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Chapter 45

CHEMICAL HYGIENE AND SAFETY PLAN

Work Process Q. Specific Controls and Procedures — Water-Reactive Chemicals



1. **General Information.** Water-reactive chemicals react violently with water, releasing heat and, in some cases, explosive by-products. Of chief concern are  GHS substances or mixtures which, in contact with water, emit flammable gases (Category 1: In contact with water, releases flammable gases which may ignite spontaneously). Examples of chemicals in this category include the alkali metals, sodium borohydride, lithium hydride, calcium hydride, phosphorus pentasulfide, borane complexes (borane-tetrahydrofuran, borane-methyl sulfide complex, etc.), and Grignard reagents. Some water-reactive chemicals in Category 1 are also pyrophoric, and must follow specific controls and procedures in Work Process R, in addition to those outlined in this Work Process.

The risks associated with water-reactive chemicals depend on the reactivity of the specific chemical, in addition to the hazards of gaseous products formed with water (flammable, toxic, or both). 



Alkali metals react vigorously with water to form  alkali  hydroxides and gaseous hydrogen. The alkali metal-water reaction is exothermic. The heat generated can ignite the hydrogen gas. The rate of reaction and the hazard severity increase as atomic weight increases. Lithium reacts slowest and poses the least hazard. Rubidium and cesium react explosively.

A DOE document, [DOE-HDBK-1081-94](#), *Primer on Spontaneous Heating and Pyrophoricity*, provides additional information.

2. **Control Measures**

- a. Activity leads must identify water reactives used in the work area. Review sources such as SDSs for specific compounds.
- b. An assessment of the hazards and controls in place is necessary to safeguard employees against these agents. Contact an [EHS Health and Safety Representative](#) to provide assistance.
- c. Work involving these materials  must  be added to a Work Planning and Control Activity. Consult the [Work Planning and Control](#) program (ES&H Manual Chapter 6).

3. Training and Information

- a. All employees who handle or may be exposed to water-reactive chemicals are required to complete [Chemical Hygiene and Safety Training](#) (EHS0348; or [EHS0345](#) for Facilities personnel, [Fire Extinguisher Safety \(web-based\)](#) (EHS0520), and [Fire Extinguisher Safety Retraining](#) (EHS0531) annually thereafter. If desired, employees may also take [Fire Extinguisher Safety \(hands-on\)](#) (EHS0522).
- b. These individuals  must  be trained in the specific hazards and controls of the water-reactives. The Activity Lead and/or Project Lead is responsible for ensuring workers are properly trained, qualified, and authorized to work.
- c. Consult [Work Process Y, Container Labeling](#), for labeling requirements for primary and secondary containers.
- d. The area entrance should be posted with a Caution Placard depicting the hazards and emergency contact information.

4. Substitution and Chemical Inventory Management

- a. Identify and use safer chemical alternatives (e.g., non-water-reactive chemicals) if possible.
- b. If a safer chemical can't be used, limit what you buy or borrow what you need from a colleague in your group or contact the Chemical Management System Coordinator (cms@lbl.gov) to assist you in finding a source of the chemical at Berkeley Lab.
- c. Conduct periodic clean-outs to prevent accumulating unneeded chemicals.
- d. Procure and use the minimum amount of material required for the operation, or
- e. Keep working quantities of chemicals to a minimum. Don't stockpile chemicals.
- f. Enter these materials into the [Chemical Management System \(CMS\)](#).

5. **Engineering Controls.** Alkali metals should be handled in a glove box made of materials that are compatible with the metal, with an inert gaseous atmosphere such as dry argon. ⚠️ Operations that could generate a flammable or toxic atmosphere must be performed in a fume hood. ⚠️

6. **Work Practices**

- a. Do not eat; drink; smoke; chew gum; apply cosmetics; or store food, beverages, and tobacco products in work areas where water-reactive materials are being used.
- b. General traffic should be prohibited in areas where alkali metal ⚠️ and water-reactive chemical ⚠️ operations are performed.
- c. Avoid all skin and eye contact with the material. Where possible, use tongs or appropriate tools to handle solids.
- d. All tools used to handle ⚠️ water-reactive chemicals including ⚠️ alkali metals must be dry, rust-free, clean, and composed of a ⚠️ compatible ⚠️ material. Tools can be dried by baking in an oven, desiccating in a vacuum, or rubbing with anhydrous dry soda ash.
- e. ⚠️ Protect water-reactive chemicals from water during use. Water may include atmospheric moisture. Air- and moisture-free handling techniques may be required. ⚠️
- f. Develop procedures that will be used to mitigate the hazards of excess water-reactive chemicals and their mixtures after the experiment is completed. Quenching procedures must be authorized through work planning and control. Do not stockpile alkali metal “scrap” that is no longer needed, even if under mineral oil.
- g. ⚠️ Oxidized alkali metals (typically a white surface coating) make the material more hazardous to handle because the oxide can flake off. NOTE: Potassium metal with a yellow or orange coating may indicate the presence of peroxides, which may detonate if cut or abraded. Do not handle these materials. Contact an [EHS Health and Safety Representative](#) for further guidance. See [Work Process P, Specific Controls and Procedures — Peroxide-Forming Compounds](#), for additional requirements. ⚠️
- h. Assume that containers with ⚠️ water-reactive chemicals ⚠️ contain flammable (e.g. hydrogen) ⚠️ and/or toxic ⚠️ gas in the head space, even if stored under mineral oil or an inert gas. Thus, no source of ignition ⚠️ must ⚠️

be present where these containers are opened. Use non-sparking tools to open containers.

7. **Personal Protective Equipment (PPE).** Skin and eye contact must be prevented.

The following PPE will be worn when handling these materials. Additional information may be found in [Work Process I, Personal Protective Equipment](#).

- a. At a minimum, safety glasses with side shields, laboratory coats (coveralls are acceptable in shop settings), and closed-toe shoes must be worn when handling these materials. For alkali metals, the shoes should be leather. This is to be considered as minimum protection and must be upgraded if necessary.
- b. Additional PPE such as chemical goggles, face shields, chemical aprons, fire-resistant aprons, disposable coveralls, [chemically resistant gloves](#), and respiratory protection must be worn if there is a greater chance of chemical exposure. An [EHS Health and Safety Representative](#) may be contacted for assistance in selecting appropriate gloves and respiratory protection. The use of respiratory protection requires a hazard evaluation and a medical clearance followed by a fit test and training by the Research Support Team.
- c. Consult [Work Process I.6, Eye and Face Protection](#), for guidance on the selection, uses, and limitations of safety glasses, chemical goggles, and face shields.
- d. Because many chemicals are skin-absorbers (i.e., agents that readily pass through the skin) it is important to select gloves that are chemically resistant to the material. Consult the PPE section, which contains a list of skin-absorbing agents and provides detailed guidance for selecting [chemically resistant gloves](#).
- e. Gloves must be selected on the basis of their chemical resistance to the material(s) being handled, their suitability for the procedures being conducted, and their resistance to wear as well as temperature extremes. Improper selection may result in glove degradation, permeation of the chemical through the glove, and ultimately personal exposure to the chemical. This is a potentially serious situation. Consult [Work Process I.5, Gloves](#), for guidance on the selection, uses, limitations, and disposal of chemically resistant gloves. An [EHS Health and Safety Representative](#) may also be contacted for assistance in selecting appropriate gloves.

8. **Storage**

- a. Consult [Work Process K, Chemical Storage](#), for hazardous material storage requirements, recommendations, and information on chemical incompatibility. It is recommended that alkali metals be stored in manufacturer-provided containers, if practical. Requirements for storing water-reactive chemicals are provided below.
- b. Separate alkali metals from incompatible chemicals. In addition to being water-reactive, alkali metals can react with oxygen, acids, halogenated hydrocarbons, and carbon dioxide.
- c. Store alkali metals under mineral oil or in an inert atmosphere.

NOTE: Lithium may react with nitrogen to form nitrides.

🚩 NOTE: Potassium may react with oxygen to form explosive peroxides. See [Work Process P, Specific Controls and Procedures — Peroxide-Forming Compounds](#), for additional requirements. 🚩

9. Emergency Procedures

- a. Consult [Work Process V, Emergency Procedures and Equipment](#), for emergency actions regarding chemical spills and personal exposure to chemicals.
- b. Employees working with water-reactive chemicals must take [Fire Extinguisher Safety \(web-based\) \(EHS0520\)](#), and [Fire Extinguisher Safety Retraining \(EHS0531\)](#) annually thereafter. If desired, employees may also take [Fire Extinguisher Safety \(hands-on\) \(EHS0522\)](#).
- c. In addition to these requirements, the following applies to spills of water-reactive compounds:
 - i. Never use combustible or reactive materials (such as paper towels) to clean up spills. Keep an adequate number of appropriate spill kits to meet anticipated needs.
 - ii. In case of a fire, the safest course of action is to notify the fire department by activating a fire alarm pull station, call x7911 or 911, and evacuate the building. Employees who are comfortable doing so may attempt to extinguish a small fire with a fire extinguisher only after activating a fire alarm pull station, and only if the employee knows what is burning to select the appropriate extinguisher, can fight the fire without sustaining injury, and fighting the fire will not prevent the employee's escape from the building if the fire is not contained.

- iii. Anhydrous dry soda ash may be used for fires involving all metals except lithium. Lith-X fire extinguishers must be used for lithium metal fires. Met-L-X metal fire extinguishers may be used for sodium, potassium, and sodium-potassium alloy (NaK) fires. Employees involved in metal work must be knowledgeable of the details of the emergency plan in case of a metal fire, e.g. the nearest pull station, evacuation routes, location of fire extinguishers, etc.

Please note that Met-L-X, Lith-X, and other Class D fire extinguishers are not suitable for flammable organic solvent fires, even if the fire was initiated by reaction with an alkali metal or water-reactive chemical.

10. Skin or Eye Contact

- a. If any alkali metal fragment or drop enters the eye, it will immediately generate considerable heat, which is likely to result in severe eye injury. In such cases, the eyes should be flushed with water from an eyewash/safety shower. Continue to flush the eye with water while someone dials 7-911 for emergency help.
- b. When alkali metal comes in contact with the skin, remove all contaminated clothing. If contact with the metal occurs at only one or two spots on the skin, it is best to wash off those areas with mineral oil. A container with at least one quart of mineral oil should be available in alkali metal work areas labeled for this purpose. If contact with the metal is widely distributed over the body, a decision on the best course of first aid must be made immediately. If the material is already burning, the individual should be drenched continually under a safety shower until emergency help arrives. If the material is not burning, the metal should be removed by wiping the skin with mineral oil. In all cases, dial 7-911 for assistance.

11. Disposal

- a. Contact the Waste Management Group Generator Assistant if you need guidance or assistance on proper disposal of water-reactive chemicals. Water-reactive chemicals must be packaged in a compatible container and meet off-site vendor's disposal waste acceptance criteria.

- b. Contact your Division's Generator Assistant to ensure that your waste is safe for pickup, storage, and transportation and meets waste disposal waste acceptance criteria.
 - c. Alkali metals (e.g., lithium, potassium, rubidium, and cesium) must be fully submerged in mineral oil *before* placement in a SAA or WAA.
 - d. Water-reactive non-alkali metal waste must be packaged in a compatible container under inert conditions (e.g., under argon or nitrogen) before placement in a SAA or WAA.
 - e. Contact your Division's Generator Assistant to assist with unique water-reactive waste before generating the waste (e.g., experimental lithium batteries or more than 500 grams of alkali metals).
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