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GUIDELINES FOR THE SAFE USE OF COMBUSTIBLE METALS

Most metals are combustible to a varying degree, depending on the physical conditions. Certain metals undergo dangerous reactions with water, acids, and other chemicals. Some metals are subject to spontaneous heating and ignition. The hazards of an individual metal or alloy can vary widely depending on the particle size and shape that is present (see Appendix A for information on specific metals). Pure metals or alloys covered by this guideline have the generally recognized properties of the metal, including the fire or explosive characteristics of the metal in its various forms and include (but are not limited to) the following chemical groups ¹:

Alkali metals: highly combustible metals that react with water to generate hydrogen, and are easily ignited; examples include sodium, potassium, lithium, rubidium and cesium

Combustible metals: any metal, composed of distinct particles or pieces, regardless of size, shape or chemical composition, that will burn

Metal alloys: multiphase solid that is formed by mixing in the molten state, in which the primary component or matrix phase is a metal and the original composition is retained during size reduction

Metal containing mixtures: physical combination of one or more metals or metal alloys with one or more solid, liquid, or semi-solid chemical elements or compounds

Pyrophoric materials: substance capable of self-ignition on short exposure to air under ordinary atmospheric conditions (additional information on pyrophoric liquid reagents is available in the University of Pittsburgh Guideline – *Safe Use of Pyrophoric Liquid Reagents*, # 04-031) ²

1. Hazards

Health hazards associated with combustible metals include (but are not limited to) ³:

- 1.1 Severe skin and eye burns upon contact
- 1.2 Metals can react with moisture on the skin to produce corrosive hydroxides
- 1.3 Fumes/vapors generated during burning are highly irritating to the skin, eyes, and mucous membranes
- 1.4 Metals ignite in air or oxygen thus producing a fire hazard and potential thermal and chemical burns
- 1.5 Reactions of various metals with water can release hydrogen thus producing a fire hazard and potential thermal and chemical burns (consult Appendix A for information on specific reactions of metals)

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2. Safety Precautions

- 2.1 Employees who work with combustible metals should receive training on the associated hazards and what to do in the event of an exposure or an uncontrolled reaction. A Safety Data Sheet (SDS) should be accessible in the immediate work area where combustible metals are used. The SDS, along with this Guideline, should be used for training employees on the hazards of combustible metals prior to initial use.
- 2.2 The quantity of combustible metals that is allowable in a room or laboratory is restricted by International Fire Codes and University Guidelines. Certain combustible metals are also classified as Chemicals of Interest per the U.S. Department of Homeland Security. Therefore, the amount of combustible metals stored in the laboratory shall be kept to the minimum necessary for the laboratory experiment or activity. EH&S (412-624-9505) should be contacted with questions concerning quantities.
- 2.3 Alkali metals shall be immersed in mineral oil (preferred) or kerosene within a noncombustible, sealed container to prevent the metals from reacting with water or moisture in the air; the storage solution should be compatible with the metal that is being immersed.
- 2.4 Work with combustible metals should always be performed inside a certified chemical fume hood or approved glove box. Care should be taken to clean the work area prior to manipulation of combustible metals. Acids, aqueous solutions, halogens, oils, oxidizing materials, ordinary combustibles and any other incompatible substances should be removed from the immediate work area.
- 2.5 Safety glasses (or chemical splash goggles) along with a face shield are required when handling combustible metals.
- 2.6 A flame-resistant lab coat is required when handling combustible metals. A chemical-resistant and flame-resistant apron is required to be worn over the flame-resistant lab coat when working with large quantities. Consult EH&S (412-624-9505) for lab coat and apron recommendations. Strict adherence to the University's Guideline – *Lab Attire* (EH&S # 03-001) ⁴ is necessary when handling combustible metals. Shorts, skirts above the knee or open-toed shoes are not permitted to be worn when handling combustible metals or other laboratory chemicals.
- 2.7 Nitrile rubber gloves are recommended when working with most combustible metals. Depending on reagent quantity and/or the type of solvent, heavier gloves may be required. Consult the specific SDS for proper glove recommendations. If you have any questions about which glove to choose, contact EH&S (412-624-9505). If gloves become contaminated with a combustible metal or damaged,

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remove them immediately (do not place the gloves near any combustible materials), thoroughly wash your hands, and check your hands for any sign of contamination.

- 2.8 An eyewash and safety shower must be nearby and accessible when handling combustible metals. The eyewash must be tested weekly to ensure it will operate appropriately when needed. If exposure to a combustible metal occurs, immediately rinse the exposed area for at least 15 minutes. Seek additional medical attention immediately after the water rinse. Call Pitt Police at 412-624-2121.
- 2.9 The following safeguards should be applied to water reactive metals (for example magnesium, potassium, sodium).
 - 2.9.1 Store in containers within cabinets that minimize water spray, pooling, or drainage from sources such as sprinklers, domestic water supplies, or process water lines.
 - 2.9.2 Ensure that the preparation area is completely dry of any moisture (pooled or surface water, etc.).
 - 2.9.3 Maintain all tools such as knives (when cutting metals), tongs or other equipment used to handle or process the metals free of water or moisture.
 - 2.9.4 Collect and properly store excess chips, fines, ribbons or other leftover pieces from processes by immersion in the appropriate medium and dispose through the University's Chemical Waste Program.
 - 2.9.5 Materials such as dry sand, clay or other dry inert materials should be available to help smother a potential combustible metal fire.
- 2.10 When using combustible metals (such as sodium) for solvent purification within a still, the solvent still should be maintained within a certified chemical fume hood and be clearly labeled as to the contents.
- 2.11 Combustible metal usage is not permitted when personnel are working alone in a laboratory per University of Pittsburgh Guideline – *Working Alone in Laboratories* (EH&S # 03-020).⁵

3. Spill and Emergency Response

- 3.1 If exposure to a combustible metal occurs, immediately rinse the exposed area for at least 15 minutes. A follow-up medical evaluation is required immediately after the water rinse. Call Pitt Police at 412-624-2121 to request medical assistance
- 3.2 Small spills of combustible metal solids should be handled with extreme care as the metal can ignite if it is allowed to dry prior to clean-up. The metal solids should be quickly cleaned from the laboratory hood and immersed in mineral oil or kerosene (when applicable) within a sealed container.

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- 3.3 If a large spill occurs, evacuate the area, close the doors, and notify appropriate chemical spill response personnel by calling Pitt Police at 412-624-2121.
- 3.4 In the event of a fire involving combustible metal, immediately close the chemical fume hood sash and notify other laboratory personnel. Activate the nearest building fire alarm, and evacuate the building.
- 3.5 Class D fire extinguishers must be installed for use by trained personnel in the vicinity of all areas where combustible metals are stored or handled. Contact EH&S (412-624-9505) to arrange installation of Class D fire extinguisher.

4. Storage

- 4.1 Combustible metals should always be stored in the original manufacturer's container; the bottle should be stored within a secondary plastic bag and then stored within a metal container with inert packing material (such as Vermiculite).
- 4.2 Alkali metals such as potassium and sodium should be immersed in mineral oil or kerosene and should not be allowed to dry out for risk of direct exposure to air and moisture.
- 4.3 Storage of a combustible metal in an approved glove box under an inert atmosphere is permitted. As with all chemicals being stored/used in a glove box, the specific combustible metal(s) must be listed on the glovebox chemical inventory that must be posted on the outside of the glovebox.

5. Waste Disposal

- 5.1 Unused combustible metals should be kept in the original manufacturer's container and disposed via the University's chemical waste program. Do not transfer combustible metals to another container for disposal purposes.
- 5.2 Combustible metal waste should never be combined with incompatible chemicals such as aqueous solutions, oxidizing agents, combustible materials, and acids. Contact with incompatible chemicals will cause the rapid generation of flammable gas and the potential for spontaneous ignition and/or explosion.
- 5.3 Contact EH&S (412-624-9505) with any questions regarding the disposal of combustible metal wastes.

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EMERGENCY PROCEDURES FOR COMBUSTIBLE METAL EXPOSURES

Individuals that are exposed to combustible metals require immediate first aid and prompt medical evaluation.

Skin contact

1. Keep tongs, tweezers, scrapers or some type of implement on hand to remove bits of metal from skin or clothing in the event of an exposure.
2. Immediately proceed to the nearest drench hose/shower and wash affected area for a minimum of 15 minutes. Use large amounts of water to flood the affected area; small amounts of water (ex. sink faucet) may cause adverse chemical reactions.
3. While washing the affected area, have someone call for emergency medical assistance – **PITT POLICE 412-624-2121**.
4. Remove all contaminated clothing.
5. After 15 minute rinse, immediately obtain emergency medical attention.

Eye contact

1. Immediately proceed to the nearest eyewash station.
2. Wash eyes with water for at least 15 minutes while holding eyelids open.
3. While washing eyes, have someone call for emergency medical assistance – **PITT POLICE 412-624-2121**.
4. After 15 minute rinse, immediately obtain emergency medical attention.

References

¹ – National Fire Protection Association (NFPA®) 484, Standard for Combustible Metals, 2015 Edition

² – University of Pittsburgh Guideline for the Safe Use of Pyrophoric Liquid Reagents (EH&S # 04-031), <http://www.ehs.pitt.edu/assets/docs/pyrophoricliquidreagents.pdf>

³ – A Comprehensive Guide to the Hazardous Properties of Chemical Substances, 3rd Edition, Pradyot Patnaik, 2007

⁴ – University of Pittsburgh Guideline for Proper Attire for Individuals in Laboratories (EH&S # 03-001), <http://www.ehs.pitt.edu/assets/docs/lab-attire.pdf>

⁵ – University of Pittsburgh Guideline for Working Alone in Laboratories (EH&S # 03-020), <http://www.ehs.pitt.edu/assets/docs/03-020WorkingAloneinLabs.pdf>

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**APPENDIX A – INFORMATION ON SPECIFIC COMBUSTIBLE METALS
(Appendix Information from FM Global Property Loss Prevention Data Sheets)**

Alkali Metals:

Sodium (Na): Specific gravity, 0.97; melting point, 208°F (98°C). In University laboratories, sodium metal is most often used to remove excess water from flammable liquids during the distillation process. It is also used in the production of other sodium-based compounds and in the reduction of organic esters.

Sodium metal reacts violently with water to produce hydrogen gas and sodium hydroxide. The exothermic heat of this reaction can lead to auto-ignition of the hydrogen gas and/or the metal itself and create a severe fire or explosion hazard. Due to its low melting point, explosions of molten sodium may occur during reaction with water. Residual liquid present following the reaction contains a high percentage of sodium hydroxide, a caustic, corrosive material.

In finely divided form, sodium ignites spontaneously in air. Molten sodium reacts with most gases and liquids except the noble gases and nitrogen, and combines vigorously with hydrogen to form the hydride. Solid sodium reacts strongly with water, alcohol, polyhalogenated hydrocarbons, halogens, acidic oxides, sulfuric acid, mercury, and certain alloys of lead, tin, zinc and bismuth.

Potassium (K): Specific gravity, 0.86; melting point, 145°F (63°C). Similar to sodium in its pyrophoricity, chemical activity, and hazards although somewhat more reactive. See sodium section. Potassium is violently reactive with sulfuric acid and most halogens. Potassium will detonate in contact with liquid bromine.

Lithium (Li): Specific gravity, 0.53; melting point, 356°F (180°C). As the hydride, lithium offers the most concentrated method of storing and transporting hydrogen. Ignition and burning occur when lithium is heated to about 356°F (180°C). Lithium reacts less vigorously than sodium with water or air, and usually does not ignite. Lithium reacts strongly with chlorinated, fluorinated, and brominated organic compounds, halogens, and sulfuric acid. In the presence of moisture, lithium reacts exothermically with nitrogen at ordinary temperatures. Above the melting point, lithium rapidly forms the nitride. Near its melting point, lithium ignites in air and burns with a characteristic intense, brilliant white flame. Following treatment with nitric acid, lithium may explode on very light impact or friction. Lithium also reacts violently with hydrogen peroxide.

Magnesium (Mg): Specific gravity, 1.74; melting point of 1202°F (650°C). Ignition temperature of magnesium is near the melting point, although ignition of some forms may occur at lower temperatures. As a dust cloud or in ribbon form, magnesium can be ignited almost instantly. Loose shavings ignite fairly readily. Magnesium is less easy to ignite the surface of a compact pile of chips. Magnesium fines wet with oils may ignite spontaneously. Fines wet with acids, water, water-soluble oils, or oils containing fatty

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acids will generate hydrogen. Powders form explosive mixtures with air that may be ignited by a spark. Fines will also react with chlorine, bromine, iodine and oxidizing agents.

Other Highly Combustible Metals

Hafnium, plutonium, thorium, uranium and zirconium are all highly combustible metals. The hazards of this group are similar to those of magnesium, and the same safeguards should be applied except as noted in the following:

Uranium isotopes 233 and 235, plutonium, and thorium are radioactive, and present the same fire and explosion hazards as other combustible metals. They have been known to ignite spontaneously. As coarse particles, metals in this group offer little hazard; but in powder form, they present severe dust explosion possibilities. Some burn readily in pure nitrogen or carbon dioxide gas, and explode on contact with oxidizing agents. Some heat spontaneously in air and must be stored and handled under a nonreactive liquid or gas. Chips and other fine particles ignite easily, and special care is needed to prevent ignition of chips by the friction of cutting. Fine particles of these metals should be shipped and stored in approved DOT containers.

When molten or when burning, all these metals react vigorously with water, foam, carbon dioxide vaporizing liquid and dry chemical extinguishing agents. Applied directly to the burning material, these agents will intensify burning and may cause an explosion. Approved dry powder extinguishing agents, dry sand, graphite chips, limestone, or talc are used to smother fires.

Hafnium (Hf): Specific gravity, 13.36; melting point, 4032°F (2222°C). Fines are pyrophoric. The metal burns with little visible flame but with a high rate of heat release. Chemical reacts with water to form hydrogen, which may ignite spontaneously. Hafnium hazards are similar to those of zirconium. Crushing and sizing should be carried out under inert gas.

Plutonium (Pu): Specific gravity, 19.6; melting point, 1170°F (632°C). Plutonium is pyrophoric, highly toxic (particularly in the oxide form when burning), and radioactive. Chips, turnings, and fine particles may ignite spontaneously. Plutonium is easily ignited by friction.

Raney®-Nickel: Specific gravity, 1.94. Supplied as slurry in water (demineralized / deionized water). Chemical as a very fine dry powder is pyrophoric. Ignites spontaneous in air, store under alcohol (ethanol, cyclohexane, or dioxane) or water; catalyst for hydrogenation reaction.

Thorium (Th): Specific gravity, 11.6; melting point, 3090°F (1700°C). Thorium is pyrophoric and radioactive. As a dry powder it has a low ignition temperature. Thorium powder is shipped under helium or argon gases in special containers. When poured

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through air, Thorium is subject to ignition by electrostatic spark. Thorium should be handled cautiously with a nonsparking spoon or scoop. Containers and tools should be grounded. Ignition has occurred due to chemical reaction between finely divided thorium and water at ordinary temperatures.

Uranium (U): Specific gravity, 18.68; melting point, 2071°F (1132°C). The fire hazard of metallic uranium is similar to but more severe than magnesium. In finely divided form, Uranium is pyrophoric. Spontaneous fires have occurred under argon, under vacuum, and under water. The high temperature reaction of uranium with steam is very violent. Radioactivity and products of combustion present a health hazard. Uranium powder should be handled in an inert atmosphere. Chips and turnings may be stored if completely immersed in water with ventilation to remove evolved hydrogen. Partial submersion or slight moistening accelerates spontaneous heating.

Zirconium (Zr): Specific gravity, 6.51; melting point 3326°F (1830°C). Fine particles in dust layers or clouds are pyrophoric, and may be ignited by heat, static or friction. Particles can be ignited in nitrogen gas above 986°F (530°C) and in carbon dioxide above 1040°F (560°C). Zirconium samples may explode during or following treatment with strong nitric acid or carbon tetrachloride. Samples have also exploded while being dissolved in a mixture of sulfuric acid and potassium acid sulfate. Particles form explosive mixtures with barium nitrate, potassium chlorate, and other oxidizing materials. In dry powder form, zirconium or zirconium-copper alloys in glass containers may explode by impact or friction if the container breaks. Zirconium ignites more easily than magnesium and is slightly less hazardous than uranium. Zirconium powder is commonly handled wet because it is then more difficult to ignite, although once ignited it will burn more violently. At least 25 percent moisture by weight should be present.

Miscellaneous Metals

Certain other metals in molten form or as fine particles present varying degrees of hazard. They may be subject to spontaneous heating, chemical activity, dust explosions, or ignition under favoring conditions.

Aluminum (Al): Aluminum is used both as a commercially pure metal and as an alloy. In finely divided powder or dust form, aluminum and its alloys are combustible in air and present a serious combustion explosion hazard. Aluminum will react violently with many chemicals. Aluminum particles and smaller turnings will react with water to form hydrogen gas which is highly flammable and explosive in favorable concentrations. The rapid vaporization of water in contact with molten aluminum can result in rapid phase transformation explosions. Halogenated extinguishing agents should not be used.

Antimony (Sb): Specific gravity, 6.62; melting point, 1166°F (630°C). Antimony ignites and burns in air above 780°F (416°C).

Barium (Ba): Specific gravity, 3.5; melting point, 1300°F (704°C). In contact with water, barium liberates hydrogen but usually without ignition.

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Beryllium (Be): Specific gravity, 1.85; melting point, 2400°F (1316°C) also called glucinum. Beryllium decreases the combustibility of molten aluminum and magnesium. As a powder, ignition may occur if the metal is heated to about 1115°F (600°C). Burning occurs with an intense flame, but can be extinguished by water. Beryllium powder should be kept away from air and moisture and stored in tight containers, preferably under argon gas. Beryllium and its compounds are very toxic and contact with skin or inhalation of dust or fumes should be avoided.

Bismuth (Bi): Specific gravity, 9.80; melting point, 520°F (271°C). Bismuth burns in air with bluish flame when vaporized and oxidizes rapidly when molten. At red heat, bismuth decomposes steam. Bismuth reduces carbon dioxide, but does not react with nitrogen or hydrogen.

Calcium (Ca): Specific gravity, 1.55; melting point, 1562°F (850°C). In contact with water, calcium liberates hydrogen but usually without ignition. Calcium is considered pyrophoric under some conditions and is normally shipped in lump form under argon.

Cadmium (Cd): Specific gravity, 8.65; melting point, 610°F (321°C). Cadmium oxidizes when heated, giving off dense brown fumes that decompose steam above 750°F (400°C). As a powder, cadmium decomposes hot water but without igniting.

Chromium (Cr): Specific gravity, 7.19; melting point, 3407°F (1875°C). Chromium presents a moderate dust explosion hazard under favorable conditions of partial size dispersion and ignition source.

Copper (Cu): Specific gravity, 8.96; melting point, 1981°F (1083°C). Copper is not known to produce explosive properties when in finely divided form.

Iron (Fe): Specific gravity, 7.86; melting point, 2802°F (1540°C). Iron presents a dust hazard under favoring conditions of particle size and dispersion in air. Iron can be easily ignited in the form of dust or steel wool or as fine turnings or chips containing oil. Structural steel has a specific gravity of 7.83 and melting point of 2605°F (1430°C). When heated above 600°F (315°C), it begins to lose strength rapidly.

Lead (Pb): Specific gravity, 11.34; melting point, 621°F (327°C). At high temperatures lead volatilizes and burns with white flame. At red heat, lead is rapidly oxidized by air and at white heat by steam.

Manganese (Mn): Specific gravity, 7.43; melting point, 2246°F (1230°C). Manganese dust can be ignited at 840°F (449°C) in air.

Molybdenum (Mo): Specific gravity, 10.2; melting point, 4750°F (2620°C). Molybdenum powder reacts vigorously with water vapor at 1300°F (704°C).

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Molybdenum presents a slight dust hazard under favoring conditions of particle size, dispersion, and strong ignition source.

Silicon (Si): Specific gravity, 2.33; melting point, 2588°F (1420°C). A silicon dust cloud can be ignited in air at 1425°F (775°C). Pure silicon metal dust has been shown to be highly explosive under certain conditions.

Strontium (Sr): Specific gravity, 2.6; melting point, 1386°F (752°C). In contact with water, strontium liberates hydrogen readily, but usually without ignition.

Tantalum (Ta): Specific gravity, 16.62; melting point 5425°F (2996°C). Tantalum presents a moderate dust explosion hazard under favorable conditions of particle size, dispersion, and ignition source.

Tellurium (Te): Specific gravity, 6.24; melting point, 846°F (452°C). Tellurium presents a moderate dust explosion hazard under favoring conditions of particle size, dispersion and ignition source.

Thallium (Tl): Specific gravity, 11.85; melting point, 572°F (300°C). At red heat, thallium decomposes water, producing hydrogen. It is very toxic.

Tin (Sn): Specific gravity, 7.29; melting point, 450°F (232°C). Tin dust can be ignited in air at 1165°F (630°C).

Titanium (Ti): Specific gravity, 4.51; melting point, 3040°F (1670°C). At red heat, 1300°F (704°C), the metal actively decomposes steam. Following strong nitric acid treatment, the metal may explode by the light impact or friction of handling with tongs. The powder can be ignited in pure carbon dioxide above 1260°F (682°C), in nitrogen above 1475°F (801°C), and in air at 626°F (330°C) to 1094°F (590°C). Powdered titanium immersed in water or wet with water at ordinary temperatures has been ignited by chemical reaction.

Tungsten (W): Specific gravity, 19.2; melting point, 6115°F (3380°C). As fine powder, tungsten may be pyrophoric. Hydrogen reduced powder may retain some absorbed hydrogen, presenting a dust explosion hazard. Tungsten reacts violently with molten nitrates, nitrites, and peroxides.

Zinc (Zn): Specific gravity, 7.13; melting point 786°F (419°C). In the form of dust, in contact with moisture, alkaline solutions, or acetic acid, zinc will heat spontaneously to ignition. Large pieces of zinc are difficult to ignite but once ignited will burn strongly. In oxygen, oxidation of the metal takes place rapidly at 300°F (149°C) and ignition occurs at 930°F (499°C) with a bluish flame. Steam is decomposed on contact with zinc at 660°F (349°C). Acids or caustic soda also liberate hydrogen on contact with zinc. In air, zinc burns to the oxide, forming white or bluish smoke. As a dust cloud, zinc can be ignited at 1110°F (600°C).