

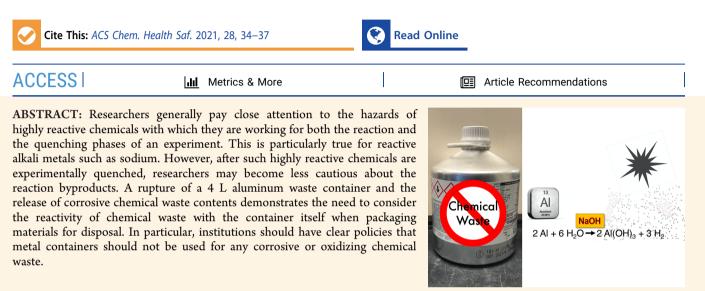
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Lessons Learned—Aluminum Waste Container Rupture

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WHAT HAPPENED?

A 4 L chemical waste container was picked up from a department by Environment, Health and Safety (EH&S) staff as part of routine hazardous waste collection and transported to the campus waste collection facility. Two days later, and before the hazardous waste was collected by a commercial vendor, the container burst, spilling out almost four liters of corrosive waste (Figure 1).

An investigation conducted by the EH&S department uncovered the following chain of events. A third-year chemistry graduate student decided to quench the laboratory's 1 L benzene still which employed the commonly used combination of sodium metal and benzophenone as the drying



Figure 1. Ruptured waste container and spilled corrosive waste.

and deoxygenation agent.¹ Following the lab's Standard Operating Procedure (SOP) and working in a fume hood, the researcher quenched the mixture in the still distillation flask by establishing an inert nitrogen atmosphere, cooling externally with ice water, slowly adding isopropanol to quench the sodium metal, and adding methanol to ensure a complete quench by dissolving clumps of sodium isopropoxide that may cover sodium metal. They finally added water to make sure there was no active sodium metal contained within the sodium alkoxide residues. This is a standard procedure, and SOPs are available from other researchers.^{2,3} After letting the quench mixture (benzene, isopropanol, methanol, water, sodium isopropoxide, sodium methoxide, and sodium hydroxide) warm to room temperature, the researcher considered how to dispose of the hazardous waste. Knowing that strongly basic chemicals should not be added to solvent waste carboys (vide infra), the student contemplated what container to use. Empty chemical and solvent glass bottles were available, but they could break, so the student decided to use an empty 4 L aluminum diethyl ether container which seemed like a robust choice (Figure 2). The container was filled with the waste, a hazardous waste tag was attached, and it was transferred to the EH&S hazardous waste collection staff.

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Figure 2. Aluminum containers, 1 and 4 L, for diethyl ether.

WHAT WAS THE CAUSE?

An initial safety review focused on the fact that sodium metal had been quenched and that all the material had been placed in the waste can. Since quenching of sodium with alcohols (or water) produces hydrogen gas (eq 1),⁴ the initial explanation

$$2Na + 2ROH \rightarrow H_2 + 2RONa \tag{1}$$

was that the quench was incomplete before the researcher placed the material into the waste can, so continued reaction of sodium metal with alcohol or water caused a buildup of hydrogen gas which led to rupture of the waste can. However, the student was certain that quenching of the sodium metal had been thoroughly completed based on observations of bubbling and the time between quenching reagent additions.

Another analysis resulted in a completely different and somewhat surprising explanation. Aluminum metal is a reducing agent and reacts with water to form hydrogen gas and aluminum hydroxide (eq 2). Further, that reaction is

$$2AI + 6H_2O \rightarrow 2AI(OH)_3 + 3H_2 \tag{2}$$

promoted by bases which serve to disrupt the protective aluminum oxide layer on the surface of the aluminum metal.^{5,6} Hence, this incident was not the result of sodium metal reacting but rather the aluminum waste container reacting with the strongly basic aqueous wastes contained within it. Hydrogen gas built up pressure, and the reaction of the aluminum weakened the container wall, so the combination resulted in a violent rupture of the container. Instances of combinations of incompatible wastes causing explosions or other serious incidents are well-known, and a computer program designed to identify waste stream incompatibilities was recently reported;⁷ however, this incident involved a redox reaction between the chemical waste and the container.

Reaction of a strongly basic aqueous solution with the aluminum metal waste container producing hydrogen gas pressure and weakening the container wall in the process was the immediate cause for the incident. This was the immediate cause, but what was the root cause? Often, root causes trace back to a lack of an SOP, lack of appropriate training, or lack of a risk assessment for a specific experimental protocol. However, in this instance it is not so clear. The student conducted an appropriate quench of the sodium metal, properly decided to dispose all of the waste in a container rather than adding the waste to the lab's solvent waste carboy (vide infra), made an effort to choose a sturdy waste container, properly labeled the waste container, and correctly transferred the waste to the campus hazardous waste EH&S personnel. Possible issues that could be considered root causes are (a) the student not being educated that an aqueous base reacts with aluminum metal to form hydrogen gas, (b) the SOP for processing hazardous waste did not rule out use of aluminum waste containers or suggest alternative, more appropriate containers, or (c) the vendors supplying solvents in aluminum containers did not provide a warning on the label that the containers are reactive and should not be used for chemical waste. However, those root causes may not be valid until an incident such as this occurs and is publicized and changes to labeling and procedures are made.⁸

Hence, the root cause is the waste management policy set by the institution which allowed the packaging of corrosive wastes in a nonsuitable container. The origin of the problem may come down to costs. Empty chemical containers are widely available and free, so academic researchers commonly use such containers to package wastes. This is not the case in many industrial research laboratories. In researching this issue the authors learned that many companies forbid the use of chemical containers to package hazardous wastes.⁹ Instead, new containers designed to hold hazardous wastes are purchased and used for this purpose. This policy not only ensures the integrity of the waste containers but also ensures that there are no potential issues from residual chemicals in the container that could react with added wastes.

WHAT CORRECTIVE ACTIONS WERE TAKEN?

After the incident investigation was completed, several corrective actions were performed in partnership with the EH&S department:

- The EH&S incident report was shared with the research laboratory group members, PI, and the department' s safety committee.
- The incident, as well as the specific hazards of sodium metal and benzene, was discussed by the PI with the laboratory group members.
- The laboratory SOP for handling hazardous waste was amended to state that aluminum cans should not be used for chemical waste.
- The incident was discussed with hazardous waste collection EH&S staff, and they were instructed that they should refuse to collect any chemical waste packaged in aluminum cans. The waste should be transferred to nonreactive glass or plastic containers.
- A summary of the incident was prepared by the department's safety committee and sent to all researchers in the PI's department.

■ HOW CAN INCIDENTS LIKE THIS BE PREVENTED?

Although this incident involved a reaction of an aqueous base with an aluminum can, it can be expected that many other corrosive chemicals could also react with an aluminum container. For example, beyond the aqueous base, aqueous acid promotes aluminum oxidation as well.¹⁰ Further, any obvious oxidants such as transition metal oxides, chlorine oxides, nitrate salts, and peracids, as well as less obvious

oxidants such as halogens, pseudohalogens, and transition metal halides, can be expected to react with aluminum containers in redox reactions as in eq 2. Further, moving beyond the specifics of this incident, metal containers in general are susceptible to reactions with oxidants and strong corrosives and so should not be utilized as containers for such waste. Hence, the following actions are recommended:

- Institutions should amend their waste SOPs to state that aluminum containers should not be allowed for containing chemical waste.
- Institutions should further mandate that metal containers should not be used for any corrosive or oxidizing chemical waste.
- Laboratory researchers should be notified on those revised procedures.
- ES&H staff should be trained to recognize this hazard and should refuse to collect any chemical waste packaged in aluminum containers.
- Researchers should be trained to evaluate the hazards of all chemicals and equipment at every stage of an experimental procedure—from setup through hazardous waste disposal.

Finally, the authors contacted companies selling diethyl ether in aluminum containers to notify them of this incident and to request that a warning notice be added to container labels. The warning notice should state "Caution: aluminum containers are reactive and should not be used to hold chemical wastes".

■ WHAT OTHER SAFETY ISSUES WERE INVOLVED?

To more thoroughly address the safety issues presented in this incident, there are a number of additional safety considerations that should be discussed. First, the academic lab had a benzene still. Benzene is a known carcinogen and is not allowed to be used in many industrial research facilities, so replacement by other solvents is highly encouraged.¹¹ Academic research laboratories should also adopt that practice. The mere presence of an active benzene still might encourage student researchers to use benzene as a solvent.

Second, the lab was using the older, and considerably more hazardous, sodium plus benzophenone distillation method of purifying and drying solvent. It is highly recommended that laboratories convert to the column purification method for solvents that entirely eliminates the hazards of reactive metals and distillation.¹²

Third, quenching of sodium, and other alkali metals, is a potentially hazardous operation; therefore, laboratories conducting this operation should have a detailed SOP. Researchers should not conduct the operation until trained and authorized to do so. Furthermore, researchers should never conduct the operation alone.¹³

Fourth, even laboratories that regularly quench sodium, or other alkali metals, following a well-established SOP should have well-defined limits on the quantity that can be quenched. Above a certain quantity of sodium metal, it should be recommended to dispose of the active metal as hazardous waste rather than attempting to quench it. Institutions should thus set limits on quantities of sodium metal that can be quenched rather than leaving it up to individual research groups to decide.¹⁴ Further, it is important that researchers be trained that laboratory treatment of chemical hazardous waste is only allowed under federal law in cases where small-scale treatment is part of a laboratory procedure, as in the last step of a chemical experiment.¹⁵ In this instance, quenching of sodium from a solvent still in the distillation flask was appropriate, but quenching of 15 g of old, unwanted sodium in a reagent bottle would not be appropriate.

Fifth, the researcher in this incident knew that highly basic chemicals should not be added to a solvent waste carboy. Halogenated solvents react with strong bases by elimination forming alkenes, alkynes, or more reactive carbenes, and incidents caused by these reactions forming flammables, gases, and heat have been reported.¹⁶ Most institutions previously required separation of halogenated and nonhalogenated waste solvents due to increased costs for treating halogenated wastes, but most waste processors now treat all solvent wastes in high temperature kiln processes which provide extremely efficient combustion.¹⁷ Thus, even if a lab separates halogenated and nonhalogenated waste solvents, strong bases should not be added to the nonhalogenated waste solvent since the mixture might be consolidated with halogenated waste in subsequent processing.

Sixth, this noninjury incident points out an education gap in appropriate procedures for hazardous waste disposal. The regulations and requirements set out in the Resource Conservation and Recovery Act (RCRA) administered by the U.S. Environmental Protection Agency (EPA) for hazardous waste disposal are extensive,¹⁸ so institutions provide training to personnel on simplified procedures for disposal of hazardous waste. A common core element of such training is the issue of chemical compatibility for mixed wastes. While the extensive and detailed EPA listing of incompatible binary combinations of hazardous wastes clearly lists caustics and metals, as well as acids and metals, as incompatible,¹⁶ researchers may not consider a metal container to be a hazardous waste to be evaluated. Hence, hazardous waste training provided by institutions should more thoroughly address the selection of an appropriate container for solid and liquid hazardous waste. Since waste is to be discarded, researchers might be inclined to use any available empty and/or less costly containers. However, such containers may be reactive with the waste, penetrated by the waste, structurally deficient to hold the waste, or not acceptable by the commercial vendors collecting the waste. Thus, clear guidance on waste containment should be provided to researchers generating hazardous waste.¹⁵

Seventh, aluminum solvent containers are actually used for safety reasons. Diethyl ether is packaged in aluminum containers since there is no reaction between diethyl ether and aluminum. However, should any explosive ether hydroperoxide form from oxidation of the diethyl ether with oxygen,¹⁹ it would react with aluminum and be reduced to ethanol, acetaldehyde, and alumina (or aluminum hydroxide if not dehydrated) (eq 3).²⁰ Thus, the aluminum container serves a protective purpose.

$$2AI + 3Et-O-CH(OOH)Me$$

$$\rightarrow Al_2O_3 + 3EtOH + 3Me-CHO$$
(3)

QUICK ACTION TIPS

If a hazardous waste, or other chemical, container is bulging or otherwise distorted, it may indicate a buildup of internal pressure. The impulsive response by a researcher might be to quickly open the container to relieve the pressure. However, manipulation of a pressurized container might induce a violent rupture before it can be opened. Therefore, an emergency response should be initiated:

- 1. All personnel in the immediate area should be evacuated.
- 2. The area should be secured so no one inadvertently enters.
- 3. EH&S should be contacted immediately.
- 4. The research supervisor should be notified.
- The research group together with EH&S staff should conduct a risk assessment and develop an appropriate course of action to follow.

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Notes

The authors declare no competing financial interest.

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