

Case Study

U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD



HYDROGEN SULFIDE EXPOSURE

No. 2003-02-C-OH
September 2003



ENVIRONMENTAL ENTERPRISES, INC.

Cincinnati, Ohio
December 11, 2002

KEY ISSUES:

- ◆ Hazard Communication
- ◆ Operating Procedures
- ◆ Management Oversight
- ◆ Mechanical Integrity

Introduction

This Case Study describes a hydrogen sulfide (H_2S) exposure incident that occurred December 11, 2002, at the Environmental Enterprises, Inc. (EEI), facility in Cincinnati, Ohio. One person was injured. The H_2S exposure was caused by using the incorrect vessel for waste treatment.

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1.0 Background

At approximately 2:00 pm on December 11, 2002, a maintenance employee entered the wastewater treatment (WWT) room at Environmental Enterprises, Inc. (EEI), in Cincinnati, Ohio, to retrieve a tool. His path brought him directly alongside the WWT clarifier, an open-top tank with a conical bottom for settling solids (Figure 1).

As the mechanic approached the clarifier, he noticed a “rotten egg” odor that became stronger as he moved forward. He suddenly felt pressure in his lungs and was unable to breathe. He attempted to flee the area, but was overcome by hydrogen sulfide (H₂S) gas and collapsed.

Fortunately, fellow employees found the victim a few moments later and pulled him to safety. He recovered, and there were no other injuries.

1.1 Incident Review Process

The U.S. Chemical Safety and Hazard Investigation Board (CSB) examined physical evidence at the site, conducted interviews, and reviewed relevant documents. CSB conducted this investigation in cooperation with the Occupational Safety and Health Administration (OSHA) and the Ohio Environ-

Figure 1
Open-top WWT clarifier



mental Protection Agency (OEPA), Division of Hazardous Waste Management. The City of Cincinnati Office of Environmental Management, the Metropolitan Sewer District of Greater Cincinnati, and the Cincinnati Fire Department Hazardous Materials/Environmental Crimes Unit were also consulted.

1.2 Properties of Hydrogen Sulfide

H₂S is a colorless, extremely toxic flammable gas. It has a rotten egg odor that most people can smell at

Cover photo:

EEI wastewater treatment vessels. The clarifier is in the back far left; the treatment tank is in the center.

CSB Case Studies summarize incident investigation data and present conclusions based on CSB analyses. They do not discuss root and contributing causes or make safety recommendations—unlike the more comprehensive CSB Investigation Reports.



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very low concentrations. However, exposure at higher concentrations deadens the sense of smell, which results in an *inability* to smell the gas. Exposure to concentrations of 500 parts per million (ppm) causes unconsciousness, and concentrations as low as 700 ppm can cause immediate death.¹

H₂S is well known in industry because it occurs naturally in some crude oils and untreated petroleum products. It also evolves from chemical reactions between sulfur-containing compounds and acids. Because H₂S is heavier than air, it sinks toward low points if released at elevations, such as from the top of an open vessel.

1.3 EEI Operations

Environmental Enterprises, Inc. (EEI), is a privately held company that has operated at its present location on Spring Grove Avenue in Cincinnati for 30 years. According to the company website, EEI processes 35,000 drums of household hazardous waste per year, recycling more than 90 percent. Corporate offices and the main testing laboratory are located nearby. EEI employs a staff of 80 at the Spring Grove facility.

The EEI hazardous waste treatment and storage facility

¹Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Hydrogen Sulfide.

receives laboratory, light industrial, and household hazardous waste (e.g., paint, cleaners, pesticides, and solvents). The aqueous portion of this waste and wastewater material is treated and filtered before being discharged to the municipal sewer.

EEI provides hazardous waste collection and transportation, hazardous waste emergency response, and onsite hazardous waste remediation services. The company also provides a “lab-pack” service, wherein EEI technicians separate, package, and transport laboratory hazardous wastes to assist facilities in meeting Federal and state regulations for disposal.

The company was an active participant in the 1994 program sponsored by the City of Cincinnati to encourage homeowners to collect and properly dispose of household hazardous waste.

1.4 Waste Treatment Operations

The hazardous waste treatment facility at EEI is a permitted treatment, storage, and disposal (TSD) facility as defined and regulated by the U.S. Environmental Protection Agency (EPA).² The treatment area (located in a separate building) consists of a

²Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities, 40 CFR 264.

♦ . . . EEI processes 35,000 drums of household hazardous waste per year, recycling more than 90 percent.

series of tanks and filters that receive, store, chemically treat, filter, and settle solids out of water-based waste streams.

Hazardous waste comes into the facility in containers ranging from small household cans and bottles to 55-gallon drums. The aqueous portion of this waste is consolidated in a storage tank. The solution is sampled and tested to determine a treatment protocol.

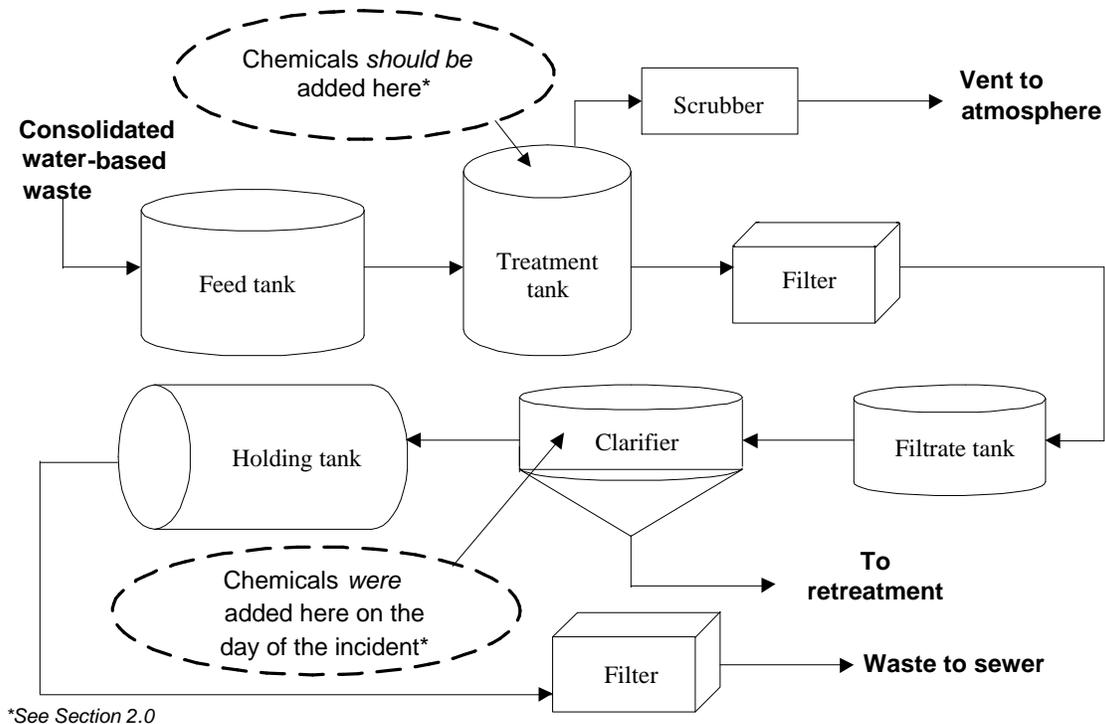
The wastewater treatment process is a polishing step that represents the final stage of hazardous waste treatment. This process is

regulated by EPA under the Clean Water Act and by the City of Cincinnati Municipal Sewer District.

EEI treats the waste by adding chemicals to react with the various contaminants, adjusting for pH, and filtering. The treated solution is held in a clarifier. If all pollutants are determined to be within permitted limits, the liquid is tested and decanted into a storage tank and filtered again. A final test is performed before discharging the material to the municipal sewer system. Figure 2 is a simplified flow diagram of the WWT process.

Figure 2

Simplified process flow diagram for WWT operation at EEI



2.0 Description of Incident

Operations on December 10, the day before the incident, were fairly typical for the Spring Grove facility. Water-based waste containing various contaminants, including heavy metals, was received into the WWT area. The waste was sampled and analyzed. An experienced waste treatment operator determined what treatment was required and began to process the material.

Late that day or early the next morning, the operator sampled the treated liquid in the clarifier. Tests revealed that the mercury content was above the discharge permit limit (0.02 ppm).

A typical method of removing heavy metals from water-based waste streams is to add a chemical to react with the metal. The product of this reaction is a salt that precipitates (i.e., settles) out of solution so that the remaining liquid can be decanted and discharged.

On December 11, the waste treatment operator added 50 pounds of sodium sulfide (Na_2S)³ flake to the water-based waste in the clarifier to precipitate mercury

sulfite (Figure 3). Because the clarifier is not equipped with a mixer or agitator,⁴ the operator connected a plant air hose to the vessel to provide mixing (this action is typically referred to as “air rolling”). After decanting, tests showed that the mercury was within limits, but the pH was high (11.4) due to the alkalinity of Na_2S .⁵

The operator then added an acidic chemical—polyaluminum chloride⁶ (PAC)—to the clarifier (Figure 4). This was intended to bring the mercury salts together into larger, heavier clusters (i.e., to flocculate) and to adjust the pH toward neutral (the permitted range is 6 to 10).⁷ Three 55-gallon drums of PAC were added over a few hours.

At approximately 2:00 pm on December 11, the facility compliance coordinator—whose primary responsibility is environmental regulations—was alerted to an H_2S

⁴The treatment tank—not the clarifier—is the proper location for this type of chemical treatment (Figure 2) because it is enclosed, vented to a scrubber, and equipped with a mixer.

⁵Excess Na_2S not consumed in the mercury salt formation reaction contributed to the high pH.

⁶Aluminum hydroxychloride: $\text{Al}_2(\text{OH})_x\text{Cl}_{(6-x)}$. The MSDS indicates that the PAC solution used at EEI has a pH of 2 to 3 and is incompatible with alkalis (i.e., basic materials, or those with high pH).

⁷City of Cincinnati Municipal Sewer District permit.

³The pH of Na_2S is 13.5 in a 10 percent solution. The material safety data sheet (MSDS) states that Na_2S is incompatible with strong acids and decomposes to release H_2S .

... The operator connected a plant air hose to the vessel to provide mixing. . .

... The operator then added . . . polyaluminum chloride to the clarifier . . . to bring the mercury salts together into larger, heavier clusters and to adjust the pH . . .

Although the employees . . . were accustomed to waste treatment odors, not everyone was aware of the dangers of H₂S.

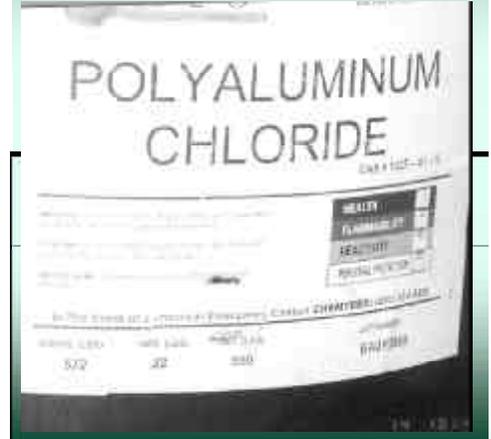
Figure 3
Sodium sulfide flake



smell. He entered the WWT area, noticed the strong odor, and left immediately to get a portable gas detector.

A few minutes later, a maintenance employee entered the WWT area to retrieve a tool that the operator had borrowed. The tool was located in an equipment cage near the treatment vessels. When the mechanic entered the room, he noticed the odor of H₂S but was not concerned because he had smelled it before, with no ill effects.

Figure 4
Polyaluminum chloride



Although the employees in the Spring Grove facility were accustomed to waste treatment odors, not everyone was aware of the dangers of H₂S. The mechanic recalls proceeding toward the tool cage; he felt as if the breath was suddenly sucked from his lungs, then felt burning and pressure in his chest.⁸ He stumbled back toward the door through which he had entered and collapsed in a main pathway, within 20 feet of the clarifier vessel.

⁸ATSDR describes H₂S as causing respiratory arrest and pulmonary edema (i.e., excess fluid accumulation).

When the compliance coordinator returned to the WWT area equipped with a hand-held gas detector, he discovered the mechanic lying unconscious on the floor and not breathing. At nearly the same instant, the gas detector began to alarm. Although the compliance coordinator did not read the display on the detector at that time, a supervisor checked the meter within the hour; the indicator showed an H₂S level of approximately 85 ppm.⁹

Ventilation fans in the WWT building are likely responsible for lowering toxic gas levels below the high concentration that was present when the mechanic was first exposed.

The supervisor for another EEI division (located in the same building) had also entered the WWT area at about the same time to investigate the odor. He and the compliance coordinator pulled the mechanic from the room. The

victim began breathing on his own; fresh air and the action of being pulled by the arms may have facilitated his recovery. The rescuing employees gave the victim oxygen until emergency responders arrived. He was taken to a local hospital for evaluation and released; he reported no lingering effects.

There were no other injuries. Because of the short duration of high H₂S concentration, the other employees who went to the WWT area to address the situation were not overcome, even though they were not wearing respiratory protection.

Figure 5 shows the sequence of events leading up to the incident.

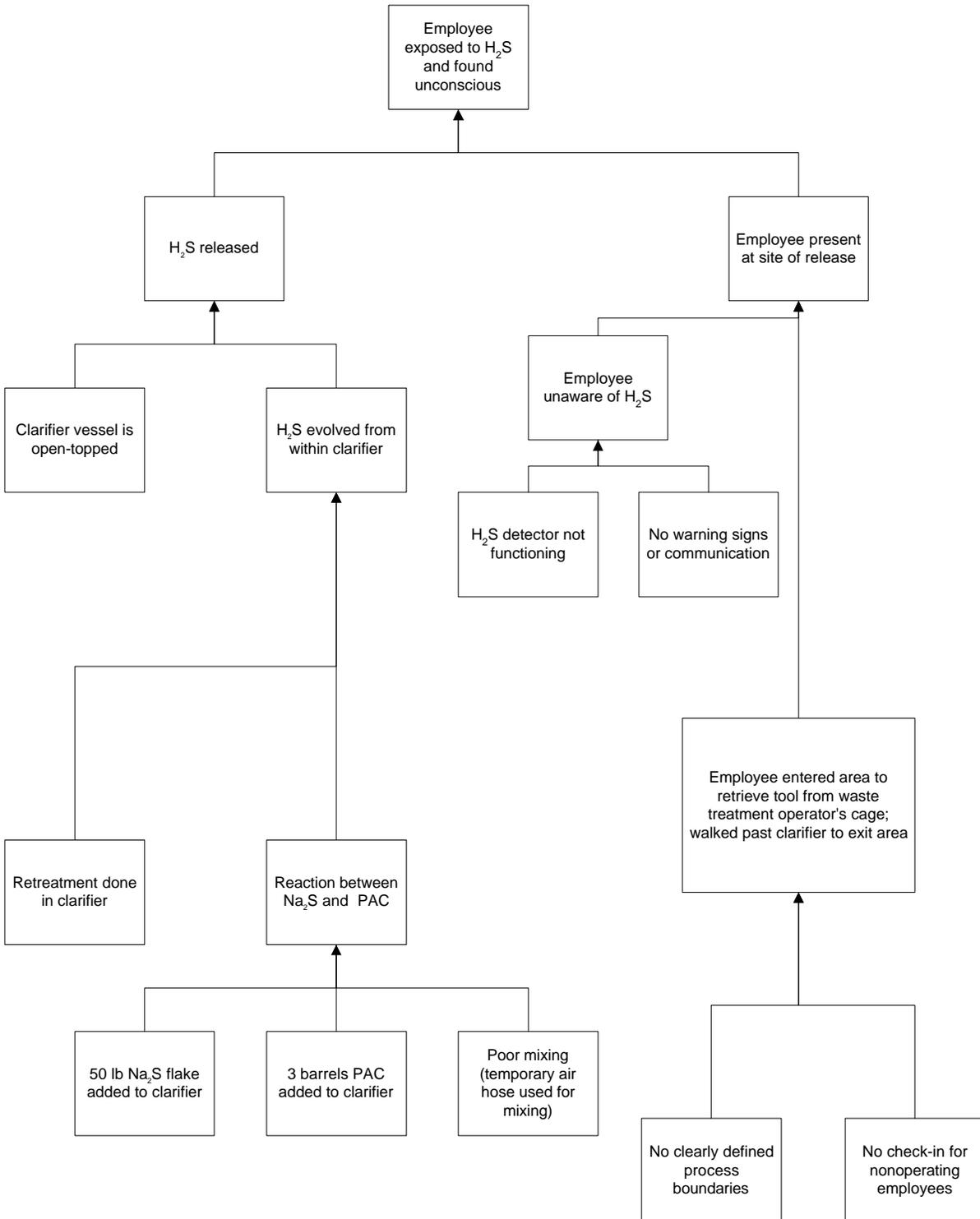
EEI estimates that approximately 2 pounds of H₂S was released. The release quantity that necessitates filing a report with Federal, state, and local officials (i.e., reportable quantity) is 100 pounds.

... The compliance coordinator ... discovered the mechanic lying unconscious on the floor and not breathing.

⁹This type of detector reads instantaneous values and does not store measurements for later retrieval. The H₂S concentration at the time the meter first alarmed could have been as low as 5 ppm or higher than 85 ppm. The OSHA short-term exposure limit for a maximum 10-minute exposure is 50 ppm.

Figure 5

Event tree, hydrogen sulfide release



3.0 Investigation Findings and Conclusions

During the course of this investigation, the CSB team worked in conjunction with representatives from OSHA, OEPA, and the City of Cincinnati Office of Environmental Management. CSB investigators reviewed procedures, training records, and other documents; inspected the facility; and interviewed employees and management personnel. The team also visited a similar waste operations facility in Cincinnati.

CSB investigators determined that this incident occurred because wastes were chemically treated in a vessel not designed for such use. In summarizing findings, this Case Study discusses procedures, training, hazard communication, previous incidents, mechanical integrity, and management oversight.

3.1 Procedures

At the time of the incident, the facility had no written procedures for operating the WWT area. Although each waste batch was unique and required customized treatment protocols, EEI relied on the knowledge of plant personnel with many years' experience in waste treatment to take appropriate actions.

In this case, the operator used air to mix the contents of the clarifier—a vessel designed to settle its contents. He should have transferred the batch back to the treatment tank, which is equipped with both adequate mixing and ventilation.

The air used in the clarifier did not provide sufficient mixing to completely dissolve the Na₂S flake and distribute the strongly acidic PAC. This produced a localized condition under which the two chemicals combined to form H₂S, which was released from the top of the open vessel.

There were no written instructions to warn operators of the hazards of adding treatment chemicals to the clarifier, nor were there procedures specifying what to do in the event that a waste failed to meet discharge limits after treatment. Subsequent to the incident, EEI developed detailed, written procedures for WWT operation.

3.2 Training

The operator responsible for the WWT area had no formal training in waste treatment or chemistry; he relied on his prior experience to determine waste treatment

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This incident may have been avoided if the operator had been aware of the possible reactions that can produce H₂S gas.

EEl did not have a formal system for investigating incidents and communicating findings to employees.

protocols¹⁰. He was aware of the hazards of H₂S but unaware of the possible reactions that could produce the gas. He operated under the assumption that H₂S would not be released from the clarifier as long as the pH stayed within a certain range.

The air hose draped into the clarifier (a vessel *designed to settle its contents*) did not provide sufficient mixing to completely dissolve the Na₂S flake, which combined with PAC to form H₂S. Fortunately, the duration of the release was limited by the amount of Na₂S available to react with the strong acid as it entered the clarifier.

If the entire reaction proceeded homogeneously (i.e., with good mixing) throughout the batch, the pH would have not been low enough to lead to the dangerous release of a large amount of H₂S.

3.3 Hazard Communication

This incident may have been avoided if the operator had been aware of the possible reactions that can produce H₂S gas. Facility staff, maintenance and administrative employees, and laboratory personnel were not trained on the

¹⁰The operator and the victim received Hazardous Waste and Emergency Response (HAZWOPER) 40-hour training in 1999; however, it was not specific on the hazards of H₂S.

hazards of the WWT process or on the properties and hazards of H₂S. Employees assumed that someone knowledgeable in WWT operations would alert them if they were in danger and needed to evacuate.

3.4 Previous Incidents

Offensive odors were considered part of the business at EEI. All facility personnel were accustomed to strong odors and the characteristic rotten egg smell of H₂S.

On at least one previous occasion, the odor of H₂S was strong enough to be detected outside the facility, by a local police officer.

Investigation of that incident by city officials resulted in a written order from the Office of Environmental Management in July 2001.

To reduce the potential for H₂S evolution, the order specified that Na₂S flake must be dissolved before being added to the waste. The order required EEI to install an H₂S detector in the WWT area.

The wall-mounted H₂S detector was installed; however, no procedures were developed or training conducted to ensure that WWT personnel understood the order. EEI did not have a formal system for investigating incidents and

communicating findings to employees. New employees were not made aware of the specifics of the city order.

3.5 Mechanical Integrity

The newly installed H₂S detector (Section 3.4) did not alarm on December 11. Through interviews, CSB learned that the detector had not been calibrated for 2 to 3 months prior to the incident. Calibration attempts following the incident revealed that the detector was not functioning because of a bad sensor.¹¹

The facility did not implement procedures or assign responsibilities for calibrating, inspecting, and maintaining the H₂S detector. The operator or mechanic performed calibration on an irregular basis, and no records were kept. (Therefore, neither employee knew for certain when the meter was last calibrated.) In the months following the incident, EEI implemented a calibration program that includes written records.

¹¹H₂S detectors employ a sensor head that is susceptible to moisture fouling and overload by repeated or strong exposure to H₂S, hydrocarbons, and other substances. To ensure proper operation, detectors must be calibrated frequently and the sensors replaced as needed.

3.6 Management Oversight

Facility staff included the plant manager, a chemical engineer with waste treatment experience; a compliance coordinator; and a staff chemist responsible for lab-pack operations. In addition to onsite personnel, degreed chemists were available at the EEI analytical laboratory located near the Spring Grove facility.

None of these personnel were consulted on the treatment protocol in use on the day of the incident. Lacking written operating procedures and oversight, the WWT operator relied solely on his experience and judgment to perform treatment.

Management oversight includes approving facility operating procedures and providing for proper technical consultation whenever employees need to deviate from procedures. If such oversight had been in effect at EEI, it could have ensured that the proper treatment methods were used, including returning all failed wastes from the clarifier to the treatment tank for chemical addition.

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The waste was chemically treated in the clarifier, a vessel not designed or intended for such use.

Communication was inadequate to inform facility personnel of the hazards of H₂S.

EEI had not implemented a mechanical integrity program to provide for calibration, inspection, and maintenance of the H₂S detector.

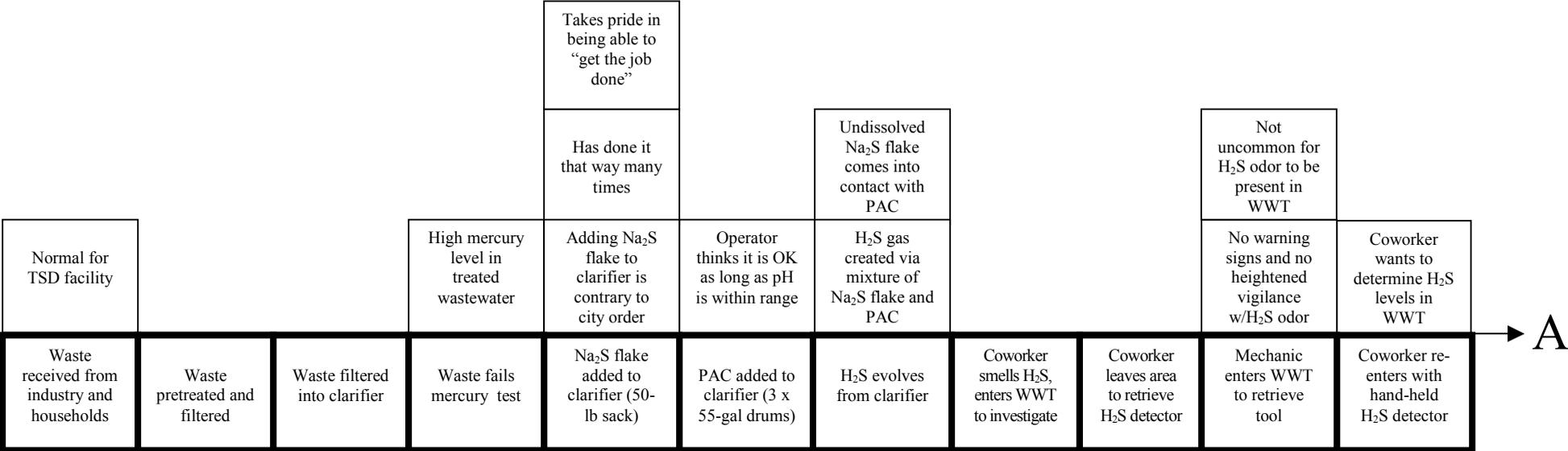
4.0 Contributing Factors

CSB investigators used a modified fault tree approach to analyze the information from this incident. The investigative team identified several contributing factors, as noted below. Refer to Figure 5 for the event tree and to Figure 6 for the event timeline.

- ◆ The waste was chemically treated in the clarifier, a vessel not designed or intended for such use. The clarifier was not equipped with a scrubber to minimize toxic gas releases and did not have an agitator to ensure adequate mixing.
- ◆ Operating procedures and operator training were inadequate. The WWT operator did not have written instructions or training on the proper treatment of wastes, the importance of using a properly designed treatment tank, or the consequences of treating waste in the open-topped clarifier.
- ◆ Management had not implemented an incident investigation program to communicate lessons learned; the operator was unaware of the enforcement order from the city that prohibited adding Na₂S flake.
- ◆ Management had not implemented controls to limit access to the WWT area during treatment or to notify facility personnel that WWT operations might present a hazard.
- ◆ Communication was inadequate to inform facility personnel of the hazards of H₂S. Employees did not respond appropriately when they smelled the characteristic odor because they did not fully appreciate the dangers of H₂S. Furthermore, employees were not warned when waste treatment operations had the potential to release H₂S. This lack of awareness of the hazards of H₂S is also evidenced by the fact that several employees entered the WWT area immediately after the incident, without respiratory protection.
- ◆ EEI had not implemented a mechanical integrity program to provide for calibration, inspection, and maintenance of the H₂S detector. The detector was not functioning on the day of the incident and failed to warn employees of a dangerously high H₂S concentration in the WWT area.

CSB concludes that the lack of effective management systems contributed to this incident, resulting in a near-fatal H₂S exposure.

Figure 5



Inadequate process safety management practices are often cited as the cause of reactive incidents.

The WWT system at EEI could benefit from *written and implemented* management systems.

5.0 Prevention

Effective management systems help prevent accidents. Although management systems can be multilayered and complex, simple systems often work adequately for small organizations such as EEI.¹² Inadequate process safety management practices are often cited as the cause of reactive incidents (USCSB, 2002). The EEI incident is a reactive incident, involving the reaction of two chemicals to cause a hazardous release.

Management systems consist of policies, procedures, and work instructions that identify and define required actions; assign responsibilities; and provide necessary training, oversight, and verification to accomplish the goals of the program. They may be informal and employ minimal documentation (CCPS, 1989).

EPA emphasizes the need for management systems in the TSD regulation (40 CFR 264.31).

Facilities must be designed, constructed, maintained, and operated to minimize the possibility of a fire, explosion, or any unplanned sudden or non-sudden release of hazardous waste or hazardous waste constituents to air, soil,

or surface water which could threaten human health or the environment.

The WWT system at EEI could benefit from *written and implemented* management systems. CSB learned that other facilities engaged in the same activities and with similar staffing structures successfully use management systems to ensure safe and environmentally responsible operations.

The following management system elements would help prevent the occurrence of similar incidents:

- ◆ A written policy defining the goals of the program (i.e., to comply with all Federal, state, and local regulations and to protect the safety of workers and the public).
- ◆ Written procedures for managing the WWT program, which include assignment of responsibilities, definition of training requirements, and work instructions.
- ◆ Management oversight guidelines for ensuring adherence to procedures and identification of hazards through regularly scheduled audits and inspections.

¹²EEI is not covered under the OSHA process safety regulation, Process Safety Management of Highly Hazardous Chemicals, 29 CFR 1910.119.

6.0 Post-Incident Remediation

- ◆ Written work instructions (i.e., operating procedures) with clearly stated safety and precautionary information, along with procedures for obtaining management approval if operators must deviate from the instructions.
- ◆ Formal training, following written outlines and conducted by qualified personnel, for all operating employees. According to the EPA regulation for TSD facilities (40 CFR 264.16):

Facility personnel must successfully complete a program of classroom instruction or on-the-job training that teaches them to perform their duties in a way that ensures the facility's compliance with the requirements of [the TSD regulation].
- ◆ An incident investigation program that includes determining the root causes of safety and environmental incidents, and communicating the lessons learned to affected employees.
- ◆ Written records of process activities for verification of program compliance and effectiveness.
- ◆ Routine inspections and audits to verify program implementation and effectiveness, along with procedures for followup activities.

Following the initial investigation of the December 11 incident, EEI took several steps to prevent a similar incident. The measures implemented by EEI include:

- ◆ Establishing written operating procedures for the WWT area.
- ◆ Training all WWT operators on proper waste treatment methods.
- ◆ Training all facility employees on the hazards of H₂S.
- ◆ Installing improved ventilation equipment in the WWT area.
- ◆ Implementing a calibration program for the H₂S detector.
- ◆ Installing signs at entrances to the WWT area to warn nonoperating employees of potential hazards.

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