safety shoes. If a person must enter an area in which either past experience or instruments indicate to be contaminated with toxic level gaseous emissions he should be equipped with an air line respirator, hose mask with blower, or self contained breathing apparatus. The face piece must protect the eyes. The best way to prevent a hydrogen sulfide gas explosion is to provide good ventilation by natural or forced draft. If a sulfur fire does occur, the National Fire Code of June 1959 [25] outlines extinguishing methods:

> 4102. Fires in vats or other containers of liquid sulphur can be extinguished by saturated steam, carbon dioxide, or water sprayed over the surface of the liquid. Pressure hose streams which may scatter the burning liquid should be avoided. It is recommended that the quantity of water used be kept to a minimum.
>
> 4103. A fire in liquid sulphur can be extinguished readily by closing the container to exclude air, formation of sulphur dioxide quickly exhausts the oxygen in the enclosure and smothers the fire. Where containers of liquid sulphur are of sufficiently small size to permit such action, it is recommended that they be so arranged that they can be sealed rapidly to exclude air in case of fire. Any covers used for this purpose should be constructed entirely of noncombustible material.

<u>A solid stream of water hitting hot sulfur in a closed tank may cause a steam explosion</u>.

Due to the high levels of H_2S expected in the sulfur tank dome, and around the inspection port of the silo, it is recommended that the tank be vented and that work practices be devised disallowing personnel to approach these areas during normal operations. It is further advised that appropriate continuous sensing devices (See Section 2.5) be substituted for visual inspection of the tank. When these areas must be entered, the work procedure should include monitoring for H_2S, SO_2, and O_2 and the use of supplied air respirators if appropriate.

PREBLENDING OF SULFUR-EXTENDED-ASPHALT BINDERS

When preblending is used, dangerous concentrations of sulfur gases can collect in the dome of surge tanks and at sampling spigots. Sulfur-asphalt blended materials, held in dead areas in the system at or above operating temperatures, can polymerize to a sludge thereby blocking outlets and causing spills. A hazard is likely to arise from storage of the preblended sulfur-asphalt paving mix for more than a few hours. Overnight storage is questionable, and storage over a weekend should not be done as conditions become increasingly conducive to the generation of gases. The possibility of an exothermic reaction taking place within the stored sulfur-asphalt mixture has been considered as a hazard that may arise. To date, no data has been generated to determine the extent or degree of risk in relation to exotherm.

Exposure, risk evaluation, and recommendations are the same as given for Sulfur Storage Tank.

MIXING UNITS

Over heated aggregates, often associated with start-up and stop-and-go operations of the drier on batch type and continuous mix hot plants, when mixed with sulfur binder can cause smoking of the mix and formation of dangerous fumes. The fumes are largely dissipated in the plant emission control system but can be detected around the pug-mill or mixing unit. The fumes may be visible as plumes of smoke during the batch loading of trucks.

In drum mixers similar situations may arise to produce undesirable emissions. In general, the asphalt can be injected into the hot aggregates downstream from the burner in a zone or location where direct contact with the burner flame is avoided. Sulfur binder may also be injected at a point downstream in a favorable temperature and aggregate drying stage.

Air currents around the mixing and loading units which escape the emission control system and stack gases can carry minute particles (colloidal) of sulfur which permeate the ambient air and can settle out, especially in a quiet, high humidity atmosphere, to form thin but visible layers of sulfur on exposed flat surfaces.

Exposures: H_2S, SO_2, S

Sources: Stack, drum mixer, pug mill, mix discharge, conveyor

Factors Affecting Exposures:

Temperature - Mix temperatures in excess of 300°F-149°C result in sharply increased H_2S and SO_2 emissions.

Dispersion - Dispersion due to wind and distance from source keeps H_2S and SO_2 emissions at low levels in the General Area.

Risk Evaluation	Mix Discharge	Other Locations in Area
H_2S	Acceptable	Acceptable
SO_2	Conditional (1.5-5ppm)	Acceptable
S	Acceptable	Acceptable

Recommendations:

A representative sample of personnel working in these areas should be monitored for H_2S, SO_2, and sulfur exposures during start up of the plant, and thereafter as required by state and federal regualtions. Safety procedures corresponding to those in current use in the asphalt industry should be adequate.

SURGE SILOS

Surge silos are widely used for the transitory storage of asphalt hot-mix. They are necessary for intermittent truck loadings for continuous mixing plants and drum mixers. Sizes range from 50 tons to several hundred tons capacity depending on the mixing operation needed. The silos are mainly vertical tanks which are loaded with the hot-mix by conveyor belt or bucket line from the mixing unit. Internal configurations of cones and baffles prevent segregation of the mix. Discharge is by gravity through a bottom cone equipped with gates. The silo is normally insulated and the outlet cone and discharge gates are heated. Evidences of steam and moisture from condensate at the discharge gates are not uncommon even though the mix temperatures may be well above the minimum for hauling and placing.

Exposures: H_2S, SO_2, S

Sources: Conveyor (loading gate), inspection ports, vents, discharge gates

Factors Affecting Exposures:

Temperatures - Mix temperatures in excess of 300°F-149°F cause a sharp increase in H_2S and SO_2 emissions.

Storage time - H_2S and SO_2 are generated continuously and the surge silos are not well ventilated, thus an increase in storage time will increase H_2S and SO_2 levels in the silo.

Risk Evaluation	Discharge Gate Area	Loading Gate, Inspection Ports and Vents
H_2S	Acceptable	Unacceptable
SO_2	Acceptable	Unacceptable
S	Acceptable	Conditional (See Recommendations Below)

Fire - During long storage periods it is possible that H_2S concentrations in the silo could exceed 4.3%, the lower explosive limit, thus producing the potential for a deflagration.

Comments: H_2S levels in the air space of the silo are almost certain to exceed 600 ppm during normal operations. Consequently, personnel in the immediate area of the loading gate, inspection ports and vents may be exposed to levels of H_2S that are immediately dangerous to life.

Recommendations:

Due to the high levels of contaminates (H_2S, SO_2, and S) expected around the loading gates, inspection ports, and vents of the silo, it is recommended that work practices be devised disallowing personnel to approach these areas during normal operations. It is further advised that appropriate sensing devices be substituted for visual inspection of the silo. When these areas must be entered, the work procedure should include monitoring for H_2S, SO_2 and O_2 before entry, and the use of supplied air respirators if appropriate. Goggles should also be worn to protect the eyes, and eye wash facilities should be provided for ready accessibility by all employees. This includes some type of portable unit such as the "squeeze bottle and eye cup" type.

STACKS

Stacks are commonly used to discharge exhaust gases from the dryer, screens, and mixer on batching and continuous mixing plants, and from the drum on drum mixing plants. Normally these gases pass through an emission control system before discharge to the atmosphere.

There are two general classifications of collector systems for dust and other pollutants on batching plants, continuous mixing plants, and drum mixing plants i.e., dry collectors and wet collectors. Both these systems are actuated by exhaust fans which draw the hot emissions from the dryer, screens, and mixer on batching and continuous mixing plants, and from the drum on drum mixing plants, into high velocity air streams in ducts.

Of the dry collectors, there are three general types in use:

One type is widely known as a cyclone. The air stream enters a large horizontal or vertical tank where both the velocity and direction are changed into a centrifugal (cyclonic) motion. This change causes the fine particulate matter to be dropped out of the air stream and returned to the mixing unit. The exhaust gases may be led out of the stack, or into a companion cyclone or cyclones in conjunction with a wet washer. The cyclones are usually fabricated by the drier manufacturer and therefore come in many sizes and internal configurations.

Another type of dry collector is widely known as a bag-house. Fabric filter bags are mounted on frames and suspended in cages within the housing. The hot dust and gas laden air streams flow from outside to inside the bags where there is usually a fan located on the discharge end of the house. The fines are separated from the discharged air stream and returned to the mixer. Baghouses are not normally used in conjunction with other types of collectors, as they are regarded as quite effective in eliminating steam plumes and particulates.

The third type of dry collector is normally used with other devices, including impinger plates and dropout or knock-out boxes. These knock-out boxes essentially consist of an expanded duct and a turn in the stream flow which serve to sharply decrease the velocity of the air stream and increase turbulence, thus precipitating out the particulate matter.

Wet collectors are basically of one general design with many air stream and water injection patterns. The basic system consists of a tank and water spray which intermixes with the hot dust and gas laden air stream introduced into the tank. The particulate matter mixed with the water forms a slurry which is drained from the bottom of the tank into a sludge or settling pond. Wet collectors are usually preceded by dry collectors and may be used singly or in tandem. They are vented through the stack or directly from the slurry discharge line.

A widely used system, particularly with drum mixers, consists of a drop-out box followed by a wet washer (scrubber) and an exhaust stack.

Dispersion of the emissions after release from the stack will prevent exposure of personnel to levels in excess of the MAC from this source, and the stack does not constitute a significant exposure to the personnel in the plant. These emissions may not meet air quality standards depending on applicable laws.

Exposures: H_2S, SO_2, S

Source: Stack

Factors Affecting Exposures:

Dispersion due to stack height, discharge velocity, and temperature.

Risk Evaluation	General Area
H_2S	Acceptable
SO_2	Acceptable
S	Acceptable

Comments: Since allowable concentrations for particualte emissions can vary from state to state, a universal acceptable level of emissions is yet to be established. Furthermore, existing emission control technology should be capable of handling any gaseous sulfur emission condition which might be encountered. Baghouses and cyclone dust collectors may allow H_2S and SO_2 gases to pass through. Therefore, it is suggested that wet scrubbers be used to collect both particulates and vapor prior to venting to the atmosphere.

Recommendations:

Monitoring of stack emissions to determine compliance with appropriate laws, and installation of appropriate control devices is recommended.

2.4.2 Mobile Sources.

As with the stationary sources, a primary hazard is presumed to exist when sulfur is heated to temperatures over 300°F (149°C) whether or not it is associated with mineral aggregates. Further hazards may arise due to the nature of the sulfur.

HAULING

Sulfur paving mixtures are hauled in trucks in the same manner as asphalt hot-mix. The truck bed is sprayed with a light lubricant as a parting compound. The truck may or may not be equipped with a cover. Regardless, exposures to H_2S, SO_2, and S are nil, and therefore rated "Acceptable."

THE PAVER

Paver screeds are normally heated for start-up and for stop-and-go operations with hot air from an oil or gas fired burner and blower system. Overheating of the screed is commonplace in the placing of asphalt mixes. Smoke and fumes can arise as the sulfur mix comes in contact with the overheated screed as well as the paver hopper. The air currents around the unloading truck and, in turn, around the paver, can carry minute particulates of sulfur even though temperatures of the loads are within the specified limits.

Exposures: H_2S, SO_2, S

Sources: Hauling trucks, paver hopper, screed, freshly laid pavement.

Factors Affecting Exposure:

Temperature - Mix temperatures in excess of 300°F (149°C) result in a sharp increase in H_2S and SO_2 emissions.

Dispersion - Dispersion due to wind and distance from the source reduce area H_2S and SO_2 concentrations but may increase particulate sulfur.

Risk Evaluation	All Locations
H_2S	Conditional (See Comment)
SO_2	Conditional (See Comment)
S	Acceptable

Comments: Field studies (Delaware and Texas) have shown that workers involved in these operations were exposed to less than 5 ppm of H_2S and SO_2 for an 8 hour time weighted average (TWA) day. However, when control of paver screed temperature on on the Kenedy County, Texas project was lost H_2S and SO_2 concentrations increased to 20 ppm [42].

Recommendations:

A representative sample of exposed personnel should be monitored for exposure to H_2S, SO_2, and particulate sulfur during initial operations. Additional monitoring and control of exposures may be suggested by the results of the initial monitoring. Care should be taken in maintaining screed temperature control. In addition, safety procedures currently followed in the asphalt industry are recommended for these operations.

2.4.3 Maintenance.

SURFACE HEATERS [48, 49, 50, 51]

Surface heating of in-place pavement is employed for the maintenance and rehabilitation of asphalt pavements. Surface heating is followed by planing, scarifying, or hot surface recycling. The pavement is softened to depths of 1/2" to 1" (12.7 to 25.4 mm) by direct application of heat from mobile combustion chambers which are moved across the surface. The burners are oil or LPG fired. In some heating units, the flame is directed toward the pavement. In other units, refraction is used to create radiant heat. Usually banks of heaters, at carefully spaced intervals in the heating chamber, provide intermittent heating and heat soaking of the surface. In most cases the heaters are located within one ft. from pavement surface. The heated pavement is then immediately planed or scarified and relaid. An asphalt softening agent, new asphalt, or both may be used to process the heated surface.

Other methods used for in-place heating of asphalt pavements include heater units mounted on motor graders to portable torches and hoods. The latter are sometimes used for maintenance patching and repair of utility cuts.

Hot surface maintenance is economical and efficient if the desired depths of pavement are heated in the shortest possible time with the least amount of fuel and without damage to the asphalt or creation of undesirable amounts of smoke as temperatutes of the pavement surfaces are often over 400°F (205°C) [52].

Exposures: H_2S, SO_2, S

Source: Pavement surface

Factors Affecting Exposures:

Temperature - Temperatures in excess of 400°F (205°C) are likely at the pavement surface, indicating that H_2S and SO_2 emissions may be significant.

Time - Elevated temperatures are held for only a short time, so H_2S and SO_2 emissions decrease rapidly.

Dispersion - Wind and distance from the source will dilute the H_2S and SO_2 concentrations before it can reach workers' breathing zone.

Risk Evaluation	General Area
H_2S	Conditional (based on judgement - data nonexistent)
SO_2	Conditional (based on judgement - data nonexistent)
S	Acceptable

Recommendations:

During initial operations a representative sample of exposed personnel should be monitored to determine exposures to H_2S, SO_2, and particulate sulfur. Based on these results additional monitoring and control of exposures may be indicated. In addition, safety procedures used in these operations in the asphalt industry are indicated.

COLD MILLING AND GROOVING [53, 54]

Cold milling and grooving of pavement surfaces are being increasingly used to restore skid resistance. The machinery used for this purpose are heavy, self-propelled mills with rotary cutter assemblies that are equipped with hard metal (tungsten-carbide steel). These cutter assemblies cut, chip, or pulverize the pavement surface in widths of a traffic lane or more, and in depths of 5" to 7" (127 to 178 mm) in one-pass operations. Forward speeds can range over 100 feet per minute. Other purposes for these machines include removal or profiling of old asphalt pavement (in which the processed material is salvaged as hot-mix recycle feed), and pulverizing in-place for base stabilization or for shoulder materials.

The process of crushing, grinding, or pulverizing may cause sulfur odors and sulfur gases to be present as well as dust particles with trace quantities of sulfur [47].

Exposures: H_2S, SO_2, S

Source: Pavement surface

Factors Affecting Exposure:

Temperature - Production of H_2S and SO_2 gases will result from friction heating of the pavement.

Dispersion - After dispersion due to wind and distance H_2S and SO_2 levels should be insignificant.

Risk Evaluation	General Area
H_2S	Acceptable
SO_2	Acceptable
S	Acceptable

Recommendations:

Safety procedures followed in the asphalt industry are recommended.

MISCELLANEOUS MAINTENANCE OPERATIONS

Operations and situations common to asphalt pavement maintenance and which may be anticipated in the maintenance of sulfur modified pavements will include scarifying, tight blading, sawing, coring, and similar scraping and cutting processes.

Detectable amounts of H_2S and SO_2 and dust particles containing elemental sulfur is likely to occur in all these processes, except, perhaps, when wet processes are used. Most likely they will appear in trace quantities only and will have no detrimental effect on personnel or the environment.

2.4.4 Hot-Mix Recycling [55] .

Hot-mix recycling of asphalt pavements has been of widespread interest in the past decade and is being increasingly practiced in the industry. Initially, the old pavement was scarified and broken up in-place by heavy grid rollers, then hauled and further crushed for the hot-mix plant feed. The addition of new aggregates, new asphalt and softening agents were mixed in with the old pavements to correct its deficiencies. However, there were several problems that arose with this operation particularly black smoke from direct contact of the drier flame with the recycle mix. In an effort to correct this problem, driers were redesigned or modified so that the recycle mix avoided direct contact by the burner flame and hot gases. One modification was to introduce the recycle mix directly from an aggregate bin as a component of the total mix, thereby completely bypassing the drier. Heat transfer from the new hot-mix material heated the recycle material in the pug mill instead. Ratios of recycle material to new materials were less than 1:1. Current methods of recycling have seemed to overcome the initial problems and are quite successful.

In general, the drum mixers are designed to prevent direct contact of the recycle mix with the drier flame. The methods employed are unique to the manufacturer. One supplier features a drum within a drum where new aggregates are charged to the inner drum and the recycle mix to the outer drum [56]. Another features a multi-feed arrangement which permits the recycle material to be introduced downstream from the new aggregates [57, 58]. Still another employs a removable cylindrical combustion chamber which is attached to the front end of the drier and equipped with cool air inlets to control temperatures of gases entering the drum [59]. A further arrangement entails a drier and drum mixer which are operated in series. New super heated aggregates from the drier are discharged into the drum to comingle with the cold recycle materials [60].

The redesign of driers and drum mixers have virtually eliminated gaseous emissions from recycle mixes within the batch plant operations. The worker exposure to H_2S, SO_2 and particulate sulfur would be the same as is common to the asphalt paving operation (hauling and placing) which has been shown to be minimal.

Exposures: H_2S, SO_2, S

Sources: Drum mixer, pug mill, mix discharge

Factors Affecting Exposures:

Temperature - Mix temperature in excess of 300°F (149°C) will result in sharply increased H_2S and SO_2 emissions.

Dispersion - Dispersion due to wind and distance from the source keeps H_2S and SO_2 emissions at low levels in the general area.

Risk Evaluation	Mix Discharge	Other Locations
H_2S	Conditional (trace-10 ppm)	Acceptable
SO_2	Conditional (trace-5 ppm)	Acceptable
S	Acceptable	Acceptable

Recommendations:

A representative sample of personnel should be monitored to determine exposures to H_2S, SO_2, and particulate sulfur. The results of the monitoring will be used to determine the need for additional monitoring and control of exposure. In addition, safety procedures followed in the asphalt industry are recommended.

2.5 Emissions Monitoring Methods.

There are presently on the market dozens of commercial instruments for continuously and periodically monitoring ambient sulfur dioxide and hydrogen sulfide. Comparisons of individual manufacturers' products have been published [61]. Although the underlying scientific principle of each is important in choosing an instrument, other factors that must be considered are type of environment, instrument performance characteristics (such as drift, readability, sensitivity - lowest limit of detectability, lagtime-time interval from change in input concentration to change in output signal, response time - time interval from change in input concentration to 90% of maximum output signal, collection efficiency, and interferences), calibration drift, accuracy, maintenance requirements - including operator cost, unattended operation performance, difficulty of servicing, and availability of manufacturer service - and effect of changes in air flow in addition to the actual manufacturing differences, hardware, electronics, and operational details [62].

Two types of monitoring may be advisable under some circumstances. Continuous monitoring of "unacceptable" areas for H_2S, with a system that activates an alarm, is indicated if personnel are required to enter these areas as part of normal (operational) working procedures. If entry of personnel is required only for maintenance purposes, then portable monitoring equipment and normal entry procedures are acceptable.

Personnel monitoring for determining actual exposure of personnel to H_2S and SO_2 during the working day is recommended for the initial operations of a new sulfur-modified asphalt pavement plant. A representative sample of personnel working in "conditional" and "unacceptable" areas should have their exposures to SO_2, H_2S, and particulate sulfur monitored using conventional personnel sampling methods. Depending on the results, corrective measures may be necessary, with additional sampling needed to determine the effectiveness of the controls. Federal and state laws may require repeated sampling at specified time intervals if exposures found during the initial sampling were higher than the allowed standard.

Three types of monitoring equipment are briefly outlined in the following pages: (a) continuous monitoring of area samples, (b) short term sampling for inspection and (c) personnel sampling. The continuous area monitoring techniques for SO_2 and H_2S are intended for air pollution monitoring and may not measure high enough levels of the contaminant to be useful in some applications of the sulfur-modified asphalt pavement industry. It is suggested that an instrument be chosen which can detect concentrations above the ceiling limit for SO_2 and H_2S. The short term area sampling devices are generally not used to measure personnel exposures. These devices are not considered to be as accurate as the area monitoring instruments though they can give peak values. Continuous personnel monitoring techniques have generally been adapted from the continuous area monitoring methods. For the most part, those systems available through instrument manufacturers are NIOSH approved. It is important to note the sensitivity (or limit of detection - LOD) and range of the monitoring method. If the upper range is not 50^+ ppm

H_2S or SO_2 then the instrument is of little value as an alarm. If the lower range is not 1 ppm or less H_2S or SO_2 the instrument is of little value for personnel monitoring.

The following is a brief description of the theory behind presently available commercial analyzers and samplers for gaseous sulfur compounds and particulate sulfur that are considered applicable to the pavement industry.

2.5.1 Area Monitoring - Continuous Sampling.

SULFUR DIOXIDE

Conductimetric Analyzers

Conductimetric analyzers were the first commercial instruments for continuously monitoring SO_2. These analyzers are based on air that is brought into contact with an absorbing solution which dissolves SO_2. The ions formed by the dissolved SO_2 increase the conductivity, which is proportional to the concentration. Conductance is measured by a pair of electrodes within the cell [63]. Some typical features of conductimetric analyzers are limit of detection (LOD or sensitivity) of 0.01 ppm with highest range at about 2 ppm, lag time of about 20 seconds, and response time of 2 minutes [64]. A major disadvantage of the conductimetric analyzers is that interference will occur to some extent by the species that forms or removes ions from solution and changes the conductivity if present in sufficiently large concentration. The degree of interference also depends on humidity, temperature, the SO_2 concentration and the particular instrument [62]. Advantages of the conductimetric analyzers for ambient air monitoring are their sensitivity, fast response, minimal maintenance, and simplicity of operation [62].

Colorimetric Analyzers

Colorimetric analyzers are based upon their reaction of SO_2 with solutions of organic dyes to form colored species. The optical absorbency of the resulting solution, measured spectrophotometrically, is within limits linearly proportional to the concentration of the colored species, in accordance with Beer's law [62]. Accuracy depends upon the rigid control of pH, temperature, reagent purity, development time, age of solutions, and concentrations of some atmospheric interferents, such as ozone and nitrogen oxides [65]. Commercial instruments have introduced modifications such as reducing the number of reagents needed in order to minimize the interference of NO_2 [66]. Typical features of this group of instruments are sensitivity of about 0.005 ppm, with highest range of about 2 ppm, a lag time of 2 minutes, and response time of 8 minutes [64]. Advantages include simplicity of operation, high sensitivity, and good specificity. Disadvantages are the replacement of reagent and pump tubing, and frequent recalibration.

Coulometric Analyzers

Coulometric analyzers are based on the reaction of SO_2 with a halogen, such as bromide or iodide, formed directly by electrolysis of a halide solution. The current necessary to replace the depleted halogen is measured and is proportional to the amount of SO_2 absorbed in the solution, and hence to the amount of SO_2 in the air [62]. Typical features of coulometric analyzers are sensitivity of 0.002 ppm, highest range of 4 ppm, lag time of 2 to 120 seconds, and response time of about 3 minutes [64]. The major advantage of the coulometric analyzer is its minimal maintenance. Reagent consumption is minor because of halide regeneration and may be replaced monthly, electrodes may need annual cleaning, and evaporated water is replaced by condensation from air or from a reservoir [62]. The disadvantage of this analyzer is that the interferent species are primarily sulfur compounds. The interference effects may be minimized by selective filters which may be built into the instrument [62].

Electrochemical Transducers

Electrochemical Transducer (ECT) analyzers measure the current generated by electrochemical oxidation of SO_2 at a sensing electrode. All the chemical reactions take place within a sealed transducer module [67], eliminating the wet chemistry of conductimetric, colorimetric, and coulometric analyzers [62]. Typical features of ECT analyzers include sensitivity of about 0.01 ppm, highest range of 5 ppm, lag time of 10 seconds, and response time from 20 to 180 seconds [64]. The advantages of ECT analyzers include simple operation, low maintenance costs, quick response, low weight and therefore ease of portability, and low power consumption [62]. Disadvantages of ECT analyzers are that the transducer needs replacement or rejuvenation approximately every 6 months; due to the gradual deterioration of the transducer frequent calibration is necessary; furthermore, the air sample is introduced by pushing instead of pulling through the transducer to avoid membrane displacement and therefore pump and lines must be carefully chosen and maintained [62].

Flame Photometry

The flame photometric detector (FPD) is based upon photoemission of sulfur bands by sulfur compounds in a hydrogen-rich flame. The sampled air is mixed with excess hydrogen to form a flame. The emitted light passes through a narrow-pass optical filter, which isolates the 394-nm S_2 band, and is detected by a photomultiplier tube [68]. These analyzers have been widely accepted for use in ambient SO_2 monitoring. The FPD is able to detect other sulfur compounds besides SO_2, and selective filters may be used to reduce interference from the other gaseous sulfur compounds [62]. The typical operational features are sensitivity of about 0.005 ppm, highest range of 1 ppm, lag time of 3 seconds and response time of 10 seconds [64]. Advantages of FPD systems include low maintenance, high sensitivity, very fast response, good selectivity for sulfur compounds, and other than compressed hydrogen, no reagents are necessary [62]. The disadvantages of these analyzers are its sensitivity to all sulfur compounds (making selective filters mandatory) and the need for a compressed hydrogen source [62].

NIOSH Approved Method

Accepted methods for area monitoring are described in NIOSH Criteria Documents on SO_2 [69].

HYDROGEN SULFIDE

Flame Photometric Detector (FPD)

The FPD is also used for measuring H_2S levels. A typical analyzer provides total sulfur (SO_2 plus H_2S) and SO_2 measurements. The H_2S

level is obtained by electronically subtracting the SO_2 concentration from the total sulfur [70].

Lead Acetate Tape and Tiles

Lead acetate is the most commonly used method of continuously monitoring H_2S in the field [71]. Its basic principle is simply the reaction of H_2S with lead acetate to form lead sulfide which distinctively blackens the sampling tape or tile proportional to the atmospheric H_2S concentration [62, 72, 76]. The advantage of using lead acetate is its simplicity. The disadvantages of this method of analysis is its inaccuracy, and stains (from the reaction) are easily bleached by light in a relatively short time [73]. Although lead acetate methods are gross indicators of concentration and tell nothing about peak concentrations, they do offer a way to verify whether hourly air quality standards are being exceeded [62].

Electrochemical Analyzers

The ECT analyzer outlined for SO_2 monitoring has also been developed for H_2S monitoring with the same advantages and disadvantages [74, 75].

NIOSH Approved Method

Accepted methods for area monitoring are described in NIOSH Criteria Documents on H_2S [77].

2.5.2 Short Term Sampling ("Grab" Sampling).

SULFUR DIOXIDE

West-Gaeke Method

The West-Gaeke Method is probably the most widely used colorimetric procedure for SO_2 determination in ambient air [78]. It is also the basis of the EPA reference procedure for manual measurement of SO_2 [79]. Air is bubbled into impingers containing a specific amount of sodium tetrachloromercurate (TCM) solution. Sulfamic acid is then added to remove interference from nitrogen dioxide. A red-purple acid complex is formed after the TCM complex is reacted with a dye reagent. Measurement of SO_2 is done spectrophotometrically at 548 nm. The West-Gaeke method is capable of measuring 0.005 ppm to 5 ppm SO_2. Possible problems that may arise with this method are interferences from chlorine, hydrochloric acid, hydrogen sulfide, thiols, thiosulfates, and aldehydes [62].

Impregnated Papers

Sulfur dioxide can be absorbed from air samples passing over filter papers impregnated with alkali plus a humectant to keep them moist [62, 80, 81, 82]. Solutions commonly used to impregnate papers are potassium hydroxide with triethanolamine, and potassium carbonate with glycerine. Absorbed SO_2 is leached from the papers and determined colorimetrically by the West-Gaeke method [62, 80]. No interference has been observed for nitrogen dioxide and hydrogen sulfide, though ozone may cause negative errors [62].

Chemiluminescence Method

The basis for this method is the chemiluminescence produced when sulfite solution is oxidized [83]. The chemiluminescence is detected by a photomultiplier tube with total light yield, measured by a photon counting system, proportional to the oxidized sulfite [62].

Detector Tubes

Detector tubes are glass tubes filled with a reagent and calibrated to coincide proportionally with the reaction taking place. Indication is based on a modified iodine-starch reaction for SO_2 concentration measurements. A bellows pump, operated by hand, supplies 100 cm^3 of air with each stroke [84]

HYDROGEN SULFIDE

Lead Acetate Filters

In the procedure for collection of H_2S on lead acetate filters, the reaction changes lead acetate to lead sulfide. The filter is dissolved by an organic solvent, and the absorbency of suspended lead sulfide is related to atmospheric H_2S concentrations [62]. This method is useful only for H_2S concentrations of 2 ppb and above [62].

Chemiluminescence

The chemiluminescent technique employed for SO_2 monitoring has also been developed for measuring H_2S emissions [86]. They are available in sensitivities from 0.05 ppm to 0.2 ppm and ranges up to 10 ppm.

Detector Tubes

The detector tube described for SO_2 monitoring is also available for measuring H_2S emissions. Indication is based on a color reaction with a lead compound on silica gel carriers. Pale brown lead sulfide is produced proportionally to the amount of H_2S in 100 cm^2 of air which is supplied by a bellows pump operated by hand [84].

2.5.3 Personnel Monitoring - Continuous Sampling.

SULFUR DIOXIDE

NIOSH Approved Method (H_2O_2)

Accepted methods for personnel monitoring are described in NIOSH Criteria Documents on SO_2 [69].

Electrochemical and Other

Generally, the sampling techniques listed under Continuous monitoring for area samples are employed in personnel monitoring of SO_2. Most companies have modified a specific technique in which they incorporate a variety of uses, such as personnel portable monitoring that can be worn around the hips to stationary monitoring of ambient air in several areas at one time.

HYDROGEN SULFIDE

NIOSH Approved Method ($Cd(OH)_2$)

Accepted methods for personnel monitoring are described in NIOSH Criteria Documents on H_2S [77].

Electrochemical and Other

The sampling techniques employed for monitoring area samples are also used in personnel monitoring. Smaller models, designed by industry, are available for personnel wear as described under personnel monitoring of SO_2.

2.5.4 Stack Sampling .

GASEOUS SULFUR COMPOUNDS AND PARTICULATE SULFUR

Monitoring methods and emission control systems are already incorporated in the asphalt paving industry in order to comply with EPA regulations and state requirements. The utilization of sulfur at the plant may raise the concentration of gases in the stack, but current emission control systems mentioned in Section 2.4.1 Stacks of this report should be sufficient to meet current EPA standards. EPA approved monitoring methods are given in EPA Method Nos. 5, 16, 17 as applicable to sulfur-modified aspahltic pavement materials [87].

3 CONCLUSIONS

The main laboratory study described fully in Volume I of this final report has found no prohibitive or safety related problems that would make construction with sulfur-asphalt mixes more hazardous than regular asphalt mixes. This statement is made on the basis that the temperature of the mix is below 300°F (149°C). The most hazardous area during the handling of sulfur for sulfur asphalt mixes is where the sulfur is stored and/or the preblended sulfur asphalt mixture is stored. These areas are not considered personnel areas and proper protection from worker access is advised. The monitoring methods presented in this report are only a discussion on some of the popular methods available and in no way constitute the only means or methods applicable to the paving industry. It is further advised, when constructing with sulfur-modified asphalt pavement material for the first time, that personnel be given some instruction as to the nature of the material as well as safe handling techniques to be employed. The more that the personnel understand what they are working with, the smoother, more efficient, and safer the operation will proceed.

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* U.S. GOVERNMENT PRINTING OFFICE: 1982 361-428/2260