

# Safety Bulletin

U.S. Chemical Safety and Hazard Investigation Board



## SODIUM HYDROSULFIDE: PREVENTING HARM

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### Introduction

Since 1971, reported incidents involving liquid solutions of sodium hydrosulfide (NaHS) have resulted in 32 deaths and 176 injuries, most notably in the leather tanning and pulp and paper industries. The most serious safety concern associated with NaHS is its capacity to produce large amounts of deadly hydrogen sulfide gas ( $H_2S$ ) when it reacts with an acid or is exposed to high heat.

Despite its pungent rotten egg odor,  $H_2S$  can deaden the nerves that detect odors, thereby preventing those exposed from being able to smell life-threatening airborne concentrations. This condition is referred to as “olfactory fatigue” and must be considered when designing NaHS safety systems.

This Safety Bulletin is published to increase awareness of the hazards associated with NaHS and to outline safety practices to minimize the potential for harm to workers and the public.

### Defining the Problem

NaHS releases highly toxic  $H_2S$  if mixed with an acid or if exposed to excessive heat. Because it is corrosive, it is also potentially harmful to the skin and eyes.<sup>1</sup>

NaHS incidents typically involve the following three elements:

- An inadvertent spill, leak, or mixing, whereby NaHS reacts with an acidic solution to produce  $H_2S$  (Figure 1).

<sup>1</sup> Although this bulletin addresses the hazards associated with NaHS solutions, its precautions also apply to other sulfide-containing substances (e.g., sodium sulfide), which are often used interchangeably with NaHS, and which also generate  $H_2S$  when mixed with acids.

- Absent or inadequate engineering controls, such as ventilation or  $H_2S$  detection devices, coupled with inadequate PPE.
- Inappropriate emergency response actions by workers and emergency responders.

This bulletin reviews selected NaHS incidents that caused death and injury, for example:

- Delivery drivers inadvertently pumping NaHS into acid storage tanks. (See Whitehall Leather, Horween Leather, and Prime Tanning case studies on pages 13–15.)

### Sodium Hydrosulfide

Common synonyms:

NaHS (NaSH)  
Sodium bisulfide  
Sodium sulfhydrate  
Sodium hydrogen sulfide  
Sodium mercaptan

CAS No.: 16721-80-5

UN No. (solution): 2922  
(Figure 2)

DOT Hazard Class: 8

EPA Hazardous Waste No.:  
D003

- Figure 1. Firefighters in NaHS and  $H_2S$  protective gear. MIT



- Figure 2. Shipping placard with UN number and DOT hazard class.



- NaHS being allowed to mix with acids in a plant sewer system. (See Georgia-Pacific and Westvaco case studies on pages 13-14.)
- Mixing of NaHS and an acid inside a common spill containment. (See Powell Duffryn case study on page 13.)

CSB Safety Bulletins offer advisory information on good practices for managing chemical process hazards. Case studies provide supporting information. Safety Bulletins differ from CSB Investigation Reports in that they do not comprehensively review all the causes of an incident.



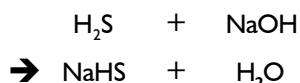
U.S. Chemical Safety and Hazard  
Investigation Board  
Office of Investigations and Safety  
Programs  
2175 K Street NW, Suite 400  
Washington, DC 20037-1848  
202-261-7600  
[www.csb.gov](http://www.csb.gov)

CSB identified the following two common management failures during its review of catastrophic NaHS-related incidents:<sup>2</sup>

- Failure to identify and mitigate hazards during process system design and engineering.
- Failure to manage hazards that were not controlled through good design and engineering.

## Physical Characteristics and Uses of NaHS

Typical NaHS solutions are produced commercially by combining H<sub>2</sub>S with caustic soda (NaOH), as shown in the following reaction:



The resulting finished solution has a pH of approximately 11.5. Depending on its solution strength (22 to 60 percent NaHS), it is heated to 71 to 82 °C to prevent crystallization. NaHS is sold commercially in both solution and flake forms, with solutions accounting for about 80 percent of total U.S. production.<sup>3</sup>

<sup>2</sup> CSB compiled incident data and safety practices described throughout this Safety Bulletin during a comprehensive review of NaHS incidents and industry handling practices.

<sup>3</sup> Total U.S. production for all forms of NaHS was approximately 269,000 tons in 2003.

Table 1 summarizes the general physical properties of NaHS solutions.

**Table 1**  
**Physical Properties of NaHS**

**Molecular weight:** 56.1

**Specific gravity:**

1.152 (a)–1.376 (b)

**pH of solution:**

strongly alkaline (11–12)

**Solution freezing point:**

–15°C(a) – 40°C (b)

**Odor:** rotten egg

**H<sub>2</sub>S flammable limits**

(% H<sub>2</sub>S in air):

Lower: 4

Upper: 44

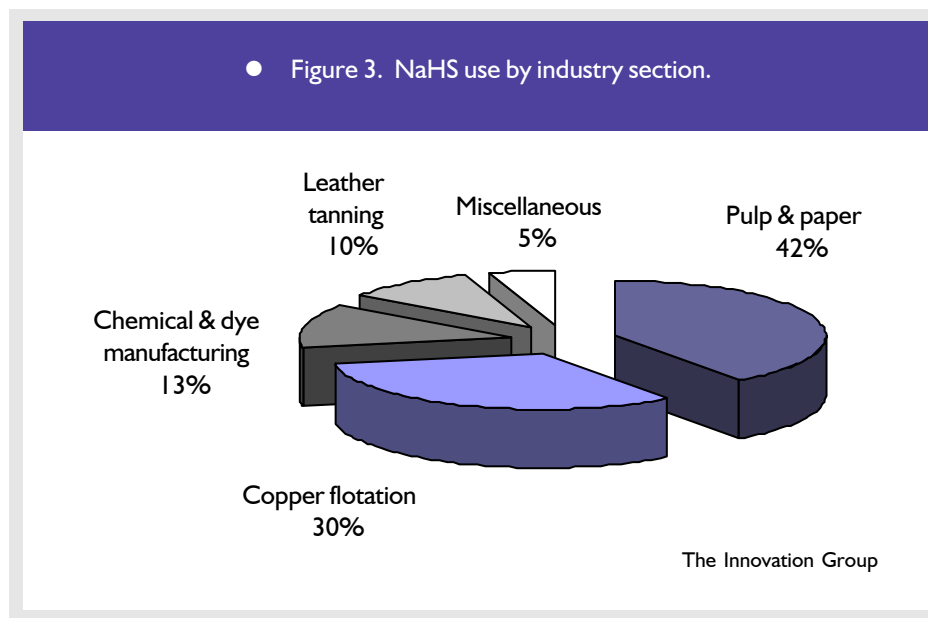
(a) 22% solution.

(b) 60% solution.

NaHS is used in a variety of industries (Figure 3):

- In the pulp and paper industry, to remove lignin from wood chips.
- In mining, as a flotation agent to separate impurities.
- In manufacturing, as a raw material or purifying agent.
- In the leather tanning industry, to remove hair from hides.

● Figure 3. NaHS use by industry section.

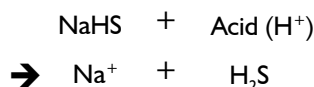


**ACGIH:** American Conference of Governmental Industrial Hygienists  
**AICHe:** American Institute of Chemical Engineers  
**AIHA:** American Industrial Hygiene Association  
**ANSI:** American National Standards Institute  
**ASSE:** American Society of Safety Engineers  
**ATSDR:** Agency for Toxic Substances and Disease Registry, DHHS  
**°C:** Degrees Celsius  
**CAS:** Chemical Abstracts Service  
**CCPS:** Center for Chemical Process Safety, AIChE  
**CDC:** Centers for Disease Control and Prevention, DHHS  
**CFR:** Code of Federal Regulations  
**CO<sub>2</sub>:** Carbon dioxide  
**CSB:** U.S. Chemical Safety and Hazard Investigation Board  
**DHHS:** U.S. Department of Health and Human Services  
**DOE:** U.S. Department of Energy  
**DOT:** U.S. Department of Transportation  
**EPA:** U.S. Environmental Protection Agency  
**ERPG:** Emergency Response Planning Guidelines, AIHA  
**H:** Hydrogen  
**H<sub>2</sub>O:** Water  
**H<sub>2</sub>S:** Hydrogen sulfide  
**HazCom:** Hazard communication, OSHA  
**IDLH:** Immediately dangerous to life or health

**MIT:** Massachusetts Institute of Technology  
**MSDS:** Material safety data sheet  
**Na:** Sodium  
**NaHS:** Sodium hydrosulfide  
**NaOH:** Sodium hydroxide  
**NAS:** National Academy of Sciences  
**NFPA:** National Fire Protection Association  
**NIOSH:** National Institute for Occupational Safety and Health, DHHS  
**NLM:** National Library of Medicine, National Institutes of Health (NIH), DHHS  
**NRC:** National Response Center, USCG  
**NTSB:** National Transportation Safety Board  
**OSHA:** Occupational Safety and Health Administration, U.S. Department of Labor  
**PEL:** Permissible exposure limit, OSHA  
**pH:** Potential of hydrogen  
**PPE:** Personal protective equipment  
**ppm:** Parts per million  
**PSM:** Process safety management, OSHA  
**PTFE:** Polytetrafluorethylene  
**REL:** Recommended exposure limit, NIOSH  
**SCBA:** Self-contained breathing apparatus  
**SO<sub>2</sub>:** Sulfur dioxide  
**STEL:** Short-term exposure limit  
**TWA:** Time-weighted average  
**UN:** United Nations  
**USCG:** U.S. Coast Guard

## Health Hazard Summary

Because NaHS is corrosive, it presents a hazard to unprotected skin and eyes. However, its most serious hazard is its propensity to produce toxic H<sub>2</sub>S gas when mixed with an acid or exposed to high heat sources such as a fire. The acid reaction chemistry is shown as:



### Inhalation

The gases released by NaHS are corrosive and may contain high levels of H<sub>2</sub>S. Inhalation of H<sub>2</sub>S is irritating to the nose and throat. At higher concentrations, it can produce olfactory fatigue, a buildup of fluid in the lungs (pulmonary edema), severe shortness of breath, and death. Table 2 outlines the health effects of inhaling H<sub>2</sub>S.

### H<sub>2</sub>S exposures may cause olfactory fatigue

Continuous exposure to low concentrations (5 to 10 ppm) of H<sub>2</sub>S or brief exposure to higher concentrations (above 50 ppm) deadens the odor-detecting nerves in the nose and lessens the ability to smell dangerous concentrations. The higher the concentration of H<sub>2</sub>S, the faster the onset of olfactory fatigue.

### Eye Contact

#### Corrosivity hazard

Because of the high pH of NaHS solutions (approximately 11.5), contact may severely irritate and burn the conjunctiva and cornea,<sup>4</sup> and may result in permanent tissue damage.

#### Hazard from generated H<sub>2</sub>S

Exposure to low concentrations of H<sub>2</sub>S over several hours or days may

<sup>4</sup> The conjunctiva and cornea are the thin, transparent tissues that cover the outer surfaces of the eye.

result in “gas eyes” or “sore eyes,” with symptoms of scratchiness, irritation, tearing, and burning. Symptoms are likely to disappear when the exposure ends. Prolonged exposure to concentrations of H<sub>2</sub>S above 50 ppm may cause permanent damage or intense tearing, blurring of vision, and pain when looking at bright light.

### Skin Contact

Skin contact with NaHS may produce pain, irritation, redness (erythema), or burns. Because symptoms of exposure severity may

**Table 2**  
**Inhalation of H<sub>2</sub>S**

Concentration (ppm)	Health Effects (a)
0.05	Rotten egg odor detectable by most humans.
0.13–30	Obvious and unpleasant odor.
50–150	Olfactory fatigue (temporary loss of smell) and marked dryness and irritation of nose and throat. Prolonged exposure may cause runny nose, cough, hoarseness, headache, nausea, shortness of breath, and severe lung damage (pulmonary edema).
200–250	Worsening and more rapid onset of the above health effects; possible death in 4 to 8 hours.
300–500	Excitement, severe headache and dizziness, staggering, unconsciousness, and respiratory failure likely in 5 minutes to 1 hour; possible death in 30 minutes to 4 hours.
500+	Rapid onset of severe toxicity, respiratory paralysis, and death. If not fatal, may cause long-term effects such as memory loss, paralysis of facial muscles, or nerve tissue damage.
800–1,000	May be immediately fatal after one or more breaths, resulting in an instant unconsciousness or “knock-down” effect.

(a) Data from NIOSH, NLM, and ATSDR.

be delayed, affected skin should be treated immediately. (See the first aid guidance on page 12.)

## Ingestion

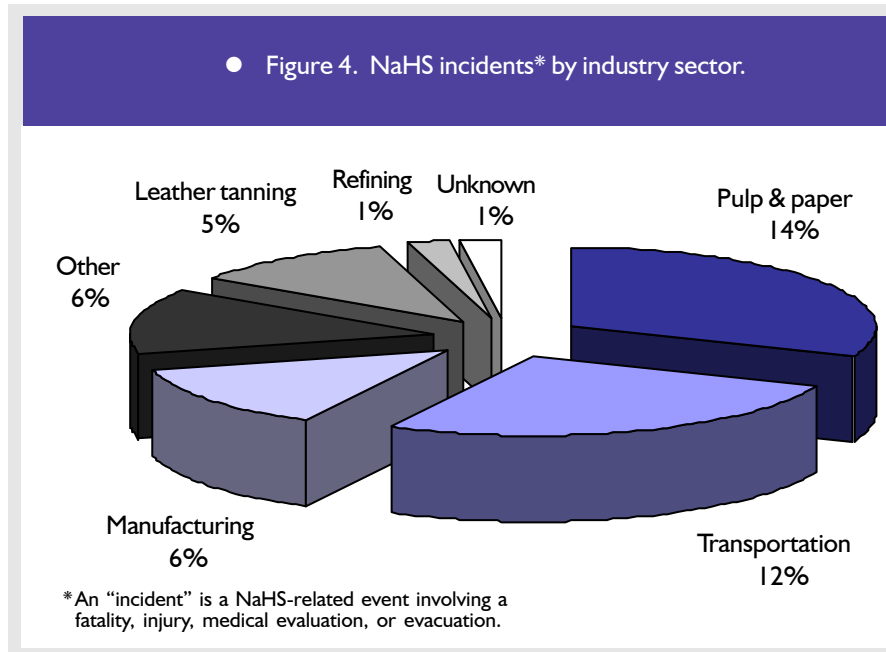
Ingesting a small amount of NaHS in a single dose will likely produce only minor throat irritation or burning of the esophagus. Ingesting a larger quantity, however – or small quantities over an extended period – may seriously damage the gastrointestinal tract. In addition, NaHS that mixes with stomach acids produces H<sub>2</sub>S and may cause the health effects associated with inhalation (Table 2).

## Incident Data

From reported data for the United States from 1971 through 2003, CSB identified 45 NaHS-related incidents (Figure 4).<sup>5</sup> Collectively, these incidents resulted in:

- 32 fatalities.
- 176 injuries.
- 351 medical evaluations.
- At least 10 plant or community evacuations.

<sup>5</sup> The earliest recorded NaHS incident identified during the CSB review occurred in 1971. Regulatory reporting requirements and industry usage practices have changed significantly since that time, which may account for incident rate fluctuations among the various industry sectors. For example, nearly all of the leather tanning incidents occurred between 1971 and 1990, and no transportation incidents were reported prior to 1990. The incidents CSB reviewed include pulping liquor incidents in which NaHS was used as the sulfide source.



Thirty-six of the incidents resulted from H<sub>2</sub>S releases, and the remainder from skin or eye exposure.

The following categories of incidents were identified during this review:

- Improper mixing or transfer: 15 (33 percent).
- Spills: 12 (27 percent).
- Mechanical failure: 7 (16 percent).
- Improper maintenance or repair: 6 (13 percent).

Five of the 45 incidents (11 percent) were attributed to unknown causes.

Incident data were obtained from OSHA, EPA, and ATSDR databases, as well as industry questionnaires, interviews, and media sources. Only those incidents that were reported and accessible are represented.

Although the incidents reviewed are not all-inclusive, their number and severity clearly indicate that NaHS presents a serious hazard in the workplace.

## Prevent Harm

Good safety management includes identifying and evaluating hazards during initial process planning and design, and continues throughout the life cycle of the operation – both for new processes and for modifications. This approach allows managers and employees to understand and address hazards prior to startup.

Hazard control measures such as work practice controls and PPE are secondary layers of protection. They should be considered only after attempting to eliminate hazards through design and engineering, or when substituting

for a less hazardous material or process is impractical.

A multidisciplinary team applying established process safety management principles should identify and evaluate hazards. These principles are outlined in the OSHA Process Safety Management of Highly Hazardous Chemicals (PSM) Standard and in CCPS publications listed at the end of this bulletin.

The PSM Standard regulates processes containing threshold quantities of highly hazardous chemicals, explosives, and flammable liquids in amounts exceeding 10,000 pounds.<sup>6</sup> NaHS is not a PSM-covered chemical because—despite its reactive potential to produce large amounts of H<sub>2</sub>S when mixed with acids or when exposed to heat—it does not meet the OSHA listing criteria.

CSB has recommended that OSHA expand PSM to include chemicals with reactive characteristics similar to those exhibited by NaHS (i.e., relatively stable chemicals that react dangerously with other substances).<sup>7</sup> (See the CSB Hazard

<sup>6</sup> See 29 CFR 1910.119 at [www.osha.gov/SLTC/processsafetymanagement/](http://www.osha.gov/SLTC/processsafetymanagement/). Highly hazardous chemicals are listed in Appendix A.

<sup>7</sup> Based on their reactive characteristics, the chemicals included in Appendix A were selected from the 1975 version of NFPA 49, *Hazardous Chemical Data*. OSHA selected only those chemicals with instability ratings of “3” or “4” (on a scale of 0 to 4). These ratings focus purely on the chemicals themselves and do not consider the consequences of mixing with other chemicals.

Investigation Report, *Improving Reactive Hazard Management* (2002; [www.csb.gov](http://www.csb.gov)).

## Design to Eliminate Hazards

Process systems must be designed to prevent NaHS from inadvertently mixing with acidic solutions. The potential for human error during handling should be identified and eliminated to the maximum extent practicable.

Interviews and literature reviews with NaHS manufacturers, trade associations, and industry representatives highlighted the following design practices:

- Always treat sewers as extensions of the process. Do NOT add wastes without analyzing for compatibility with other sewer contents.
- Separate acid- and NaHS-containing waste streams, or design the system to handle mixing so as to prevent an uncontrolled or otherwise hazardous release of H<sub>2</sub>S.
- Construct separate containments for NaHS and acid storage containers and process equipment.
- Install waste-stream/sewer monitors with alarms to warn employees of system upsets or unfavorable acid conditions.
- Install ventilation systems and H<sub>2</sub>S detectors and alarms at locations where hazardous concentrations may occur.

- Design storage tank vents to minimize the potential for worker exposure.
- Design transfer connections and procedures to prevent inadvertent mixing. Limit access to these connections to trained and authorized personnel through reliable and effective controls, which should include procedures and physical barriers (e.g., locking devices or unique fitting configurations).
- Construct process system components from materials capable of withstanding the corrosivity and temperatures associated with NaHS solutions. NaHS manufacturers recommend the following materials:<sup>8</sup>
  - ◆ Storage tanks and steam coils: 304 stainless steel.
  - ◆ Pumps: 304L or 316L stainless steel.
  - ◆ Packing: PTFE-impregnated carbon fiber.
  - ◆ Piping: 304L stainless steel, insulated and heat-traced in locations where freezing may occur.
  - ◆ Gaskets: Spiral-wound 316L stainless steel or a PTFE ring.
  - ◆ Plug valves: Lubricated or made with a PTFE sleeve and seal.

<sup>8</sup> This information illustrates the types of materials manufacturers recommend for use in NaHS process systems. It is not intended as a substitute for recognized and generally accepted good engineering practices for the specific facility design, construction, or maintenance.

## ● H<sub>2</sub>S hazard: separate NaHS and acids

Allowing spilled NaHS to inadvertently mix with an acid (pH < 7) poses a significant risk of harm. Similarly, if a sewer system is not designed to control H<sub>2</sub>S, allowing NaHS to run off to a sewer containing acids also poses a significant risk. Large amounts of toxic (and flammable) H<sub>2</sub>S may evolve very rapidly!

### Manage Hazards

Eliminating hazards through process design and engineering is the optimal hazard management system. However, additional systems are required when design and engineering do not eliminate these hazards. CSB identified the following management systems as particularly applicable to NaHS users.<sup>9</sup>

#### Communicate hazards to employees

The OSHA HazCom Standard (29 CFR 1910.1200) is based on the simple concept that employees have both a need and a right to know of the hazards associated with chemicals to which they are exposed. They also need to know

<sup>9</sup> The safety programs outlined in this section relate to circumstances identified in the incidents CSB reviewed. Other relevant safety programs—such as management of process change, line breaking, lockout/tagout, and process and equipment integrity—are also extremely important components of a successful accident prevention program.

how to protect themselves from adverse health effects due to chemical exposure. The general requirements of this standard are outlined at [www.osha.gov](http://www.osha.gov).

The HazCom requirements pertaining to NaHS MSDSs and H<sub>2</sub>S training are outlined below:

- **MSDSs:** Employers are required to obtain an MSDS for each hazardous chemical (present or produced at the facility) and to make them readily available to workers. The information contained in MSDSs may vary significantly among NaHS manufacturers.<sup>10</sup> Operations and safety personnel should, therefore, attempt to acquire a better understanding of NaHS hazards through such resources as this Safety Bulletin, MSDSs and product information from multiple NaHS manufacturers, and databases such as the NLM Hazardous Substance Data Base.<sup>11</sup>
- **Training:** Employers are required to train their employees and inform contractors (including delivery drivers, construction workers, and emergency responders) of site-specific NaHS and H<sub>2</sub>S hazards, including plant hazard labeling systems and locations of MSDSs.<sup>12</sup> This is often

<sup>10</sup> See [www.csb.gov](http://www.csb.gov) and [www.osha.gov](http://www.osha.gov) for discussions of MSDS inconsistencies and inaccuracies.

<sup>11</sup> [toxnet.nlm.nih.gov/index.html](http://toxnet.nlm.nih.gov/index.html).

<sup>12</sup> See *Safety Requirements for H<sub>2</sub>S Training Criteria* (ANSI Z390.1-1995, available at [webstore.ansi.org/ansidocstore/default.asp](http://webstore.ansi.org/ansidocstore/default.asp)) for a model H<sub>2</sub>S training program.

accomplished in the form of a facility safety orientation.

### Provide personal protective equipment

Facilities should rely on PPE only after conducting a hazard assessment, as required by the OSHA Personal Protective Equipment, General Requirements Standard (29 CFR 1910.132).<sup>13</sup> Employees should participate in the selection of PPE because of the potential for stress and discomfort created by restrictions to movement, vision, and dexterity. Where practical, PPE should be simple to operate and reasonably comfortable to wear for the duration of the exposure.

- **Chemical protective clothing:** PPE required to protect workers from the corrosive hazards associated with NaHS includes eye and face protection, chemical protective gloves, protective clothing, and foot protection ([www.cdc.gov/niosh](http://www.cdc.gov/niosh)).
- **Respiratory protection:** Because of the toxicity and potential for olfactory fatigue associated with H<sub>2</sub>S (see Table 3), extended exposure above any of the OSHA PELs<sup>14</sup> requires use of an SCBA or airline respirator equipped with a full-face piece and operated in pressure-demand or

<sup>13</sup> [www.osha.gov/SLTC/personalprotectiveequipment/](http://www.osha.gov/SLTC/personalprotectiveequipment/).

<sup>14</sup> See Table Z-2, 29 CFR 1910.1000, [www.osha.gov/pls/oshaweb/owadisp.show\\_document?p\\_table=STANDARDS&p\\_id=9991](http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9991).

**Table 3**  
**H<sub>2</sub>S Exposure Limits**

<b>OSHA (PEL)</b>	
Ceiling (a)	20 ppm
10-minute peak (b)	50 ppm
8-hour TWA	10 ppm
<b>NIOSH</b>	
IDLH (c)	100 ppm
REL (10-minute ceiling) (d)	10 ppm
<b>ACGIH</b>	
15-minute STEL (e)	15 ppm
8-hour TWA	10 ppm

- (a) Concentration generally not to be exceeded during the work shift.
- (b) Workers may be exposed above the ceiling level up to this concentration for a maximum of 10 minutes.
- (c) Exposure to environments exceeding these airborne concentrations is likely to cause death or permanent adverse health effects or to prevent escape. Use of SCBA in pressure-demand or positive-pressure mode is required (see 29 CFR 1910.134).
- (d) Exposure should not exceed the REL for any continuous 10-minute period during the work shift.
- (e) According to ACGIH, exposure should not exceed this level for any continuous 15-minute period during the work shift.

positive-pressure mode. Such respiratory protection could be required when transferring materials to or from tankers, cleaning process equipment, responding to NaHS releases, and performing emergency rescue.

According to OSHA, employers are responsible for determining exposure for all employee activities, including those that expose contractors and

visitors.<sup>15</sup> If respiratory protection is required, employers must comply with the OSHA Respiratory Protection Standard (29 CFR 1910.134).<sup>16</sup>

Before relying on respirators, facilities must have determined that it is impractical to eliminate or control hazards through substitution of a less hazardous chemical, design and engineering controls, or work practice or administrative controls.

NIOSH has certified certain full-face air purifying respirators (i.e., a facemask equipped with a filter) for emergency escape purposes, but only where H<sub>2</sub>S concentrations do not exceed 100 ppm.<sup>17</sup> For all other situations, NIOSH prescribes supplied-air respirators. These requirements are outlined in the NIOSH *Pocket Guide to Chemical Hazards* (2003; [www.cdc.gov/niosh/npg/npg.html](http://www.cdc.gov/niosh/npg/npg.html)).

- **Air monitoring for H<sub>2</sub>S:** In environments that are normally safe, but which pose the risk of hazardous H<sub>2</sub>S exposure, the only way to ensure worker safety is to continuously monitor the air. In recent years, H<sub>2</sub>S monitors have become much smaller, more

<sup>15</sup> A person trained in industrial hygiene sampling practices must perform exposure monitoring to ensure compliance with the OSHA PEL.

<sup>16</sup> [www.osha.gov/SLTC/respiratoryprotection/](http://www.osha.gov/SLTC/respiratoryprotection/).

<sup>17</sup> OSHA relies on NIOSH as the testing and certifying body in 29 CFR 1910.134. NIOSH requires end-of-service life indicators for filters used to protect against chemicals with poor warning properties, such as H<sub>2</sub>S. There are currently no approved filters for extended protection against H<sub>2</sub>S.

rugged and reliable, simpler to operate, and much less expensive. Examples of available devices are noted below:

- ◆ Personal H<sub>2</sub>S detectors with audible, vibrating, and visual alarms: These detectors can be clipped into a shirt pocket or worn on a hard hat. They are relatively inexpensive and reliable, and have low-maintenance electrochemical sensors and long-lasting batteries.
- ◆ Stationary H<sub>2</sub>S detection and notification systems: These systems provide alarm notification 24 hours a day and can be used to automatically notify emergency responders. Freestanding solar- and battery-powered systems are also available that can be equipped with radio transmitters to send real-time monitoring results to a remote alarm or warning device.

### *Enter confined spaces safely*

Because H<sub>2</sub>S is heavier than air, it tends to concentrate near or below ground level, especially where there is limited air movement. Sump pits, storage and process tanks, valve trenches, and sewers are particularly susceptible to high concentrations of H<sub>2</sub>S and may require atmospheric testing, communications equipment, and standby emergency rescue personnel.

OSHA regulates confined spaces in the Permit-Required Confined



Spaces Standard (29 CFR 1910.146).<sup>18</sup> Further information and guidance on this standard is provided in the references section of this bulletin.

### *Handle and store NaHS safely*

The hazards associated with NaHS require employers to establish facility-specific safe handling and storage practices and procedures for both employees and contractors. These practices and procedures include:

- Controlling access and supervising product delivery and transfer.
- Installing local exhaust ventilation on process or storage equipment where personnel exposure is likely and ensuring that such systems are operating properly before starting a process.
- Installing fixed H<sub>2</sub>S monitors with alarms in NaHS storage and offloading areas where concentrations could exceed safe levels.
- Providing PPE and emergency eyewash and shower facilities where there is a risk of exposure to NaHS.
- Ensuring that NaHS-containing wastes are not flushed to acid-containing sewers without controls to prevent a release of H<sub>2</sub>S.
- Storing NaHS separately from low pH (acidic) materials to avoid inadvertent mixing.

- Clearly labeling NaHS containers, process piping, and critical process piping valves that may contain NaHS with essential hazard information.
- Warning against exposure of NaHS to excessive heat or storage near open flames or other ignition sources that might generate or ignite flammable H<sub>2</sub>S.
- Ensuring that storage containers and process equipment materials are compatible with the alkalinity of NaHS. Manufacturers of NaHS warn against using copper, zinc, or aluminum.
- Implementing an emergency notification system to inform emergency responders and potentially impacted offsite residents of threatening incidents.

## Emergency Response

Emergency responders must immediately take precautions in the case of a fire or spill involving NaHS. If there is evidence of an H<sub>2</sub>S release – either the presence of its characteristic rotten egg odor or affirmative H<sub>2</sub>S monitoring results – emergency responders should:

- **Restrict access to the spill/release site:** Allow only emergency personnel equipped with proper PPE to enter the area (i.e., NIOSH-approved, full face-piece SCBA in pressure demand mode, and protective outer garments).

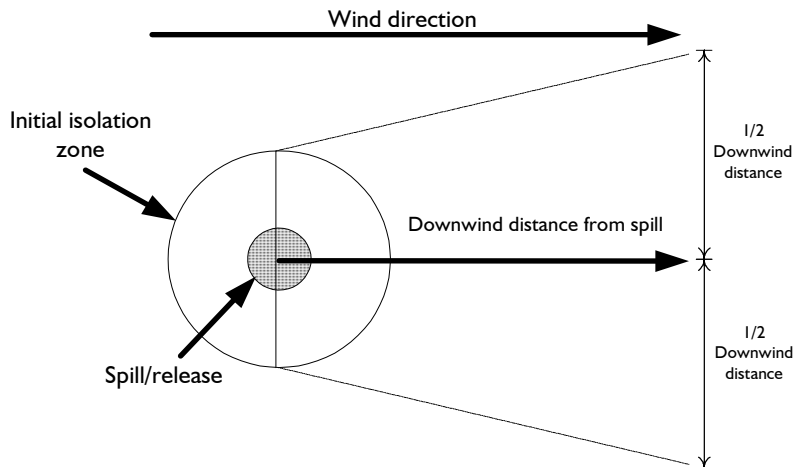
- **Decide whether to evacuate or shelter-in-place:** This decision is made under urgent conditions. Factors that must be considered include population distribution, risk of exposure, adequacy of available shelters, evacuation time requirements, and other factors such as the characteristics of the chemical released and weather conditions. This issue has been studied thoroughly by researchers at the Oak Ridge National Laboratory, as documented in *Planning Protective Action Decision-Making: Evacuate or Shelter-in-Place?* (USDOE, 2002; [www.osti.gov/bridge/](http://www.osti.gov/bridge/)).

A decision to evacuate should be based on the reasonable assurance that movement is in the best interest of those being evacuated:

- ◆ **Evacuation:** Downwind of a release – before starting to move upwind – unprotected personnel should move directly crosswind to one-half of the downwind distance from the spill. The crosswind distance varies in relation to the size of the spill and downwind distance. See Figure 5 and Table 4 for the initial isolation and protective action distances recommended by the DOT Emergency Response Guidebook (2000; [hazmat.dot.gov/guidebook.htm](http://hazmat.dot.gov/guidebook.htm)).

<sup>18</sup> [www.osha.gov/SLTC/confinedspaces/](http://www.osha.gov/SLTC/confinedspaces/)

● Figure 5. Initial isolation and evacuation diagram.



- ◆ **Shelter-in-place:** This is a precaution to keep people safe while remaining indoors. It calls for taking refuge in a preferably small, interior room with no or few windows; closing windows and doors; turning off heating and air-conditioning systems; and listening to local TV/radio for emergency response directions.

Offsite residents or plant personnel who may be required to shelter-in-place must be provided with instructions and training, and must have necessary supplies on hand (e.g., food, water, tape, vinyl sheeting) prior to an incident. Detailed

information regarding shelter-in-place is available at [www.cdc.gov/](http://www.cdc.gov/) and [www.redcross.org/](http://www.redcross.org/).

- **Conduct continuous downwind monitoring:** Determine if  $H_2S$  concentrations exceed the AIHA ERPGs<sup>19</sup> (ERPG-3 or -2 values from Table 5) or the OSHA PEL; and continue to evacuate or shelter-in-place as required.

### Firefighting

Contact between  $NaHS$  and an acid – or exposure to excessive heat – liberates  $H_2S$ , which presents an inhalation and fire

<sup>19</sup> NAS has developed acute exposure guideline levels that may be more protective than AIHA ERPGs. Interim exposure levels for  $H_2S$  are available at [www.epa.gov/oppt/aegl/](http://www.epa.gov/oppt/aegl/).

**Table 4**  
 **$H_2S$  Initial Isolation and Protective Action Distances**

#### Small Spill (a)

1. Isolate spill area **100 feet** in all directions
2. Protect persons downwind  
Day (b) – 0.1 mile (528 feet)  
Night – 0.2 mile (1,056 feet)

#### Large Spill (c)

1. Isolate spill area **700 feet** in all directions
2. Protect persons downwind  
Day (b) – 0.9 mile (4,752 feet)  
Night – 2.7 miles (14,256 feet)

(a) From a small package (55 gallons or smaller) or a small leak from a large package.

(b) Sunrise to sunset.

(c) From a large package or from many small packages.

Source: USDOT, 2000.

**Table 5**  
**H<sub>2</sub>S Emergency Response**  
**Planning Guidelines**

	<b>60-Minute Concentration (ppm)</b>
ERPG-3 (a)	100
ERPG-2 (b)	30
ERPG-1 (c)	0.1

- (a) ERPG-3 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.
- (b) ERPG-2 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their ability to take protective action.
- (c) ERPG-1 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.

Source: AIHA, 1991.

hazard. In addition, burning H<sub>2</sub>S produces sulfur dioxide (SO<sub>2</sub>), which is a severe respiratory irritant that can be life threatening. If a fire involves NaHS, the DOT Emergency Response Guidebook (2000) recommends the following:<sup>20</sup>

- Small fires:
  - ◆ Use dry chemicals, CO<sub>2</sub> or water spray.<sup>21</sup>
- Large fires:
  - ◆ Use dry chemicals, CO<sub>2</sub>, alcohol-resistant foam, or water spray.
  - ◆ Move containers of NaHS from fire area if possible to do so without risk.
  - ◆ Contain contaminated fire control water for later disposal.
- Fires involving a tank, railcar, or tank truck:
  - ◆ Fight the fire from the maximum distance possible, or use unmanned hose holders or monitor nozzles.
  - ◆ Do NOT allow water to enter containers of NaHS.

<sup>20</sup> See Guide 154 for NaHS.

<sup>21</sup> Some manufacturers and fire safety professionals caution against using extinguishers containing CO<sub>2</sub> and dry chemical extinguishing media because they form acids when mixed with water and may exacerbate the generation of H<sub>2</sub>S when used on fires involving NaHS. They recommend using water in flooding quantities to fight the actual fire, and water spray or foam to control vapors. If CO<sub>2</sub> or dry chemical extinguishers are used, responders must wear proper respiratory protection (i.e., SCBA).

- ◆ Cool containers with flooding amounts of water until well after the fire is extinguished.
- ◆ Withdraw immediately in case of a rising sound from venting safety devices or discoloration of the tank.
- ◆ ALWAYS stay away from burning tanks.

## Spill Response

In the event of a NaHS spill:

- Do NOT allow NaHS to come in contact with acids.
- Contain the spill. Do NOT flush to a sewer unless the sewer is designed and engineered to control the H<sub>2</sub>S that may be released.
- Remove sources of ignition so that any H<sub>2</sub>S released will not ignite.
- Provide maximum ventilation.
- Recover spilled material on adsorbents, such as sand or vermiculite, and place in covered containers for reclamation or disposal.
- For spills that exceed the 5,000-pound reporting threshold,<sup>22</sup>

<sup>22</sup> NaHS is listed in Table 302.4 of the Superfund, Emergency Planning and Community Right-to-Know Act (40 CFR 302) as a hazardous substance with a reportable quantity of 5,000 pounds, based on 100 percent purity (approximately 1,077 gallons of 43 percent solution). See [www.epa.gov/swercepp/factsheets/epcra.pdf](http://www.epa.gov/swercepp/factsheets/epcra.pdf) for more information.

notify NRC at 1-800-424-8802 or [www.nrc.uscg.mil](http://www.nrc.uscg.mil).<sup>23</sup>

## Emergency Responders

Emergency responders must wear NIOSH-approved, full face-piece SCBA in pressure-demand or positive-pressure mode and chemical-resistant outer garments when there is a threat of airborne concentrations of H<sub>2</sub>S exceeding the PEL. To avoid endangering emergency responders, NaHS- or H<sub>2</sub>S-contaminated outerwear should be discarded and victims decontaminated prior to placing them in a confined space, such as a medical transport vehicle.

## Emergency rescue

If H<sub>2</sub>S is present, do NOT attempt to rescue a fallen worker without proper PPE.

## First Aid

Each year a large number of fatalities result from failed rescue attempts by those who rush into dangerous environments to help fallen workers. *First responders and emergency medical personnel must protect themselves before rendering aid to others.*

<sup>23</sup> This is a regulatory threshold reporting quantity established by EPA with an emphasis on identifying adverse environmental impact. Spills and releases of much smaller quantities of NaHS can lead to catastrophic consequences. For example, the spillage of about 100 gallons of NaHS led to the Georgia-Pacific incident, reviewed on page 13.

Emergency responders responsible for facilities that handle NaHS should familiarize themselves with the ATSDR *Medical Management Guidelines for H<sub>2</sub>S* (2003; [www.atsdr.cdc.gov/MHMI/mmg114.html](http://www.atsdr.cdc.gov/MHMI/mmg114.html)). Do NOT enter an unknown or potentially hazardous environment without ensuring that it is safe by sampling the air and/or wearing proper PPE.<sup>24</sup>

## Inhalation of H<sub>2</sub>S

Move the victim into fresh air and administer oxygen as necessary.<sup>25</sup> Victims of overexposure to H<sub>2</sub>S (or NaHS vapors that may contain H<sub>2</sub>S) should immediately receive emergency medical attention.

## Eye Contact

In the event of eye contact with either NaHS or high concentrations of H<sub>2</sub>S, immediately irrigate the eyes with copious amounts of water for at least 20 minutes, or until the arrival of emergency medical personnel. An ophthalmologic examination should be conducted as soon as possible because the extent of some injuries related to corrosive eye exposure may not be apparent for 48 to 72 hours.

<sup>24</sup> Eight contractor employees were injured during the Georgia-Pacific incident when they remained in the zone of danger to assist with the rescue of fallen workers.

<sup>25</sup> In some states, administering oxygen requires emergency medical certification.

Chemical shower and eyewash facilities must meet the requirements outlined in the OSHA Medical Services and First Aid Standard (29 CFR 1910.151(c)).<sup>26</sup> Applying elements of the Emergency Eyewash and Shower Equipment standard, ANSI Z358.1-2004, fulfills OSHA requirements and provides adequate protection to workers.<sup>27</sup>

## Skin Contact

Immediately remove contaminated clothes and irrigate exposed skin with copious amounts of water for at least 15 minutes, regardless of symptoms. A physician may need to examine the exposed area if irritation or pain persists or worsens.

## Ingestion

Do NOT induce vomiting or attempt to neutralize ingested NaHS. Immediately request emergency medical assistance by calling 911 and the national Poison Control Center emergency hotline at 1-800-222-1222.

<sup>26</sup> [www.osha.gov/pls/oshaweb/owadisp.show\\_document?p\\_table=STANDARDS&p\\_id=9806](http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9806).

<sup>27</sup> ANSI Z358.1-2004 is available for purchase at [webstore.ansi.org/ansidocstore/default.asp](http://webstore.ansi.org/ansidocstore/default.asp).

## Selected Case Studies

### **Georgia-Pacific, Naheola pulp and paper mill, Pennington, Alabama (2 killed, 8 injured)**

On January 16, 2002, two workers were killed and eight injured while performing maintenance near a NaHS transfer terminal. NaHS had recently been pumped from 15 tanker trucks into storage tanks. Because of a leaking pump, NaHS accumulated in a containment pit that was connected to the plant acid sewer.

When the containment pit was drained, a relatively small quantity of NaHS<sup>28</sup> reacted with acid in the sewer to produce H<sub>2</sub>S. The H<sub>2</sub>S leaked through a faulty manway cover seal into the area where the contractors were working.

The CSB investigation concluded that Georgia-Pacific management was unaware that the containment pit drained to the acid sewer. However, neither Georgia-Pacific nor the previous plant owners had adequately evaluated the potential for hazardous chemical mixing in the sewer system and the release of deadly amounts of H<sub>2</sub>S. Consequently, plant personnel, contract workers, and emergency responders were unaware of and unprepared for the dangers.

<sup>28</sup> CSB investigators estimated that 100 gallons of NaHS was allowed to accumulate in the pit.

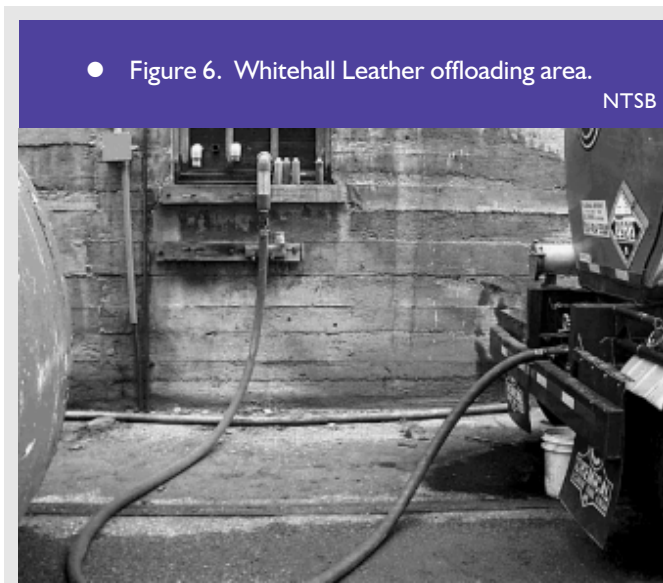
### **Whitehall Leather Company, Whitehall, Michigan (1 killed, 1 injured)**

On June 4, 1999, the driver of a tanker truck filled with NaHS inadvertently pumped the tanker contents into a storage tank partially filled with “pickle acid” (hydrochloric acid). The tanker truck had arrived at the plant during the night shift.

The shift supervisor – never having received a shipment of NaHS and believing it to be pickle acid – directed the driver to unload it into a pickle acid storage tank (Figure 6). The resulting reaction released H<sub>2</sub>S, which killed the driver and injured a plant employee.

### **Powell Duffryn terminal fire, Savannah, Georgia (337 medical evaluations, community evacuation)**

On April 10, 1995, the force from an explosion in a solvent storage tank fractured NaHS transfer piping. Up to 300,000 gallons of NaHS spilled and mixed with a similarly large quantity of acidic cleaning solution (Figure 7). The NaHS and



● Figure 6. Whitehall Leather offloading area.

NTSB

acid solution tanks were colocated inside an earthen containment.

The reaction released an enormous volume of H<sub>2</sub>S, which caused 337 people to seek medical evaluations and forced 2,000 downwind residents to evacuate. The evacuation lasted more than 30 days as H<sub>2</sub>S continued to evolve from NaHS-saturated soil.

This incident illustrates the failure of management systems to identify and evaluate the hazards associated with collocating incompatible materials inside a single spill containment. The EPA investigation report (1998) is available at [yosemite.epa.gov/opa/admpress.nsf/0/8e314f057b62e118852565fe006fa986?OpenDocument](http://yosemite.epa.gov/opa/admpress.nsf/0/8e314f057b62e118852565fe006fa986?OpenDocument).

● Figure 7. Powell Duffryn fire.

EPA



**Stone Savannah River pulp and paper mill, Wentworth, Georgia (1 killed, 4 injured)**

On December 8, 1990, one worker was killed and four injured when a large quantity of  $H_2S$  formed during acid cleaning of a 20,000-gallon pulping solution pressure filter.  $H_2S$  was routinely produced inside the process vessel when the cleaning solution was used to dissolve NaHS-containing pulping filtrate. Local exhaust ventilation normally controlled the  $H_2S$ .

However, on the day of this incident,  $H_2S$  leaked from the system and accumulated inside the walled containment where workers were operating valves. According to witnesses, the workers immediately smelled  $H_2S$  and tried to escape, but were overwhelmed before being able to climb out of the valve pit. This incident highlights

the dense gas properties of  $H_2S$  and the atmospheric hazards that may be present in confined spaces.

**WESTVACO paper mill, Covington, Virginia (10 injured)**

On May 4, 1988, 10 employees were hospitalized for  $H_2S$  exposure when a 300,000-gallon storage tank containing pulping solution

collapsed (Figure 8). The plant sewer system routinely controlled storm runoff, spills, and discharged wastes.

However, when the NaHS-containing pulping solution entered the sewer, it reacted with waste acids and produced  $H_2S$ —which escaped via drains, vents, and manways. The 10 injured employees were working at various locations near the vents and manways.

**Horween Leather Company, Chicago, Illinois (8 killed, 43 injured)**

On February 14, 1978, eight workers were killed, 43 were injured, and 57 sought medical evaluation after being overwhelmed by  $H_2S$ . The incident began when a substitute delivery driver unloaded a tanker truck of NaHS into a storage tank containing an acid. He was unfamiliar with plant operations and NaHS hazards, and was unsupervised by plant personnel.

● Figure 8. WESTVACO paper mill tank failure.

Crawford Akers Photography



A large volume of H<sub>2</sub>S was immediately generated, which led to evacuation of the entire plant and surrounding community. Although the tank fill line coupling was designed to prevent inadvertent mixing, the driver created a makeshift coupling when he was unable to attach the line from the truck.

**Prime Tanning Company,  
Berwick, Maine (6 killed)**

On April 2, 1971, six workers died when NaHS was inadvertently pumped into a tank containing acidic chrome tanning liquor, which has a pH of 3 to 4. The NaHS delivery drivers had been instructed where to offload their tanker truck.

When the drivers discovered that the truck's fill nozzle would not fit the tank's coupler, they used an adapter nozzle. There was no labeling on the tank to identify its contents or to warn of the potential hazard. Approximately 160 gallons of NaHS had been transferred to the tank before one of the drivers noticed that workers inside the plant were collapsing. NaHS had mixed with the chrome liquor to produce H<sub>2</sub>S.

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