As Seen in PE Pollution Engineering

Hazardous Materials – THE THINGS WE'VE SEEN

There is no shortage of dangerous chemical or compressed gas cylinder situations. Such explosive conditions are avoidable and it is imperative that they are properly handled when found.

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Most organizations have established procedures for handling, storing and disposing hazardous materials. The plans are written and reviewed, and then communicated to the staff. The plans are sufficient; it is staff training, communications and practices that fail.

As an environmental services and hazardous material response company, Clean Harbors has run across many dangerous situations – situations caused by neglect, lack of knowledge and procedural failures. This article will outline four scenarios.

That doesn't go in the fire

A utility operation was shipping hazardous materials for disposal. Thinking that rubidium contained in a stainless steel vessel could be incinerated, the utility sent the highly pyrophoric metal, along with other more stable materials, to an incineration plant. Except rubidium must be removed from stainless steel containers *before* incineration.

Rubidium is the third most reactive metal listed in the periodic table. It spontaneously ignites on contact with air. When in contact with water, it releases explosive hydrogen gas, which is severely corrosive to tissue and acutely destructive to the respiratory tract, skin and digestive tract. Eye contact may result in permanent damage and complete vision loss.

The above drum is bulging. It must be handled with extreme care to avoid a major mishap.

The company had listed the rubidium on its bill of lading. In order to process the material, the vessel was placed in a containment tent within a nitrogen atmosphere. The container was slowly dismantled, and the rubidium removed and placed under mineral oil for incineration according to EPA regulations.

LESSON: **Mixed Incompatibles**.

Occasionally, environmental services companies are contracted to handle drums containing incompatible materials. There may be a drum that is off-gassing or bulging so, according to Department of Transportation regulations, the material cannot be shipped. The situation requires an on-site resolution. Bulging drums can be tricky. The author's company employs a remote drum opener to remove the bungs with a pneumatic wrench if the barrel is not seriously deformed. Otherwise, a drum punch is used to alleviate the pressure.

Double-bubble can lead to toil, trouble

Sometimes errors are made when labs try to neutralize their own wastes. Some states issue permits for neutralization, so it is not an uncommon practice for them to try to do it on their own. For example, staff at a university lab decided to neutralize azobisisobutylonitrile, which is highly explosive, toxic and reactive to heat. Recommended storage temperature is 2°C to 8°C. They proceeded under the premise that they could add any organic solvent to the material. However, the Material Safety Data Sheet (MSDS) listed aldehydes, strong oxidizing agents, alcohols, alkali metals, heptane and acetone as materials to avoid. They chose acetone, which may have caused the compound to auto-detonate. A bomb squad responded.

LESSON: **Peroxide Formers**.

Elbow bottles such as those shown above are used in many situations but are often not well marked as to content.

Sometimes, gas cylinders are improperly stored and corrosion can leave them extremely unstable.

Environmental consultants frequently encounter peroxide formers, such as tetrahydrofuran, Diethyl ether, p-dioxane, potassium metal, etc. Peroxide formers can be managed to mitigate hazards as long as proper testing protocols and management practices are followed. This requires careful recordkeeping from the point when the material is received in the lab so that routine tests (experts recommend every three months) can be performed and inhibitors added as appropriate.

Unfortunately, what often happens is that universities, hospitals, research labs or industrial labs receive these materials and fail to routinely test and add the inhibitors. When environmental experts are called in to handle peroxide former materials, they have to test each container if the records are unavailable or unclear, or if it has been more than a year since the last testing or inhibiting additions. This process requires a remote opener and special handling since the hazard associated with peroxide formers is in opening the container. That is enough of an insult to the material to cause a deflagration.

Good environmental stewardship seldom goes 'boom'

In another example, an industrial company improperly stored borane-T3-THF complex containers in an outdoor storage lot and several of the containers had exploded due to the generation of flammable hydrogen gas. The MSDS overview noted that the compound is flammable, may form explosive peroxides and reacts violently with water, liberating extremely flammable gases. The MSDS also specifies storage at 2°C to 8°C under a nitrogen gas atmosphere.

The borane had been used and the septums on the containers were punctured. At first the company and the manufacturer suspected peroxides as the cause but, in fact, the explosions were caused by moisture seeping through the perforated septums and temperature fluctuations. Due to the improper storage of the material safe removal required special handling, including on-site destruction and specialized equipment.

LESSON: **Compressed Gas Cylinders**.

Many of the situations that environmental experts are called in to handle involve compressed gas cylinders. These cylinders are widely used and it is easy for even trained lab personnel to think that everything is stable and secure because the materials are in an approved, hardened container. Another reason that disposal experts see a lot of cylinders is that they are the most costly material to dispose of – beyond explosives, well beyond standard hazardous waste.

It is easy to accumulate a large number of cylinders and extremely pricey to clean them up. Frankly, many companies with their short-term financial orientations just keep pushing it off to the next quarter.

Inoperable valves are sure signs of deteriorating cylinders. This occurs when they sit idle for a long period of time, especially under improper storage conditions. Inoperable valves require specialized equipment to access the material inside the cylinders, whether the material is known or unknown. Sometimes it is necessary to use tapping rings or saddles around the cylinders and drill through the sidewalls to extract samples to identify the contents. Needless to say, this is time-consuming and expensive.

It is also common to see a lot of lecture (elbow) bottles in universities, R&D facilities and in virtually any type of industrial setting. They are often filled with extremely hazardous material, including hydrogen cyanide and pentaborane. The values are often not specific and the bottles may look the same, but they may contain a wide range of gases, from agent-of-warfare material to inert or atmospheric gases. Gas companies generally do not want them back.

Weathering can remove all markings on a gas cylinder. A special tent must be used and filled with nitrogen gas to avoid explosions in order to safely test and remove the contents.

Terror on the Back 40

The author's company was called to remove about 4,000 gas cylinders from what the gas supplier company called its "Back 40"[1] storage lot. Amazingly, the call only came because the company was shutting down the facility and preparing the property for sale. Many cylinders had deteriorated in the storage lot and were on the verge of leaking. They could not be transported without special packing. The disposal experts set up a mobile lab to evaluate the gases and prepare the cylinders for transport. They had to sample unknowns, and remove material that was dangerously unstable, such as cylinders containing hydrogen cyanide, tetrafluorohydrazine, and pentaborane. The material was over-packed, and put in cylinder recovery vessels, which are specialized containment vessels that allow the cylinders to be shipped in accordance with the DOT permits for the author's company.

There is no shortage of dangerous chemical or compressed gas cylinder situations. They all relate back to poor record-keeping, improper storage or outright neglect. It is best to develop well-defined hazardous materials handling and storage standard operating procedures. It also makes sense to establish an ongoing relationship with a hazardous materials disposal company that will routinely pack and remove materials before they become a handling risk. Just as important, it is imperative to impress safe handling and storage procedures on in-house staff – and it does not hurt for management to walk around a bit to see for themselves if they have their own Back 40 hidden somewhere. ***PE***

Reference:

1. "Back 40," refers to wild, rough or undeveloped terrain adjacent to a developed area. It is a reference to the U.S. Public Land Survey System, which was used to organize undeveloped Frontier land in the 18th and 19th centuries, among which one division was segmented into four 40-acre plots.

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