



## EH&S Guidance Document:

# Water Reactive Materials



*e.g. HAZMAT Class 4.3 – Dangerous When Wet*

Water reactive materials are substances that can react violently when exposed to water, including the water found naturally in the air. This reaction may release a gas that is flammable and/or presents a toxic health hazard. In addition, the heat generated is often enough for the item to spontaneously combust or explode.

The most common water reactives are solid alkali metals (lithium, sodium, potassium), chlorosilanes, and Grignard reagents, but a more detailed list can be found in section I of this document. Improper use of these materials in research labs has led to injuries and even death. Other common hazards of these materials can include corrosivity, toxicity, and shock-sensitive peroxide formation. The increased hazard level of this type of material requires additional safety measures be taken in order to ensure safe usage. Be aware, water reactive materials can frequently have pyrophoric qualities (i.e. can ignite spontaneously when exposed to air). If working with materials like this, please review the separate guidance document for pyrophoric materials available through EH&S.

Principal investigators (PI) should develop and implement a standard operating procedure (SOP) detailing techniques and steps for processes with water reactives, as well as site-specific emergency procedures. Researchers can only use water reactive reagents after they have read and fully understood this guidance document. However, reading these procedures does not substitute for hands-on training. New users must work under the close supervision of an experienced user, and follow all requirements listed in this document.

### **BEFORE WORKING WITH THESE MATERIALS, YOU MUST:**

- **Read and understand this guidance document and the material's safety data sheet (SDS) in order to be fully aware of all hazards present and how to safely work with the material.**
- **Create a lab specific standard operating procedure (SOP) for work with water reactive materials.**
- **Receive procedure specific training from your PI and/or supervisor that addresses unique lab protocols, your lab's water reactive SOP, the location of safety equipment, and proper emergency procedures.**
- **Before conducting the actual procedure, always perform a dry run (without the water reactive material) to identify and resolve possible safety hazards.**
- **Whenever possible, work with these materials should not occur when campus is closed or outside of normal campus hours (7am-5pm Monday-Friday).**
- **Always implement the "buddy system" and work alongside someone also trained in the hazards, use, and emergency procedures of water reactive materials.**

*(See detailed emergency procedures in Section II)*



## **I. IDENTIFICATION, PROPER USE, PPE, STORAGE & DISPOSAL**

### **Identification**

- Common examples of water reactive materials include:
  - Solid Alkali Metals (*Lithium/Li, Sodium/Na, Potassium/K (especially Sodium Potassium alloy NaK), Cesium/Cs, and Rubidium/Rb*)
  - Grignard reagents (*RMgX*)
  - Alkali metal amides (*NaNH<sub>2</sub>*) and some alkaline earth metal (*CaH<sub>2</sub>, Ca<sub>3</sub>C<sub>2</sub>*)
  - Alkali metal hydrides (*Sodium Hydride/NaH, NaBH<sub>4</sub>, LiH, LiAlH<sub>4</sub>*)
  - Chlorosilanes (*HSiCl<sub>3</sub>, SiCl<sub>4</sub>*)
  - Metal alkyls (*Li and Al alkyls*)
  - Halides of nonmetals (*BCl<sub>3</sub>, BF<sub>3</sub>, PCl<sub>3</sub>, PCl<sub>5</sub>, SiCl<sub>4</sub>, S<sub>2</sub>Cl<sub>2</sub>*)
  - Inorganic acid halides (*POCl<sub>3</sub>, SOCl<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub>*)
  - Anhydrous metal halides (*AlCl<sub>3</sub>, AlBr<sub>3</sub>, TiCl<sub>4</sub>, ZrCl<sub>4</sub>, SnCl<sub>4</sub>*)
  - Organic acid halides and anhydrides of low molecular weight (*Oxalyl chloride, acetic anhydride*)

### **Usage and Workspace**

- Before working with water reactive materials, read all relevant safety data sheets (SDS) and understand all hazards present.
- This guidance document and the material's safety data sheet (SDS) should be made directly available in the lab.
- Always wear proper personal protective equipment whenever transferring or handling water reactive materials (see PPE section below for details)
- All work with water reactive materials must be performed in a glove box or a fume hood with the sash at the lowest possible height for safe usage (no higher than 14 inches).
- Water reactive alkali metals should only be used in a dry environment away from sparks or any source of ignition. Ideally, this should be while in a glove box or AtmosBag.
- Work away from any water sources or potential water splashes.
- Keep the area free of other chemicals and flammable objects.
- Prior to working with any water reactive materials, you must identify which gas may be formed in case of exposure to water and learn the risks associated with this gas.
- Identify the closest safety shower and eyewashes, and ensure they are easily accessible.
- Identify the closest class-ABC fire extinguisher, and ensure it is available within 10 seconds travel time. It is highly recommended to purchase a class-D fire extinguisher as well, especially for work with combustible metals. You will also require a "fire bucket" of sand nearby, to be used to snuff out materials that catch fire.
- The reaction rate of solid material (and therefore heat and gas generation) depends on the material's surface area. Therefore, smaller particle size increases the hazard potential. Avoid formation of dusts and aerosols.
- After completion of a cutting process, the weigh boat or other weighing container should be rinsed carefully with a solvent (i.e. methanol, isopropanol), which will react with the excess metal much more slowly than with water. Accumulate this rinse for hazardous waste disposal.
- At the end of each project, thoroughly inspect the area for residual reactive material.



### Usage and Workspace (cont.)

- Whenever possible, work with these materials should not occur when campus is closed or outside of normal campus hours (7am-5pm Monday-Friday). Experiments should be planned so that they occur when campus is officially open in order to ensure there will be more people and resources available to help in an emergency.
- When working with these materials, you are required to implement the “buddy system” with a colleague that is also educated in the hazards, use, and emergency procedures of the materials at hand.
- All lab personnel, not just those using the material, should be informed of the dangers of water reactive materials and the emergency procedures necessary in case of an accident.
- We recommend you notify everyone in the lab whenever water reactive materials are in use.
- Purchase only the smallest amounts necessary for your work, and dispose old materials promptly. Reagents should be periodically examined to ensure containers and seals are in good condition. Try to seek alternate procedures that do not require water reactive materials.

### Personal Protective Equipment (PPE)

- **Eye Protection:** Safety glasses/goggles are required at all times. Wear a full-face shield whenever possible or if the risk of explosion is higher. EH&S can provide one upon request.
- **Hand Protection:** Gloves must be worn when handling these materials. A pair of nitrile gloves is typically adequate for working with small quantities, but be aware they are still flammable. Thicker chemical resistant gloves are required when working with large quantities, but make sure they are compatible with the materials you are using.
- **Skin and Body Protection:** Minimize exposed skin as much as possible. Full-length pants and closed toed shoes are required. A lab-coat is highly recommended. For work with water reactives that release hydrogen or flammable gas on contact with water, EH&S can provide your lab with a flame retardant and chemically resistant lab coat. This lab coat must be worn whenever handling pyrophoric materials. Due to the high cost of these lab coats, EH&S is not able to provide them for every lab user and are not able to replace them, so please make sure to have these coats accessible to all lab members and kept in good condition. Contact EH&S for more information. A chemical-resistant apron is also advisable to be worn whenever handling large quantities.

### Storage and Engineering Requirements

- Keep water reactive alkali metals (Li, Na, K) stored under mineral oil or paraffin oil at all times. The oil level can decrease over time, so frequently check your stored materials to ensure the metal remains fully submerged.
- Keep containers tightly sealed and in a dry, well-ventilated place. Opened containers must be carefully resealed and kept upright to prevent leakage. Ensure that manufacturer’s labels and warnings remain intact.
- Keep containers stored within an inert atmosphere whenever possible.
- Provide extra containment by storing in the manufacturer’s original shipping container.



## Disposal

- To ensure any water reactive waste is disposed of safely and efficiently, please contact EH&S for specific disposal guidance for the waste you are generating.
- Solid alkali metals (Li, Na, K) should remain submerged in mineral oil for EH&S disposal.
- Never leave a container with a residue of a water reactive material open to the atmosphere.
- Any contaminated glass/materials should have all surfaces coated in mineral oil and placed in an appropriate container (e.g. double plastic bagged) for disposal through EH&S.
- Empty containers must be rinsed three times with a compatible solvent and left open in the back of a fume hood overnight. Any rinses must be collected for disposal through EH&S.
- As an alternative, unrinsed empty containers can be disposed of through EH&S as hazardous waste. The unrinsed empty containers must be capped.
- Be sure not to mix the waste with any incompatible waste streams.
- Reuse of empty containers is not permitted.

## **II. EMERGENCY PROCEDURES**

Always use extreme caution due to the constant potential for spontaneous ignition.

DO NOT use water to attempt to extinguish a water reactive material fire as it can worsen the combustion and/or ignite unaffected material. Dry chemical class-D fire extinguishers are best for combustible solid metal fires.

**In the event of combustion, reaction, or a flash fire,  
CALL 911 immediately for emergency assistance!**

### Small Spills

1. If anyone is exposed at all, remove all affected clothing and rinse exposed skin/eyes for at least 15 minutes in a nearby emergency shower/eyewash.
2. Small spills of water reactives inside a chemical fume hood or glove box can be cleaned up by laboratory staff if they fully understand the hazards and are confident in their ability to clean up the spill safely. Follow these precautions for cleanup, otherwise go to step 3:
  - a. Ensure you have a fire extinguisher and a “fire bucket” of sand nearby. A class-D extinguisher is preferred, however a common class-ABC can suffice.
  - b. Carefully remove nearby flammable materials from the spill.
  - c. Powdered lime (calcium oxide, CaO) or the dry sand from the fire bucket should be used to completely smother and cover any spill that occurs.
  - d. Carefully quench materials by slow addition of isopropanol.
  - e. After complete quench, collect and double bag spill residues for disposal through EH&S.
3. Alternatively, If the spill is small, nobody was injured, and there is no chance for the situation to worsen, vacate the lab and contact EH&S at 303-492-6025. If after normal campus hours, contact 911.



## Large Spills

1. Life Safety First!
  - Remove all affected clothing and rinse exposed skin/eyes for at least 15 minutes in a nearby emergency shower/eyewash.
2. Evacuate the immediate area.
3. Pull the nearest fire or chemical alarm in the hallway as you vacate the building.
4. Execute a 911 call from a safe location to notify emergency personnel of the issue.
5. Remain available for emergency personnel.

## Exposure

- **Skin:** Prolonged exposure can cause severe burns to the skin or worse depending on its specific chemical characteristics.
  1. Remove any contaminated clothing, in case of flash fire.
  2. Rinse skin with copious amounts of water for at least 15 minutes. If larger areas of skin are affected, rinse under the emergency safety shower for at least 15 minutes or until emergency personnel arrive.
  3. Seek medical attention, especially if you experience any burning or irritation thereafter.
- **Eye:** Prolonged exposure can cause severe burns to the eyes.
  1. Immediately flush the eyes with water as absolute priority! Flush eyes at the emergency eyewash station for 30 minutes. Occasionally lift the upper and lower eyelids to ensure thorough rinsing.
  2. Seek medical attention, especially if you experience any burning or irritation thereafter.
- **Inhalation:** Inhaling gas/vapors can cause chemical burns to the respiratory tract.
  1. Remove victim from exposure area to fresh air immediately.
  2. If not breathing, call 911 and do NOT use mouth-to-mouth resuscitation. Use artificial respiration if available. If breathing is difficult, give oxygen.
  3. Immediately seek medical attention.
- **Ingestion:** Swallowing materials may cause severe/permanent damage to the digestive tract
  1. Do NOT induce vomiting!
  2. Immediately seek medical attention.

*-End of Guidance Document-*