POTENTIAL RISKS OF HYDROGEN SULPHIDE THROUGH THE BITUMEN MANUFACTURE AND DELIVERY PROCESS

SEPTEMBER 2023

ISBN 987-2-930160-94-8
D/2023/7512/125

Eurobitume, December 2023, info@eurobitume.eu

TABLE OF CONTENTS

ISBN: 978-2-930160-87-0
D/2023/7512/118

3rd edition 2023

Published by the European Bitumen Association
Boulevard du Souverain 165
B - 1160 Brussels, Belgium

T: +32 2 566 91 40

info@eurobitume.eu
www.eurobitume.eu

1. BACKGROUND

Hydrogen sulphide (H_2S) is naturally present in crude oils and can be formed during the refining process and in storage tanks downstream of the refinery. Another source may be additives used in bitumen modification processes. Although the presence of H_2S in bitumen liquid phase is not always identified, the gas can still be present and can accumulate in enclosed spaces during hot storage or transport. In the event of prolonged storage, especially at high temperatures, the headspace of storage and truck tanks can contain significant amounts of H_2S that may reach dangerous concentrations.

2. SCOPE

The objective of this document is to raise awareness of all people involved through the bitumen supply chain (i.e. managerial personnel working in relevant functions in all stages of the bitumen supply chain, e.g. refineries, bitumen depots, bituminous binder plants, asphalt plants, bitumen roofing industry, hauliers, etc.; HSE personnel involved in evaluating and controlling workplace exposures; inspecting authorities) of risks related to the handling of bitumen associated with the presence of H_2S in the vapour phase of bitumen and the importance to limit personal exposure to H_2S.

The scope of this document is description of the risk for selected operations and provide general recommendations on how to manage the associated risks. This review covers storage, transfer, loading, transport and discharge of bituminous binders in refineries, depots, polymer modified binder manufacturing facilities and customer sites. This document covers all types of bitumen: conventional bitumen grades, oxidised bitumen and polymer modified bitumen (PmB). It does not include manufacture, storage, transport or application of asphalt mixtures.

It is recognised that various measures may be taken during the manufacture of bitumen to reduce the quantity of H_2S potentially present. These may include stripping (driving off the molecules with another gas), use of additives e.g. for scavenging (neutralisation of H_2S), or degasification in storage (the gas dissolved in the bitumen naturally tends to escape from the liquid mass over the course of time). Use of such techniques to reduce the hazard and risk from H_2S in bitumen is beyond the scope of this document.

3. HYDROGEN SULPHIDE (H_2S) AND ASSOCIATED HEALTH AND PHYSICAL HAZARDS

H_2S is a gas that can be entrapped in and released from hot bitumen. It is probably best known for its recognisable “rotten eggs” smell that is detectable at very low concentrations.

Hydrogen sulphide (H_2S):

- Is toxic, acting on the nervous system, and irritating, acting on eyes and the respiratory system
- Can deaden the sense of smell, so odour is not a reliable way to detect its presence
- Is highly flammable
- Can react with iron oxide (rust) on the walls and ceilings of tanks to form pyrophoric iron sulphide, a known ignition source in the presence of oxygen

Bitumen manufacturers should ensure that hazards associated with their products are adequately communicated to customers, together with risk reduction measures. This information should be included in Safety Data Sheets (SDS).

EXPOSURE LIMITS for H_2S

There are two occupational exposure limits (OEL) for H_2S. They represent a concentration to which most workers may be repeatedly exposed, day after day, without significant adverse health effects:

- 8-hour time weighted average (TWA) represents exposure concentration of a toxic substance permitted over an 8-hour working day and a 40-hour working week
- Short-Term Occupational Exposure Limit (STEL) represents a 15-minute TWA exposure that should not be exceeded at any time during the workday

In any case of H_2S, the limits are primarily based on avoiding transient sensory irritation in the eyes, nose, and throat.

In the European Union, the Commission Directive 2009/161/EU (1) establishes a third list of Community Indicative Occupational Exposure Limit Values (IOELVs) for the protection of workers from chemical risks, to be set at Community level. IOELVs are health-based, non-binding values. H_2S is included in this Directive, which means that Member States are required to establish a national occupational exposure limit value taking into account the Community limit value, but may determine its nature in accordance with national legislation and practice.

The IOELV for H_2S are:

- TWA (8h): 5 ppm (7 mg/m^3)
- STEL (15 min): 10 ppm (14 mg/m^3)

A list of organisations who set national regulations for H_2S is given in Appendix 1.

OELs are intended to protect most of the working population from adverse health effects but some exceptions may occur with unusually sensitive individuals. For some substances, as is the case for H2S, brief exposures to high vapour concentrations may cause adverse health effects. STELs, peak concentrations, and IDHL (Immediately Dangerous to Life and Health) are designed to address these effects. The IDLH is considered a maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection should be permitted, while air purifying respirators may not be used. In determining IDLH values, the US National Institute for Occupational Safety and Health (NIOSH) considered the ability of a worker to escape without loss of life or irreversible health effects along with certain transient effects, such as severe eye or respiratory irritation, disorientation, and incoordination, which could prevent escape.

Peak exposure defines transient increases in workers´ exposure levels that may exceed 3 times the value of the TLV-TWA (Threshold Limit Value-TWA) level for no more than 15 minutes at a time, on no more than 4 occasions spaced 1 hours apart during a workday. Under no circumstances should they exceed the 5 times the value of the TLV-TWA level when measured as a 15-minute TWA. In addition, the 8-hours TWA is not to be exceeded for an 8-hour work period.

Table 1 lists the data from WHO (World Health Organisation) Concise International Chemical Assessment Document (CICAD) 53 (2).

Table 1. Typical physiological responses/effects following exposure to a range of concentrations of hydrogen sulphide (H_2S) [based upon World Health Organisation, CICAD 53]

Exposure (mg/m^3)	Effect / observation	Reference
0.011	Odour threshold	Amoore & Hautala, 1983[2]
2.8	Bronchial constriction in asthmatic individuals	Jappinen et al., 1990[3]
5.0	Increased eye complaints	Vanhoorne et al., 1995[4]
7	8 hour Time Weighted Average Occupational Exposure Limit	Scientific Committee on Occupational Exposure Limits (SCOEL)
14	Short-Term Exposure Limit	SCOEL
5–29	Eye irritation	IPCS, 1981[5]
28	Fatigue, loss of appetite, headache, irritability, poor memory, dizziness	Ahlhorg, 1951[6]
139	Immediately Dangerous to Life and Health (IDLH)	NIOSH[7]
>140	Olfactory paralysis (Sense of smell cannot be relied upon to detect H_2S)	Hirsch & Zavala, 1999[8]
>560	Respiratory distress (breathing difficulty)	Spolyar, 1951[9]
≥700	Death	Beauchamp et al., 1984[10]

EXPLOSIVE LIMITS for H2S

H_2S is highly flammable. Its Lower Explosive Limit (LEL) is 4 % (40 000 ppm H_2S concentration). H_2S may reach LEL mostly in unventilated crosslinked PMB maturation tanks (during crosslinking reaction period). Forced ventilation is recommended for these cases.

4. EXPOSURE REDUCTION

Exposure should be minimized by using technical/engineering controls such as increase of automation of tasks with risk of exposure to high concentrations of H_2S, for example introducing new techniques to enable opening of the manhole remotely. Administrative controls such as development of efficient procedures to minimize the time the worker is exposed to the hazard are also recommended.

The following hierarchy of controls should be considered to reduce exposures to H_2S and associated risks:

1. Engineering controls – feasible technical means such as ventilation, increase of automation of tasks (for example introducing new techniques to enable opening of the manhole remotely).
2. Administrative controls – such as reduction in duration of exposure of workers, implementation of formal respiratory protection and confined space entry programs, etc.
3. Personal Protection Equipment (PPE) – see section 6.6 for more details.

Examples of preventative activities that can be taken to reduce worker exposure to H_2S are given below:

- Site Hazard and/or Risk Assessments
- Based on this assessment, signs should be provided that warn the loader and unloader that H_2Smay be present
- Ventilating the area to decrease risk
- Personal or area H_2S detectors should be made available to those performing the loading if other risk management measures are not already in place
- Appropriate control measures should be applied at delivery sites to reduce the residual quantity of H_2S potentially present; this may include delineation of zones, information panels, driver training, documentation, use of adequate local ventilation
- Endeavour to stand upwind and avoid breathing the vapours that escape when the manhole is opened or closed. After unloading bitumen, personnel should allow gases and vapours to dissipate before closing the manhole

5. EVALUATION OF RISKS

Eurobitume has collected H_2S concentration data from its members, as well as peak measurement data from ATMD and Routes de France. The data collected show significant variation in average and peak H_2S concentrations, which could be explained by various factors including:

- Variation in measurement techniques and sampling protocols (which can vary in accuracy and can be affected by interference from other, non-H_2S, compounds present in the atmosphere).
- Measurements taken at variable distances from the H_2S source. Where distance from the source vs personal exposure measurements were recorded, it indicated that the concentrations of H_2S decreased rapidly over increasing distance from the source.
- Variability of local conditions at the time of the measurements, e.g. temperature, wind direction, precipitation etc..
- It is recommended to automate, as far as possible, each potentially hazardous task.

These data are not sufficient to give a robust assessment of risk, but show that the concentration of H_2S in gas phase can reach dangerous or lethal levels in the headspace of the truck trailer or storage tank headspaces. Consequently, the potential for exposure to significant amounts of H2S is greatest during operations associated with headspace of heated storage tanks and delivery trucks and in activities conducted close to manholes and ventilation outlets. Therefore, possibility exists for extremely high exposures in a very short period, even if the short- and long-term OELs are not exceeded. Caution should be taken when opening manholes and where drivers/operators could be in closer proximity to the source of high H_2S concentrations.

If sulphur is added to bitumen or modified products, the risk of exposure to H_2S becomes elevated. This also applies if sulphur-cured products had preceded bitumen deliveries.

6. RISK MANAGEMENT THROUGH THE BITUMEN SUPPLY CHAIN

Directive 89/391/EEC (3) places an obligation on employers to "take the measures necessary for the safety and health protection of workers, including prevention of occupational risks and provision of information and training". It is, therefore, the responsibility of all employers to ensure that employees and other workers on a worksite are aware of the hazards that may be present and that risk management measures are developed to ensure that workers are not exposed to unacceptable risks while carrying out their duties.

Normal operations in open or well-ventilated areas are unlikely to present serious hazards from H_2S during bitumen operations. However, since bitumen may contain H_2S, normal operations of loading/unloading, tank sampling and any activities close to manholes or ventilation pipes should take the potential presence of H_2S into account. Employers should carry out a comprehensive risk assessment taking into consideration the following items. The risk assessment should include risks facing specific types of workers and decide on the protective measures to be taken and, if necessary, the protective equipment to be used.

Exposure measurement or estimation is a key part of risk assessment. In some cases, such emissions may exceed TWA and STEL Occupational Exposure Limits. Likewise, certain tasks within bitumen production and delivery chain may exceed IDLH or peak concentration limits.

6.1. Identification of areas

Instances, circumstances and locations where exposure to H_2S may occur should be clearly identified. Such areas include, amongst others, those where work is conducted around non-contained processes like open manholes, ventilation pipes, sampling stations, etc.

A specific identification sign could be added if concentrations can reach IDLH (Immediately Dangerous to Life and Health).

6.2. Warnings

Warning signs should be provided for areas where there is a risk of hazardous concentrations of H_2S, e.g. warning signs at storage tanks, loading sites, etc.

6.3. Access control

Entry and exit of people into the areas where hazardous levels of H_2S might be present should be controlled, e.g. by sign in/out system via permit officer in control room, electronic sign in/out system. In certain circumstances, a two-way radio communication system could be useful.

6.4. Loading facilities and ventilation

In order to minimize the potential for breathing dangerous levels of H_2S, where possible operators and drivers should position themselves upwind when opening manholes or access hatches.

For areas where there is a risk of hazardous concentrations of H_2S, either natural or forced (e.g. local exhaust) adequate ventilation should be provided.

6.5. Temperature management

Temperature is one of the factors influencing release of H_2S from liquid bitumen, therefore storage temperature should be maintained at a level no higher than operationally necessary.

6.6. Protection of personnel

Personnel performing tasks where high levels of H_2S may be present should be made aware of the hazards associated with H_2S and properly trained to safely perform required tasks (e.g. loading and unloading). Appropriate personal protective equipment (PPE) should be used to address the identified hazards. An example of PPE may include wearing respiratory protection (e.g. a filtering face-piece respirator with acid gas cartridges, supplied-air, or self-contained respirators) when performing tasks or working in areas where it is expected that personnel may encounter higher levels of H_2S (e.g. confined spaces, non-routine operations).

All persons working in areas where exposure during opening of confined spaces can occur must wear a H_2S personal alarmed monitor. This also applies to situations when operations are carried out remotely, as systems may fail.

6.7. Management of activities

Applying a "permit to work" programme may help eliminate or manage exposure to hazardous levels of H_2S.

- Confined space entry programs, including personal alarms, should include control of H_2S beyond general confined spaces entry topics (sufficient oxygen, etc.). H_2S at ambient temperature is more dense than ambient air, therefore H_2S will concentrate in low points (especially when poorly ventilated) and concentration is likely to increase towards the bottom of the space. Bitumen cistern´s atmosphere should be checked carefully from manhole down to the bottom, for example using an H2S detector attached by a wire before entering, even after careful ventilation.
- Procedures for entering other areas where there is risk of high exposure to H_2S.
- Escape routes equipped with windsocks that enable people to safely leave the area in the event of a release.
- If possible, work upwind of any potential H_2S sources.
- Evacuation of non-essential personnel to a safe location if the concentration of H_2S exceeds the occupational exposure limit (OEL). Note that OELs may vary by country or jurisdiction, see Appendix 1.
- Implement applicable formal respiratory protection program, as defined by relevant regulators.
- Personnel should allow gases and vapours to dissipate before getting very close to tank openings. Avoid breathing the vapours very close to tank openings. For opening the manhole, ground-based positioning of operators is recommended. When opening the manhole, take a position as far as possible from the lid.

6.8. Training

Personnel should be educated about H_2S including:

- Where such substances may be present
- How personnel can be exposed
- Potential effects on health following exposure
- How such substances can be detected
- Use and limitations of PPE (Personnel Protection Equipment)
- Use of gas alarmed monitors, including limitations, false readings and conditions of use)
- Alarms and Emergency procedures

Training should raise awareness and provide competence. The effectiveness of training provided should be ensured.

7. RESCUING EXPOSED PERSONNEL

In the event that a person has been overcome and has lost, or is losing consciousness:

- Only personnel authorised and trained in rescue should approach the victim.
- Contact facility personnel immediately to inform them of the emergency and initiate a call to emergency medical services; if facility personnel cannot be reached, immediately call the emergency services.
- If possible, remotely stop any loading or transfer operations.
- Do not approach the victim without using supplied-air respirators (SAR) or self-contained breathing apparatus (SCBA). If you have the appropriate respiratory protective equipment, remove the victim from the contaminated area crosswind of the release.
- Rescue should be conducted with backup personnel also equipped with supplied-air respirators.
- When in a safe area, arrange for first aid and initiate a medical response.
- Keep the victim lying down.
- If you are trained to do so, start cardiopulmonary resuscitation (CPR) if the victim's heart has stopped beating.
- If the victim's eyes are affected by H_2S, flush them thoroughly with clean, cool water.
- Seek medical attention as soon as possible in every case of overexposure. The effects of overexposure to H_2S may be delayed and extended medical observation may be necessary.
- Review established emergency medical procedures with local primary medical care provider(s) and/or first responder staff.

8. CONCLUSIONS

On the basis of the information obtained from data submitted by its member companies, Eurobitume considers that there are some activities that may lead to potentially hazardous exposures to hydrogen sulphide (H_2S) during the loading and discharge process.

Operations of loading/unloading, tank sampling and any activities close to manholes or ventilation pipes should, therefore, take the potential presence of H_2S into account. Consequently, it is strongly recommended that all employees dealing with bitumen should be informed and trained to recognise potentially dangerous situations in relation to H_2S and employers should carry out a comprehensive risk assessment and provide appropriate PPE.

APPENDIX 1 – SELECTED ENTITIES ISSUING OCCUPATIONAL EXPOSURE LIMITS

Country	Authority
Austria	Grenzwerteverordnung 2011 - GKV 2011
Belgium	Belgisch Staatsblad 30 juni 2011; N. 2011-1687
Bulgaria	РБ МТСП и МЗ Наредба №13/2003
Czech Republic	178/2001 (12/2007)
Denmark	Arbejdstilsynet; Grænseværdier for stoffer og materialer, augustus 2007 (publicatie C.0.1)
Estonia	Sotsiaalminister 10/2007
Finland	Työterveyslaitos, Sosiaali- ja terveysministeriö 07/2009
France	Valeurs limites d'exposition professionnelle aux agents chimiques en France; INRS ED 984; juin 2008 (mandatory based on the decree May, 2012)
Germany	TRGS 900; version april 2011
Hungary	EüM-SxCsM 12/2007
Ireland	Health & Safety Authority
Italy	EU OEL/ list of indicateve OEL values 12/2009
Latvia	LV National Standardisation and Meteorological Centre 05/2007
Lithuania	Del Lietuvos Higienos Normos 10/2007
Luxembourg	EU OEL; List of Indicative OEL values 12/2009
Netherlands	Zoek een grenswaarde : In de Databank Grenswaarden Stoffen op de Werkplek kunt u opzoeken welke grenswaarde er is vastgesteld
Norway	Nye administrative normer for forurensning I arbeidsatmosfaere; utgave desember 2011
Poland	Ministra Pracy i Polityki Społecznej (Poland, 7/2009)
Portugal	Instituto Português da Qualidade
Slovakia	Nariadenie Vlady Slovenskej republiky
Spain	Límites de Exposición Profesional para Agentes Químicos en España, 2012; Ministerio de Trabajo e Inmigración, INSHT
Sweden	AFS 2005:17
Switzerland	SuvaPro Grenzwerte am Arbeitsplatz 2009
UK	Health & Safety Executive EH40/2005
OSHA[USA]	United States Department of Labor
ACGIH[Ad]	American Conference of Governmental Industrial Hygienists (United States)
NIOSH[AD]	National Institute for Occupational Safety and Health (United States)
SCOEL	Scientific Committee on Occupational Exposure Limits

[Ad] Advisory bodies
[USA] North American Value

APPENDIX 2 – HYDROGEN SULPHIDE (H_2S) BIBLIOGRAPHY / REFERENCES

(1) Commission Directive 2009/161/EU of 17 December 2009 establishing a third list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Commission Directive 2000/39/EC

(2) World Health Organization: Concise International Chemical Assessment Document 53 [https://apps.who.int/iris/bitstream/handle/10665/42638/9241530537.pdf?sequence=1]

(3) Council Directive 89/391/EEC of 12 June 1989 on the Introduction of measures to encourage improvements in the safety and health of workers at work

Eurobitume documents

- Safe Handling of Bitumen – Eurobitume, 2015
- Managing H_2S Risks during bitumen operations - Eurobitume, 2020
- Guide to the Safe Delivery of Bitumen – Eurobitume, 2018

Other publications on Hydrogen Sulphide

- Guidance of safe use in the REACH dossier for bitumen – CONCAWE REACH Dossier for bitumen
- Recommendation from the Scientific Committee on Occupational Exposure Limits for Hydrogen Sulphide, SCOEL, June, 2007
- Management Practices for Asphalt Facility Control of Hydrogen Sulfide Exposure, Asphalt Institute, 2006
- Energy Institute Model Code of Safe Practice; Part 11 – Bitumen Safety Code, 2023, 5th Edition, ISBN 9781787253605
- HYDROGEN SULPHIDE: UK OCCUPATIONAL EXPOSURE LIMITS; Michael G Costigan, Occup. Environ. Med. 2003;60;308-312, 2003
- Sensory and Cognitive Effects of Acute Exposure to Hydrogen Sulfide - U.S. Department of Health and Human Services, National Institutes of Health: ENVIRONMENTAL HEALTH PERSPECT (ehponline.org:; doi:10.1289/ehp.10531 (available at https://www.ncbi.nlm.gov) Published online 30 October 2007
- Sulfure s'hydrogène (hydrogen sulphide) – INERIS – 29/09/2011

References

1. Concise International Chemical Assessment Document 53, HYDROGEN SULFIDE: HUMAN HEALTH ASPECTS, World Health Organization, Geneva, 2003
2. Amoore JE, Hautala E., Odor as an aid to chemical safety: odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution. J Appl Toxicol. 1983 Dec;3(6):272-90
3. Jäppinen P , Vilkka V, Marttila O, Haahtela T. Exposure to hydrogen sulphide and respiratory function. Br J Ind Med. 1990 Dec;47(12):824-8.
4. Vanhoorne M, De Rouck A, De Bacquer D (1995) Epidemiological study of eye irritation by hydrogen sulfide and/or carbon disulphide exposure in viscose rayon workers.
   Annals of Occupational Hygiene, 3:307–315.
5. IPCS (1981) Hydrogen sulfide. Geneva, World Health Organization, International Programme on Chemical Safety (Environmental Health Criteria 19).
6. Ahlborg G (1951) Hydrogen sulfide poisoning in shale oil industry. Archives of Industrial Hygiene and Occupational Medicine, 3:247– 266.
7. https://www.cdc.gov/niosh/npg/pgintrod.html
8. Hirsch AR, Zavala G (1999) Long term effects on the olfactory system of exposure to hydrogen sulphide. Occupational and Environmental Medicine, 56:284–287.
9. Spolyar LW (1951) Three men overcome by hydrogen sulfide in starch plant. Industrial Health Monthly, 11:116–117.
10. Beauchamp RO Jr, Bus JS, Popp JA, Boreiko CJ, Andjelkovich DA (1984) A critical review of the literature on hydrogen sulfide toxicity. Critical Reviews in Toxicology, 13:25–97.
11. https://echa.europa.eu/registration-dossier/-/registered-dossier/15585

Eurobitume
Boulevard du Souverain 165
B-1160 Brussels
Belgium
T: +32 2 566 91 40
E: info@eurobitume.eu

eurobitume

www.eurobitume.eu
www.linkedin.com/company/eurobitume
www.twitter.com/eurobitume