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DOE HANDBOOK

PRIMER ON SPONTANEOUS HEATING AND PYROPHORICITY



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OVERVIEW

The *Department of Energy (DOE) Primer on Spontaneous Heating and Pyrophoricity* was prepared as an information resource for DOE and contractor personnel who may have these types of materials at their site. An understanding of spontaneous heating and pyrophoricity hazards is necessary for DOE facility personnel to operate and maintain facilities and facility support systems in a safe manner.

The *Primer on Spontaneous Heating and Pyrophoricity* contains an introduction and sections on the following topics:

- Principles of Combustion;
- Spontaneous Heating/Ignition of Hydrocarbons and Organics;
- Pyrophoric Gases and Liquids;
- Pyrophoric Nonmetallic Solids;
- Combustible and Pyrophoric Metals; and
- Accident Case Studies.

The information contained in this Primer is by no means all encompassing. However, enough information is presented to provide the reader with a fundamental knowledge level sufficient to recognize most spontaneous ignition hazards and how to prevent ignition and widespread fires. Additional resource materials for this topic are listed in the bibliography section at the end of this Handbook.

INTRODUCTION

Some materials, such as phosphorus, ignite spontaneously when exposed to air. Other materials, such as coal, may take several weeks to ignite under similar conditions. This ignition time difference is the defining point between pyrophoricity and spontaneous heating. It is well known that fires caused by these phenomena do occur, sometimes resulting in personal injury and significant damage to facilities. By its very nature, spontaneous heating and pyrophoricity are among the most insidious types of fire hazards because here is usually no outward evidence of the potential for fire. Therefore, an understanding of the principles of spontaneous heating and pyrophoricity is necessary for instituting appropriate fire prevention measures. This Primer introduces DOE operations and maintenance personnel with basic information necessary to identify and prevent spontaneous ignition hazards.

Upon completion of this Handbook, the reader should be able to:

- Identify the four required elements of the Fire Tetrahedron necessary to support combustion.
- Define the following terms: combustion, oxidation, spontaneous heating, pyrophoricity, hypergolic, and specific area.
- Describe the effects that atmospheric oxygen, moisture, heat transfer, and specific area have on spontaneous heating and ignition.
- Identify five metals and three gases known to be pyrophoric.
- Identify acceptable methods for long-term storage of spontaneously heating and pyrophoric materials.
- Identify the appropriate measures for preventing fires caused by spontaneous heating and pyrophoricity.
- Identify references for obtaining further information on oxidizers, pyrophoric materials, hypergolic substances, and fire extinguishing agents.
- Identify proper emergency response, including extinguishing agents for various spontaneously igniting materials, and self-extinguishing without interaction.
- Describe the importance of good housekeeping in limiting fire damage.

DEFINITIONS

Combustion:	A chemical process of oxidation that occurs at a rate fast enough to produce heat and usually light in the form of either a glow or flame.
Hypergolic	Any substance that will spontaneously ignite or explode upon exposure to an oxidizer.
Ignition Temperature:	Minimum temperature a substance should attain in order to ignite under specific test conditions.
Oxidization:	A reaction driven by the removal or transfer of electrons between atoms or molecules.
Oxidizer:	Any solid or liquid that readily yields oxygen or other oxidizing gas; or that readily reacts to promote or initiate combustion of combustible materials. Additionally an oxidizer, under certain circumstances, can undergo a vigorous self-sustained decomposition due to contamination or heat exposure. ¹
Oxidizing Agent:	Any material that readily yields oxygen or other oxidizing gas; or that reacts chemically to oxidize combustible materials.
Pyrolysis	A process in which material is decomposed into simpler molecular compounds by the effects of heat alone; pyrolysis often precedes combustion. A chemical property characterized by the ability of a material to undergo a spontaneous ignition in air.
Pyrophoric	A material that, even in small quantities and without an external ignition source, can ignite at or below 54.4°C (130°F) in contact with air.
Specific Area:	Amount of surface area per unit weight of a material, usually expressed in cm ² /g (in ² /lb).
Specific Surface Area:	The ratio of reactive surface area to the mass of the material (typically a factor of 3-5 times higher than the Specific Area previously defined).
Spontaneous Heating:	Process whereby a material's temperature increases due to its exothermic reaction with oxidants without drawing heat from its surroundings.

¹ See NFPA 400-2013, *Hazardous Materials Code* for more information on Oxidizer classifications, including a list of the most common oxidizers.

characterized metal existing in large pieces that have higher ignition temperatures. Thus, a piece of plutonium is not considered pyrophoric or capable of self-ignition.

An investigation of two instances in which kilogram-sized plutonium pieces were observed to "spontaneously ignite" in air at room temperature showed that they had been exposed to unlimited sources of hydrogen for extended periods, and that the samples were thermally insulated when ignition occurred. The amount of hydride present on these pieces apparently generated sufficient heat to cause ignition. These observations emphasize the need for well-characterized materials.

Storage and Handling

Plutonium should be stored as pure metal (Pu) or in its dioxide (PuO₂) form in a dry, inert or slightly oxidizing atmosphere. The formation of oxide from metal is accompanied by a large volume expansion (up to 70%) which may bulge or breach the primary container. Case studies show that mechanical wedging resulting from this expansion can even breach a second metal container, resulting in localized contamination release and possible exposure of personnel. Oxidation of the metal and rupture of the container by mechanical wedging are prevented if the storage container is hermetically sealed. Plutonium radioactively decays producing alpha particles and helium molecules. Over long-term storage, helium buildup can contribute to the pressurization of containers.

Plutonium sesquioxide and hydride should be converted to plutonium dioxide before storage. Primary and secondary containers should be hermetically sealed and contain no plastics or other materials that decompose as a result of radiation exposure.

For a more complete discussion of plutonium storage, refer to DOE-STD-3013-2012, *Stabilization, Packaging, and Storage of Plutonium-Bearing Materials* (March 2012).

Where plutonium must be handled, placing larger pieces on a thick stainless steel slab will generally conduct heat away from the material fast enough that spontaneous ignition does not occur.

Extinguishing Plutonium Fires

Plutonium fires should not be approached without protective clothing and respirators unless the fire is enclosed in a glovebox. The most effective agent for extinguishing plutonium fires has been found to be magnesium oxide sand. Gloveboxes that contain pyrophoric forms of plutonium should also contain a supply of magnesium oxide sand that is adequate for manual extinguishment. Magnesium oxide sand extinguishes a plutonium fire by providing a heat sink that cools the plutonium below its ignition temperature and by providing a barrier that limits the availability of oxygen. Burning plutonium should be completely covered with the sand to as great a depth as possible. Extinguishment - studies have shown that covering plutonium with one to two inches of magnesium oxide sand, or using a mass of magnesium oxide sand roughly three times that of the plutonium has been effective at extinguishing a plutonium fire. Additionally, if a mass of plutonium is burning within a stainless steel glovebox, agents typically non-compatible with plutonium (Clean Agents, CO₂, etc.) can be used on the exterior of the glovebox to cool the burning mass; in some cases, this is sufficient to extinguish a plutonium fire by reducing the temperature of the burning mass below its ignition temperature.

Argon is a very effective extinguishing agent, if the oxygen content in the atmosphere is maintained at 4% or less. Above 4% oxygen, flooding with argon will not extinguish a plutonium fire. This is an important point, since it is nearly impossible to reduce the oxygen content to 4% or less during argon flooding in most fume hoods. Argon may be used effectively to cool the burning plutonium prior to application of the magnesium oxide sand.

Other agents have been tested for use on plutonium fires; however, none has proven to be as effective as magnesium oxide. Typical foam or dry chemical agents are not effective extinguishing agents. Fusible salt agents have been shown to be effective on small-scale plutonium fires. However, the expansion that accompanies the oxidation of plutonium has caused the fusible salt coating to crack, allowing the plutonium to re-ignite.

As a last resort, water can be used as an extinguishing agent for fires of ordinary combustibles that are exposing plutonium. Where criticality safety considerations preclude the introduction of moderators such as water, suitable alternative fire protection measures need to be identified within fire hazard plans to coordinate or incorporate such measures into emergency response activities. Proper housekeeping, which includes removal of combustibles from pyrophoric forms of plutonium, is the most important aspect of fire loss minimization.

Uranium

Properties

Uranium is a radioactive metal that is also combustible in finely divided forms. Its radioactivity does not influence its combustibility, nor is the radioactivity influenced by burning the material. Metallic uranium that is handled in pieces does not present a significant fire risk unless exposed to a severe and prolonged external fire. Once ignited, pieces of metal burn very slowly. In the absence of strong drafts, uranium oxide smoke tends to deposit in the immediate area of the burning metal. Unless covered with oil, pieces of uranium will burn with virtually no visible flame. Burning uranium reacts violently with carbon tetrachloride, 1,1,1-trichloroethane, and the Halons.

Uranium in finely divided form is readily ignitable, and uranium scrap from machining operations is subject to spontaneous ignition. This reaction can usually be avoided by storage under dry (without moisture) oil. Grinding dust has been known to ignite even under water, and fires have occurred spontaneously in drums of coarser scrap after prolonged exposure to moist air. Because of uranium's thermal conductivity, larger pieces generally have to be heated entirely to their ignition temperature before igniting. Moist dust, turnings, and chips react with water to generate hydrogen gas. Uranium surfaces treated with concentrated nitric acid are subject to explosion or spontaneous ignition in air.

The pyrophoric characteristics of uranium are similar to those of plutonium except that uranium forms do not ignite as easily as those of plutonium do. Both form pyrophoric oxides and hydrides. Both react violently with water and are best stored in their oxide form (UO_2 , PuO_2) in dry, inert atmospheres. Uranium metal (U) releases hydrogen gas (H_2) when allowed to react with water. The hydrogen may then react with the metal to form uranium hydride (UH_3) which may in turn react with oxygen in the air to form stable uranium oxide (UO_2) and hydrogen gas (H_2).

The heat generated from corrosion, if dissipated in a water storage environment, may not be sufficient enough to ignite the uranium if properly configured. This is a dynamic process and an SME should be consulted for an appropriate hazard analysis.

Storage and Handling

The storage of the many forms of uranium is beyond the scope of this primer. For a more complete discussion of uranium storage, refer to DOE-STD-3028-2000, *Criteria for Packaging and Storing Uranium-233-Bearing Materials* (July 2000).

Extinguishing Uranium Fires

Uranium fires should be extinguished with the same techniques and precautions as plutonium fires (see corresponding paragraph on plutonium).

Combustible Metal Extinguishing Agents and Application Techniques

A variety of metals burn, particularly those in finely divided form. Some metals burn when heated to high temperatures by friction or exposure to external heat; others burn from contact with moisture or in reaction with other materials. Because accidental fires may occur with these materials, it is important to understand the nature of the various fires and the hazards involved.

The hazards involved in the control or complete extinguishing of metal fires include extremely high temperatures, steam explosions, hydrogen explosions, toxic products of combustion, explosive reaction with some common extinguishing agents, breakdowns of some extinguishing agents with the liberation of combustible gases or toxic products of combustion, and, in the case of certain nuclear materials, dangerous radiation. Some agents displace oxygen, especially in confined spaces. Therefore, extinguishing agents and methods for their specific application should be selected with care. Metal fires should not be approached without suitable personal protective equipment, including but not limited to: self-contained breathing apparatus and protective clothing, unless immediate application can be performed to suppress or control a small fire.

The use of water on a combustible metal fire is hazardous and great care must be taken to ensure the application of water does not deleteriously affect the fire. The application of water or a water-based extinguishing agent may result in a violent reaction which has the potential to spread burning material to an adjacent area; this can cause significant safety risk to firefighting personnel or others that may be located near the fire incident.

Numerous agents have been developed to extinguish combustible metal (Class D) fires, but a given agent does not necessarily control or extinguish all metal fires. Although some agents are valuable in working with several metals, other agents are useful in combating only one type of metal fire. Despite their use in industry, some of these agents provide only partial control and cannot be considered actual extinguishing agents. Certain agents that are suitable for other classes of fires should be avoided for metal fires, because violent reactions may result (e.g. water on sodium; vaporizing liquids on magnesium fires).

Certain combustible metal extinguishing agents have been used for years, and their success in handling metal fires has led to the designations "approved extinguishing powder" and "dry powder." These designations have appeared in codes and other publications where it was not possible to employ the proprietary names of the powders. These terms have been accepted in describing extinguishing agents for metal fires and should not be confused with the name "dry chemical," which normally applies to an agent suitable for use on flammable liquid (Class B) and live electrical equipment (Class C) fires. Class B extinguishing agents may not be safely applied to combustible metal (Class D) fires. Other extinguishing agents discussed herein have been used only experimentally in limited areas or at specific installations, and require much judgment in application. NFPA 10 should be used when placing fire extinguishers. Where a hydrophilic (attracts moisture and can chemically bond with it) Class D agent is placed in a container other than a fire extinguisher, it must be in an air-tight container to avoid attracting moisture from the air, which would reduce the effectiveness of the agent.

For fires that occur in chemical processing areas, the use of chemicals involved in the processing can be used to control or extinguish the fire with little or no adverse effect on the chemical processing. For example, Lithium metal is produced in a salt bath of lithium chloride and potassium chloride operating at approximately 450°C (842°F). If a fire should occur in the salt bath, adding more lithium or potassium chloride to the salt bath will lower the temperature of the salt bath and control the "operational excursion." If an operator was to try to control the fire with a commercial fire extinguisher, the agent could poison the salt bath that would have to be drained, relined, and brought back to operations, which is costly in both downtime and expense. For this reason and others, it is important to ensure an adequate fire hazard plan is in place.

The successful control or extinguishment of metal fires depends heavily upon the method of application, training, and experience. Class D agents are not all effective on all Class D fires and selection must be based on the material being protected. To avoid re-ignition, do not move the remains of a metal fire until it has cooled sufficiently. Personnel using a Class D fire extinguisher or a container containing the Class D agent must be properly trained since the methods differ from conventional Class A:B:C extinguishers. Practice drills should be held on the particular combustible metals on which the agent is expected to be used. Prior knowledge of the capabilities and limitations of agents and associated equipment is always useful in emergencies. **Fire control measures or extinguishing agents must be immediately available to ensure they are effective.** In industrial plant locations where work is performed with combustible metals, public fire departments and industrial fire brigades have the advantage of fire control drills conducted under the guidance of knowledgeable individuals.

Combustible Metal Fire Extinguishing Agents

A number of proprietary combustible metal extinguishing agents have been submitted to testing agencies for approval or listing. Others have not, particularly those agents developed for special metals in rather limited commercial use. Those extinguishing agents described as follows have been shown to be effective for use on fires involving magnesium, aluminum, sodium, potassium, and sodium-potassium alloy. NFPA 484 offers guidance on the selection of the appropriate extinguishing agent for use on combustible and pyrophoric metals in the Table "Combustible Metal Fire-Extinguishing Agents Quick Reference Chart" of Annex A.

Met-L-X and Super-D Powder

These hygroscopic (absorbs water) dry powders, with particle sizes controlled for optimum extinguishing effectiveness, are composed of a sodium chloride base with additives. The additives include tricalcium phosphate to improve flow characteristics and metal stearates for water repellency. A thermoplastic material is added to bind the sodium chloride particles into a solid mass under fire conditions.

Met-L-X and Super-D powder are noncombustible, and secondary fires do not result from its application to burning metal. There are no known health hazards resulting from the use of these agents. They are also nonabrasive and nonconductive.

Stored in sealed containers or extinguishers, Met-L-X and Super-D powder are not subject to decomposition or a change in properties. Periodic replacement of extinguisher charges is unnecessary. Extinguishers range from pressurized portable hand units, pails, cans, wheeled units, and stationary or piped systems. The wheeled units and piped systems employ nitrogen as the propellant. If the agent is stored in pails or cans, other than a fire extinguisher, it is applied either by scooping the material onto the fire or by dumping the agent from the container directly. This method is only appropriate where the combustible metal is found in small quantities. With either extinguishing method, sufficient agent must be applied to completely cover the burning material.

These powders are suitable for fires in solid pieces (such as castings) because of their ability to cling to hot vertical surfaces. To control and then extinguish a metal fire, the nozzle of the extinguisher is fully opened from a safe distance and a layer is cautiously applied over the burning material. Some extinguishers have a low flow application that can be applied to finely divided particles with less risk of dispersal of the dust. Once control is established, the nozzle valve is used to throttle the stream to produce a soft, heavy flow. The metal can then be completely and safely covered from close range with a heavy layer. The heat of the fire causes the powder to cake, forming a crust that excludes air and results in extinguishment.

Met-L-X and Super-D extinguishers are available for fires involving magnesium, sodium, potassium, and NaK. In addition, they have been successfully used where zirconium, uranium, and titanium present serious hazards.

Na-X Powder

This powder was developed to satisfy the need for a low chloride content agent that could be used on sodium Potassium and NaK metal fires. Na-X has a sodium carbonate base with various additives incorporated to render the agent nonhygroscopic (does not absorb moisture) and easily fluidized for use in pressurized extinguishers. It also incorporates an additive which softens and crusts over an exposed surface of burning sodium metal. Na-X is noncombustible, and does not cause secondary fires when applied to burning sodium metal above temperatures ranging from 649 to 816°C (1,200 to 1,500°F). No known health hazard results from the use of this agent on sodium fires, and it is nonabrasive and nonconductive.

Stored in hand portables and wheeled and stationary extinguishers, Na-X is listed by UL for fires involving sodium metal up to a temperatures of 649°C (1,200°F). Na-X has been tested on sodium metal (spills and in depth) at fuel temperatures as high as 816°C (1,500°F). Stored in the supplier's sealed metal pails and extinguishers, Na-X is not subject to decomposition, so periodic replacement of the agent is unnecessary.

Other Combustible Metal Extinguishing Agents

Foundry Flux

In magnesium foundry operations, molten magnesium is protected from contact with air by layers of either molten or crust-type fluxes. These fluxes, which are also used as molten metal cleaning agents, consist of various amounts of potassium chloride, barium chloride, magnesium chloride, sodium chloride, and calcium fluoride. The fluxes are stored in covered steel drums. When applied to burning magnesium, these fluxes melt on the surface of the solid or molten metal, excluding air. The thin layer of protection can be provided by properly applying relatively small amounts of flux.

Fluxes are valuable in extinguishing magnesium spill fires from broken molds or leaking pots and in controlling and extinguishing fires in heat-treating furnaces. In open fires, the flux is applied with a hand scoop or a shovel. Areas of furnaces that are difficult to reach can be coated by means of a flux-throwing device similar to those used to throw concrete onto building forms.

While fluxes would rapidly extinguish chip fires in machine shops, such use is not recommended. The fluxes are hygroscopic and the water picked up from the air, combined with the salt, causes severe rusting of equipment.

Copper Powder

Advances in the science of alternative propulsion systems have led to the development of copper powder as a viable extinguishing agent for combustible metals. Work sponsored by the Naval Sea Systems Command was conducted to evaluate the adequacy of existing lithium fire suppression agents and to develop new agents should deficiencies exist.

Copper powder was found to be superior to known lithium fire extinguishing agents in extinguishing capacity. The dry powder is of uniform particle size and extinguishes a lithium fire more quickly and efficiently than existing agents. The process of extinguishment is by formation of a copper-lithium alloy, which is nonreactive and forms preferentially on the surface of the molten lithium. The alloy becomes an exclusion boundary between air and the molten metal, preventing re-ignition and promoting cooling of the unreacted lithium.

Copper powder can be applied from portable, hand-held extinguishers. The nominal size a hand-held extinguisher is 14 kg (30 lb); 68 and 160 kg (150 and 350 lbs) for wheeled units; and is available in fixed systems as well. Argon is used as the propellant. The method of application is similar to that of other metal fire powders, in that the fuel surface is coated with the copper powder in an initial pass, with a throttled application following once control is achieved. Typical application densities are 3.6 kg (8 lbs) of copper powder per pound of lithium for complete extinguishment of the lithium. An 18-kg (40-lb) lithium fire can be fully controlled in 30 seconds and completely extinguished in 9 minutes. Copper powder also has been used to extinguish magnesium and aluminum fires.

Lith-X/G-Plus Dry Powder

These dry powder agents are composed of a special graphite base with additives. The additives render them free flowing so they can be discharged from an extinguisher. The technique used to extinguish a

metal fire with these agents is the same as that used with NaCl based agents. These powders do not cake or crust over when applied to burning metal. They exclude air and conduct heat away from the burning mass to effect extinguishment. They do not cling to hot metal surfaces, so it is necessary to completely cover the burning metal with the agent.

Both agents will successfully extinguish lithium fires and are suitable for the control and extinguishment of magnesium and zirconium chip fires. Lith-x is also suitable for magnesium, sodium, and potassium zirconium, titanium, and NaK fires.

TMB Liquid

TMB is the chemical abbreviation for trimethoxyboroxine. The agent contains methanol to render it free flowing. It is classed as a flammable liquid for shipping purposes. The liquid is colorless and hydrolyzes readily to form boric acid and methanol. Contact with moist air or other sources of water need to be avoided to prevent hydrolysis.

This agent is applied with a specially adapted 9.5 L (2-1/2 gal) stored pressure extinguisher which delivers either spray or a straight stream. Typical application of TMB to a metal fire yields a heat flash because of the breakdown of the chemical compound and ignition of the methanol. A molten boric oxide coating on the hot metal prevents contact with air. A stream of water may be used to cool the mass as soon as metal flames are no longer visible; this should be done cautiously to avoid rupture of the coating. Indoor application (such as in machine shops) is not recommended because of the large volume of boric oxide smoke produced. Boric oxide is only slightly toxic.

While TMB has been used primarily on magnesium fires, it has shown value in application to fires in zirconium and titanium. Although TMB applied as a spray has been used to control small sodium and sodium-potassium alloy fires, it is not recommended for fires in sodium, sodium-potassium alloy, and lithium. TMB reacts violently with lithium and sodium-potassium alloy. It will extinguish sodium in-depth, but the protective coating formed by the TMB absorbs moisture very rapidly and in time may penetrate through to the sodium, resulting in a violent reaction. Field experience has been limited to aircraft fires.

Pyromet Powder

Pyromet powder is composed of specially processed sodium chloride, diammonium phosphate, protein, and a waterproofing and flow-promoting agent. The powder is discharged under pressure provided by a carbon dioxide gas cartridge. The unit contains 11 kg (25 lb) of powder. The applicator consists of a tubular extension from the control valve, terminating in a cone-shaped nozzle. A mechanism in the nozzle absorbs the discharge pressure by swirling the powder as it is expelled. This enables the operator to let the powder fall gently on the burning metal rather than to scatter burning material under the blast of a jet of powder.

Pyromet has proven effective in handling fires involving sodium, calcium, zirconium, and titanium, as well as magnesium and aluminum in the form of powder or chips.

TEC Powder

TEC (ternary eutectic chloride) powder is a mixture of potassium chloride, sodium chloride, and barium chloride that is effective in extinguishing fires in certain combustible metals. The powder tends to seal the metal, excluding air. On a hot magnesium chip fire its action is similar to that of foundry flux. In tests reported in *Fire Technology*, TEC powder was the most effective salt for control of sodium, potassium, and sodium-potassium alloy fires. TEC should not be used on plutonium, uranium, and alkali metal fires because it is hygroscopic.

Nonproprietary Combustible Metal Extinguishing Agents

Specially formulated extinguishing powders are generally used to suppress fires involving metals. Because of the reaction many metals have with water, sprinklers and the use of other water-based agents are not appropriate and, in some cases, quite dangerous. However, many of the special agents for metal fires are at times unsatisfactory because they are corrosive, applied manually rather than by an extinguishing system, capable of clogging extinguishing nozzles, and expensive. When these specialized proprietary extinguishing agents are undesirable, the following nonproprietary agents may be used.

Talc (Powder)

Talc, which has been used industrially on magnesium fires, acts to control rather than extinguish fire. Talc acts as an insulator to retain the heat of the fire, rather than as a coolant. It does, however, react with burning magnesium to provide a source of oxygen. The addition of organic matter (such as protein) to talc assists in the controlling action, but does not prevent the reaction which releases oxygen to the fire.

Carbon Microspheres

Studies have been undertaken to examine the effectiveness of carbon microspheres or microspheroids to extinguish fires involving alkali metals, such as sodium, sodium-potassium, and lithium. These microspheres are petroleum-coke-based particles with a diameter of approximately 100 to 500 microns. The particles possess high thermal conductivity, chemical inertness, and excellent flow characteristics and are capable of being directed onto fires from dry-chemical-type extinguishers and conventional nozzles.

Tests have shown that carbon microspheres compare favorably in performance to other metal extinguishing agents. In particular, experiments with carbon microspheroids incorporating neutron absorbers have been effective in extinguishing fires involving nuclear fissionable materials, such as uranium metal powder. The excellent flow characteristics and noncoking properties of these microspheres suggest an effective way to extinguish radioactive metal fires within the inert atmosphere glovebox enclosures used in the nuclear industry.

Graphite Powder

Graphite powder (plumbago, G-Plus Dry Powder) has been used as an extinguishing agent for metal fires and acts as a coolant. Unless the powder is finely divided and closely packed over the burning metal, some air does get through to the metal and extinguishment is not as rapid as with G-1 powder.

Sand

Dry sand has often been recommended as an agent for controlling and extinguishing metal fires. At times it seems to be satisfactory, but usually hot metal (such as magnesium) obtains oxygen from the silicone dioxide in the sand and continues to burn under the pile. Sand is seldom completely dry. Burning metal reacting with the moisture in the sand produces steam and, under certain conditions, may produce an explosive metal-water reaction. By laying the sand around the perimeter of the fire, fine dry sand can be used to isolate incipient fires of aluminum dust.

Cast Iron Borings

Cast iron borings or turnings are frequently available in the same machine shop as the various combustible metals. Clean iron borings applied over a magnesium chip fire cool the hot metal and help extinguish the fire. This agent is used by some shops for handling small fires where, with normal good housekeeping, only a few combustible metal chips are involved. Contamination of the metal chips with iron may be an economic problem. Oxidized iron chips need to be avoided to prevent possible thermite reaction with the hot metal, and the iron chips need to be free from moisture.

Sodium Chloride

Alkali metal fires can be extinguished by sodium chloride, which forms a protective blanket that excludes air over the metal so that the metal cools below its burning temperature. Sodium chloride is an agent that is used for extinguishing sodium and potassium fires. It can also be used to extinguish magnesium fires.

Soda Ash

Sodium carbonate or soda ash (not dry chemical) is recommended for extinguishing sodium and potassium fires. Its action is similar to that of sodium chloride.

Lithium Chloride

Lithium chloride is an effective extinguishing agent for lithium metal fires. However, its use should be limited to specialized applications because the chemical is hygroscopic to a degree and may present problems because of the reaction between the moisture and the lithium.

Dolomite

If zirconium or titanium in the form of dry powder becomes ignited, neither can be extinguished easily. Control can be affected by spreading dolomite (a carbonate of calcium and magnesium) around the burning area and then adding more powder until the burning pile is completely covered.

Boron Trifluoride and Boron Trichloride

Boron trifluoride and boron trichloride have both been used to control fires in heat-treating furnaces containing magnesium. The fluoride is considerably more effective. In the case of small fires, the gases provide complete extinguishment. In the case of large fires, the gases effect control over the flames and rapid burning, but reignition of the hot metal takes place on exposure to air. A combined attack of boron trifluoride gas followed by application of foundry flux completely extinguishes the fire. For details of gas application, see NFPA 484.

Inert Gases

In some cases, inert gases (such as argon and helium) will control zirconium fires if they can be used under conditions that will exclude air. Gas blanketing with argon has been effective in controlling lithium, sodium, and potassium fires. Caution should be exercised when using the agent in confined spaces because of the danger of suffocation of personnel.

Water

When burning metals are spattered with limited amounts of water, the hot metal extracts oxygen from the water and promotes combustion. At the same time, hydrogen is released in a free state and ignites readily. Since small amounts of water do accelerate combustible metal fires (particularly where chips or other fines are involved), use of common portable extinguishers containing water is not recommended except to control fires in adjacent Class A materials.

Water, however, is a good coolant and can be used on some combustible metals under proper conditions and applications to reduce the temperature of the burning metals below the ignition point. The following paragraphs discuss the advantages and limitations of using water on fires involving various combustible metals.

Sodium, Potassium, Lithium, NaK, Barium, Calcium, and Strontium Fires – Water cannot be used on fires involving these metals. Water applied to sodium, potassium, lithium, sodium-potassium alloys (NaK), barium, calcium, and strontium will induce chemical reactions that can lead to fire or explosion even at room temperatures.

Zirconium Fires – Powdered zirconium wet with water is more difficult to ignite than the dry powder. However, once ignition takes place, wet powder burns more violently than dry powder. Powder containing about 5 to 10% water is considered to be the most dangerous. Water should not be applied to burning zirconium since violent reactions may result.

Plutonium, Uranium, and Thorium Fires – As a last resort, water can be used as an extinguishing agent for fires of ordinary combustibles that are exposing these metals. Where criticality safety considerations preclude the introduction of moderators such as water, suitable alternative fire protection measures need to be identified within fire hazard plans to coordinate or incorporate such measures into emergency response activities.

Magnesium Fires – Automatic sprinklers will extinguish a typical shop fire where the quantity of magnesium is limited. However, water should not be used on any fire involving magnesium - a few burning chips can be extinguished by dropping them into a bucket of water.

Burning magnesium parts such as castings and fabricated structures can be cooled and extinguished with coarse streams of water applied with standard fire hoses. A straight stream scatters the fire, but coarse drops (produced by a fixed nozzle operating at a distance or by use of an adjustable nozzle) flow over and cool the unburned metal. Some temporary acceleration normally takes place with this procedure, but rapid extinguishment follows if the technique is pursued. Well-advanced fires in several hundred pounds (100 lb equals 45 kg) of magnesium scrap have been extinguished in less than 1 minute with two 37.5 mm (1-1/2

in.) fire hoses. Water fog, on the other hand, tends to accelerate rather than cool such a fire. Application of water to magnesium fires needs to be avoided where quantities of molten metal are likely to be present; the steam formation and possible metal-water reactions may be explosive.

Titanium Fires – Water cannot be used on fires in titanium fines and should be used with caution on other titanium fires. Small amounts of burning titanium (other than fines) can be extinguished and considerable salvage realized by quickly dumping the burning material into a large volume of water to completely submerge it. Hose streams have been used effectively on fires in outside piles of scrap, but violent reactions have been reported in other cases where water was applied to hot or burning titanium, resulting in serious injury to personnel. Additional information on the use of water on titanium fires can be found in NFPA 484.

LABORATORY SCALE OPERATIONS

Laboratory operations routinely use small quantities - less than 0.23 kg (1/2 lb) of reactive materials including spontaneously ignitable and pyrophoric chemicals (reagents). Safe handling of these chemicals is critical to the prevention of fires within laboratories and the prevention of injuries to laboratory personnel.

Types of pyrophoric reagents include:

- Alkali metals – Some alkali earth metals and other pure metals that are finely divided (metal catalysts, small particulates and nanoparticles) react with water vapor to generate hydrogen and heat.
- Metal hydrides – These react in the same manner as alkali metals, generating heat and hydrogen.
- Organometallics – These are reagents with carbon metal bonds that generate a volatile organic compound and heat when they react with moisture. The most common examples are alkyl lithium reagents, Grignards (C-MgX), and phosphines. Some compounds that have carbon transition metal bonds are also known as pyrophoric reagents.

There have been several fire events in laboratories both within and outside the DOE Complex that have occurred over the last 20 years that could have been prevented if the pyrophoric reagents were handled properly. The consequences of these events have ranged from minor to significant, including at least one fatality. The 2015 edition of NFPA 45, *Standard on Fire Protection for Laboratories Using Chemicals* has requirements to address the safe handling of pyrophoric reagents to prevent fires and to minimize the risk of significant injury from accidents involving pyrophoric reagents. The following information is intended to address safe handling of pyrophoric reagents.

Operations involving solid reagents are typically performed in an inert atmosphere glovebox or glovebag. Argon is primarily used as the inerting gas in a glovebox/bag arrangement that usually includes an oxygen sensor to verify that oxygen is not present when pyrophoric reagents are in use. Liquid reagents can be used in an inert atmosphere within a glovebox/bag. Pyrophoric liquids that are used outside of an inert atmosphere glovebox/bag have to be handled in closed systems that have been inerted and include an appropriate transfer method.

After operations with pyrophoric reagents have been completed, all laboratory equipment and waste materials that have been in contact with pyrophoric reagents need to be neutralized or passivated to prevent a fire. Very small quantities (microscopic) of pyrophoric reagents will react with oxygen and/or moisture in air and the resulting heat of reaction can start a fire. Most fires associated with laboratory operations with pyrophoric reagents has been caused by inadequate neutralization or passivation of test tubes, glass ware, spatulas, wipes, needles, tubing and other tools prior to exposing them to air. Neutralize pyrophoric liquids in accordance with manufacturer's recommendations, typically by wetting the surfaces of the test tubes, glassware, needles and tubing with a solvent and rinsing with a secondary solvent. For pyrophoric solids, the passivation of wipes, spatulas and other tools can be performed by slowly exposing them to low concentrations of oxygen over a 24-hour period.

Laboratory incidents involving pyrophoric reagents are provided at the end of this Handbook. Additionally, there have been three minor events described below that were caused by pyrophoric waste that was not

properly neutralize/passivated prior to disposal at DOE labs:

- Paper in a garbage can was smoldering in a lab and was extinguished with water. The event was caused by an exothermic reaction that occurred when the residue of chemical slurry containing ethylhexylcarbazole and platinum-loaded carbon in a pipette dried out and reacted with the air to create heat (PNNL Non ORPS-reportable Event).
- Research staff was investigating a burning odor when they found a smoldering chemical wipe in a trash receptacle inside the lab. The smoldering chemical wipe was extinguished with water. The smoldering chemical wipe was a result of a chemical reaction after the wipe was used to clean Raney nickel slurry from a metal spatula and the wipe was discarded in the trash. An investigation uncovered the fact that Raney nickel is provided in slurry with water because, when it is dry, it is a pyrophoric reagent that undergoes an exothermic reaction upon contact with air (PNNL Non ORPS-reportable Event).
- A researcher found a burned trash can in a lab and used water to quench the smoldering papers. The cause of the burned trash can was determined to be the result of the disposal of several chemical wipes that were removed from an inert atmosphere glovebox without being passivated. The glovebox was used to handle less than 10-micron size metal powders. The metal powder is pyrophoric when exposed to air and the heat of reaction ignited the chemical wipes (see ORPS report: SC-PNSO-PNNL-PNNLBOPER-2014-0005).

Recommendations for the safe handling of pyrophoric reagents includes but not limited to:

- Personal protective equipment that should be worn when working with pyrophoric reagents outside of an inert atmosphere of a glovebox typically include fire retardant lab coats, fire retardant gloves, safety glasses, and a face shield.
- Operations involving pyrophoric reagents are to be performed only by those with experience in their hazards and properties or under close supervision by those with experience in their hazards and properties.
- Avoid working alone with pyrophoric reagents.
- Handle pyrophoric reagents in systems or enclosures that prevent the chemicals from igniting in accordance with the Safety Data Sheet. Use septum sealed bottles and sealed vessels when pyrophoric liquids are dispensed in a fume hood. Use syringe or double tipped needles to transfer pyrophoric liquids between containers in accordance with manufacturer's recommendations and established safety practices. Glassware, reaction vessels, needles, and other lab equipment must be cleaned of residual moisture and contaminants, and purged with a high purity inert gas prior to use with pyrophoric reagents.
- Use an inert atmosphere glovebox for open dispensing of pyrophoric liquids or handling of pyrophoric solids.
- Passivate or neutralize test tubes, glass ware, spatulas, wipes, needles, tubing and other tools that have been in contact with pyrophoric reagents prior to removing them from an inert atmosphere or disposal in accordance with established safety practices and the recommendations in the chemical's Safety Data Sheet.

INCIDENT CASE STUDIES

Current Edition (2014) Case Studies

The following case studies are considered as an update to the previous handbook Edition and are not inclusive of all DOE spontaneous heating or pyrophoric events that have occurred within the DOE complex between updates. For more information on these events, please access the applicable Occurrence Reporting and Processing System (ORPS) number through either the internet or the ORPS Administrator. For additional case studies, please refer to the NFPA web site listed the bibliography section of this Handbook.

Laboratory (Reagent) Incident – National Renewable Energy Laboratory (2002)

ORPS Report No.: GO-NREL--NREL-2002-0001

At approximately 1301 (MST) on December 27, 2002 a fire was discovered by facility maintenance personnel in a chemical fume hood located in Solar Energy Research Facility (SERF) Lab C-221. The building fire alarm system and the NREL Emergency Notification System were activated. An orderly evacuation of the facility was completed. Firefighters and equipment responded to the scene and assessed the situation. The assessment determined that the fire was contained within the chemical fume hood and that a variety of chemicals, albeit small amounts, was involved. A small flow of liquid was observed coming from the hood and pooling on the floor of the lab. The liquid was identified as de-ionized water, which was leaking from plastic piping that was apparently damaged by the fire. The single most likely cause appears to have been a delayed reaction involving unreacted pyrophoric material, tris (trimethylsilyl) phosphine (TTMSP), inside one or more of the pipettes that had been transferred from the glovebox to the chemical fume hood. Pipettes are used to transfer pyrophoric materials during sample preparation inside the glovebox. The glovebox is maintained under an inert atmosphere (helium) to prevent the reaction of pyrophoric materials. There is no fire detection or suppression system inside the hood. The laboratory is equipped with a fire sprinkler system. This system did not activate, as the fire did not escape the hood. Passive fire protection features such as laboratory compartmentalization and ventilation configuration prevented the spread of smoke beyond the laboratory.

Environmental Restoration Incident – Rocky Flats Environmental Technology Site (2004)

ORPS Report No.: EM-RFO--KHLL-371OPS-2003-0011

On May 6, 2003, D&D activities were taking place in room 2325 in Building 371. Specific actions included cutting sheet metal panels from glovebox 8 to provide an airflow path in an attempt to provide ventilation into the glovebox to reduce airborne levels of plutonium during subsequent clean out and size reduction of the glovebox. Workers noted smoke and evidence of a fire inside the glovebox structure, and took actions in an attempt to control the situation. The workers discharged a number of portable fire extinguishers into the glovebox, only to have the fire re-ignite. Concurrent with these actions, the job supervisor notified the facility Configuration Control Authority (CCA) of the event, who contacted the Fire Department, initiating their response. Further attempts to control the situation were initiated by the workers until the Fire Department arrived on scene and, using water, extinguished the fire and stabilized the situation. Actual

damage to the glovebox and other equipment was minimal, however four of the fire fighters received skin contamination as a result of the firefighting efforts. Because of the use of respirators, they did not receive any radioactive material uptake or significant dose (maximum of 20 mrem). Bioassay analysis of other potentially affected building personnel did not show any significant personnel contamination or radioactive material uptakes.

Environmental Restoration Incident – Idaho National Laboratory (2004)

ORPS Report No.: EM-ID--CWI-ICDF-2005-0004

On September 20, 2005, at the Idaho National Laboratory CERCLA disposal facility, a worker was preparing to mix zinc powder with sulfamic acid in a 5-gallon bucket to be used for treating mercury-contaminated soil when flames erupted from the bucket. A co-worker extinguished the flames using MET-L-X, and all employees left the area. The fire department verified that the fire was out, and no one was injured.

Processing Maintenance Incident – Y-12 (2005)

ORPS Report No.: NA--YSO-BWXT-Y12NUCLEAR-2005-0036

On November 22, 2005, at Y-12, workers were performing maintenance on a crusher-grinder when finely divided material ignited unexpectedly. Thirteen employees were evacuated from the facility. An investigation team learned that several factors caused the fire: the material had been exposed to air for six weeks; actuation of the crusher cylinders stirred up the material, exposing the unoxidated material beneath a layer of passivated material; and the material had been exposed to moisture. One of the employees was transported to an offsite medical facility for observation; the rest were uninjured.

Laboratory (Reagent) Incident – Los Alamos National Laboratory (2005)

ORPS Report No: NA--LASO-LANLFIRNGHELAB-2005-0012

On December 8, 2005, at Los Alamos National Laboratory, a worker in an explosives laboratory was handling a piece of fiberglass matting which was coated with 1 gram of a nanoaluminum-fluoroelastomer mixture when it unexpectedly ignited, causing second-degree burns on the worker's right hand. The mat that ignited was one of a group of mats to which the mixture had been applied, vacuum-dried at 80°C, and cooled to near room temperature. Although facility personnel had worked with this mixture before, they had never used it bonded to fiberglass matting. The accident investigation team determined that the most likely ignition source was energetic buildup within the material and that the hazards of handling the nanoaluminum material had not been properly characterized.

Laboratory (Reagent) Incident - Savannah River National Laboratory (2006)

ORPS Report No.: EM-SR--WSRC-LTA-2006-0002

On January 10, 2006, at Savannah River National Laboratory, a principal investigator and first-line manager were cleaning an attritor mill vessel (shown in Figure 1-1 on a lifting table) when a fire flashed and caused first- and second-degree burns to the right side of the manager's face and head and his left hand. The manager was treated at a local hospital and released.

The attritor mill had been used to blend and finely grind metal hydride into powder for use in hydrogen storage technologies. Grinding the metal hydride into fine particles renders it pyrophoric (i.e., capable of spontaneously combusting in air) because its increased surface area oxidizes more readily.

After preparing the necessary quantity of metal hydride powder, the principal investigator and manager wiped down the attritor mill several times in an argon-inerted glovebox. They then removed the vessel from the glovebox and began wiping it down with isopropyl alcohol. When the vessel was taken out of the glovebox, residual particulate reacted and flashed. The principal investigator extinguished the fire with MET-L-X® powder.

Following its evaluation of the January 2006 fire, the Accident Investigation Board determined that it occurred when metal hydride powder in the vessel bolt holes reacted with air and isopropyl alcohol vapors. The root cause was the failure to fully analyze the hazards of working with metal hydrides, particularly cleanup activities after processing.

Processing Incident – Y-12 (2005)

ORPS Report No.: NA--YSO-BWXT-Y12NUCLEAR-2007-0012

On March 15, 2007, at about 9:15 a.m., a uranium machine turnings (chips) fire occurred during a dry chip transfer operation in Building 9204-2E. The fire was small (~210 g U), was self-extinguished, and did not activate any fire alarms or automatic suppression systems. The operation occurred just outside the linear glovebox laboratory hood. Three assembly operators and their supervisor were involved in the activity, and a Radiological Control technician was in support. The resulting smoke prompted evacuation by involved operators, support personnel, and building occupants. Smoke generated from the fire quickly dispersed. Radiological exposure to the maximally exposed individual may have exceeded the company administrative control level, but is not expected to exceed any regulatory exposure limits.

Laboratory (Reagent) Incident - Pacific Northwest National Laboratory (2013)

Researchers in the Applied Process and Engineering Laboratory were testing a method to decompose ammonia borane (AB) and release hydrogen for use in fuel cells. They created an experimental apparatus that used a slurry of AB powder mixed in silicon oil and tried various methods of pumping the mixture through a metal tube (reactor) wrapped with heat tape to release the hydrogen. Plugging was a problem and they took the apparatus apart and cleaned it after each test. During the third test, at 150C, they noticed the syringe pump was skipping--indicating that the tube was plugged. They stopped the test according to operating procedure and noticed a foam-like substance leaking from a Teflon coupling (circled at right). As the foam bubbled and dripped to the floor of the hood, it was burning with a short, green-colored flame. They shut down power to all heater equipment, put out the flame with a fire extinguisher, and called 375-2400. Lessons Learned: When developing standard operating procedures (SOPs) and obtaining a chemical process permit (CPP), include planned procedures for emergency response for all potential byproducts and, especially any that may be hazardous, despite a low probability of occurrence. This should always include pulling the fire alarm before using a fire extinguisher to put out a small fire.

Laboratory (Reagent) Incident - Argonne National Laboratory East (2014)

ORPS Report No.: SC--ASO-ANLE-ANLECSE-2014-0001

On February 20, 2014 at Argonne National Laboratory East, a worker had finished quenching residual material from a reactive material synthesis in an atmosphere-controlled glovebox. Believing that all the reactants were either removed or quenched, the worker moved the vials, pipettes and wipes to a hood to be rinsed out and disposed of. When the worker opened the last vial, he did not notice any reaction occurring so he started to rinse out the vial with Isopropyl alcohol. Upon contact, the isopropyl alcohol ignited with the fire traveling up the solvent stream and involving all other ignitables within the hood. The fire set off smoke alarms in the lab, alerting the fire department and evacuating the facility. Upon investigation it was theorized that stearic acid must have somehow not come in contact with the remaining reactive material. One reactive by-product that was believed to remain was iron diamide, which reacted with the Isopropyl alcohol causing enough heat to ignite the combustible materials within the hood.

Previous Edition (1994) Case studies**Silane Gas Cabinet Fire**

A 6.1 x 9.1 m (20 x 30 ft) room with concrete block walls was used for distribution of process gases to clean room areas. Silane cylinders were located in 12-gauge metal gas cabinets. The ventilation system for the cabinets was in the process of being upgraded and automatic sprinklers protected the cabinets.

The silane cylinder involved was installed about 30 minutes prior to the incident. Employees in the area heard a loud "pop" from the process gas distribution room. Upon investigation, they found the windows of the cabinet broken, the doors open, and fire coming from the cylinder valve. The sprinkler activated properly and confined the fire to the cylinder head.

The escaping silane was caused by an improper connection of the cylinder to the distribution piping. There was evidence that the connection was cross-threaded, allowing the leakage. The flow of silane could not be shut off because of damage to the cylinder manifold connections. The fire continued to burn for about 8-1/2 hours until all silane in the cylinder had been consumed.

Coal Fire at a DOE Site

In 1992, a DOE site experienced a coal fire initiated by spontaneous ignition. Because of the nature of the fire and initial ineffectiveness of the means used to fight it, the fire required more than 28 hours to completely extinguish from the time a hot spot was first detected in a coal bunker. The initial strategy involved trying to remove coal from the bunker by feeding it more rapidly to the boiler and by using a drag chain to move more of it to the field. The drag chain failed in 30 minutes, however. Subsequent efforts to control the fire with carbon dioxide applied through inspection ports at the bottom of the bunker and from the tripper (switchgear) room high above the bunker were ineffective, and may have worsened the situation. The drag chain emptying coal from the bunker worked intermittently after being repaired, and finally stopped. Boiler plant personnel then began to remove burning coal by hand shovel.

Twenty-one hours after the fire was discovered, it had involved a large amount of the bunker. At one point, flames appeared at the tripper room windows, which were approximately 22.86 m (75 ft) above the seat of the hot spots. A strong concern for a steam explosion delayed the application of water, but the decision was finally made to use water, which was applied without incident and eventually ended the fire.

Zirconium Incidents (Smith, 1956)

Up to May 1955, no serious fires had been encountered during storage of scrap zirconium turnings, chips, plates, rods, etc. Such scrap had been stored (pending contemplated future recovery) in segregated open-top bins. Several days after a heavy rain, a fire of unknown origin took place in one of the bins with flames extending 30.48 m (100 ft) into the air. Shortly afterwards, contents of other (but not necessarily adjoining) bins suddenly and intermittently flared up. Material in all bins soon became involved and 72,121 kg (159,000 lb) of zirconium were consumed. The heat was sufficiently intense to crack windows and ignite wood located over 45.72 m (150 ft) away. Particles of burning zirconium were carried over one-quarter mile through the air.

In 1951, some water-wet scrap zirconium powder in wooden barrels was placed in outside storage pending development of scrap-recovery processes. During the next several years, a few minor spontaneous fires broke out in this material. In January 1956, the material in several deteriorated wooden barrels was wet with water and repackaged in steel drums. In May 1956, employees working in the area noted that one of the steel drums lying on its side contained a black material "similar to carbon dust." What happened is uncertain, but a spontaneous explosion occurred accompanied by streaks of red fire with black smoke extending 30.48 m (100 ft) into the air. A pronounced concussion wave was noted and the sound of the blast was heard several miles away. Two employees were killed; one having been blown 24.38 m (80 ft) through the air, and a third lost an arm. The drum contained zirconium, probably in the form of a fine powder. Using extensive precautions, the remaining drums of scrap zirconium were subsequently burned. During this operation, one of the drums exploded.

Two men died and two others were seriously injured in 1954 in a spontaneous explosion initiated during removal of the friction-top lid from a polythene-bag-lined, 3.79 L (1 gal) metal can containing zirconium powder 16 percent wet with water. A ball of flame enveloped the entire area, accompanied by a concussion wave.

A .907 kg (2 lb) sample of carbon-tetrachloride-moistened powdered zirconium was placed in a glass flask, vacuum applied, and the flask very gently heated with a Bunsen burner. The zirconium suddenly began to heat up and detonated with a blinding flash. The explosion was attributed to a small amount of water.

Uranium Incidents (Smith, 1956)

In January 1955, an attempt was made to roll two 453.6 kg (1,000 lb) uranium slabs into 0.254 mm (0.01 in) thick strips. After initial heating to 621°C (1,150°F) in a lithium-carbonate-potassium/carbonate salt bath, several 30 percent reductions were made by rolling. It was observed that heavy work passes had caused overheating. The strip, then 19.05 mm (3/4 in) thick, was cooled to 648.89 °C (1,200 °F). The strip again excessively heated during the next three reductions and became so ductile on entering the fourth that it

pulled into two parts. The strip at this stage was cherry red, but by the time it had been removed to the mill floor it was observed to increase in temperature to a white heat followed by melting and burning.

In February 1956, a technician was attempting to roll a plate consisting of zirconium-clad uranium, which, in turn, was clad in a low-carbon-steel jacket. During preheating, the furnace temperature control [which had been set to 788°C (1,450°F)] failed, allowing the temperature to rise to 982°C (1,800°F).

During subsequent rolling, molten iron - zirconium eutectic alloy within the steel jacket was forced to one end of the strip where it burst into flames as it sprayed out over an area approximately 3.048 m (10 ft) wide, 3.048 m (10 ft) high, and 7.62 m (25 ft) long. One employee was seriously injured.

In the early program for the large-scale manufacture of metallic uranium, fine powder was allowed to collect under roughly 7.62 m (25 ft) feet of water. At approximately one-month intervals, and without prior warning, a geyser about 9.14 m (30 ft) high would suddenly develop over the powder and then immediately subside.

A series of cases is known in which pieces of metallic uranium, plutonium, and thorium have displayed unusual pyrophoricity, e.g., spontaneously igniting at room temperature. Spontaneous fires in uranium chips are, however, much more common and in one case ignition occurred six months after the chips had been placed in storage. One investigator of spontaneous fires in briquette uranium chips opened a drum filled with briquettes that had been in outside storage for several weeks. After noting that the drum contents were normal and at approximately room temperature, he was warned by an operator to stand back. A few seconds later, a flame shot to a height of about 7.62 m (25 ft) and then immediately subsided. Upon reinspecting the drum interior, he noted that all of the briquettes were at an incandescent temperature.

A series of incidents have been experienced in which uranium and titanium alloys have displayed explosive surface films following acid treatment. Studies at Argonne National Laboratory showed that such explosions could be averted through use of adequate fluoride ion concentrations in nitric acid etching baths. Witnesses have described metal-surface explosions of this type as involving a brilliant flash of white light, accompanied by a sound similar to that of a 22-caliber rifle shot.

Thorium Incidents (Smith, 1956)

For several years scrap thorium powder had been disposed of by burning in successive small amounts. In July 1956, employees were engaged in burning scrap thorium powder that had previously been washed with several aqueous solutions and vacuum-dried 3 days earlier. Some of the thorium was placed in a special hood and ignited without incident. An employee took a "golf-ball-size" piece of thorium from a metal pail containing 13.61/18.14 kg (30/40 lbs), replaced the pail lid, and placed the piece on a small thorium fire. An immediate sharp explosion blew the employee 6.096 m (20 ft) across the room. Almost immediately, a second blast involving the thorium in the pail was accompanied by a jet of orange fire and big cloud of dust. A third explosion occurred in a nearby vacuum dryer containing about 3.18 Kg (7 lbs) of moist thorium powder. One employee suffered fatal burns, while three others suffered serious injuries.

In preparing an experimental charge for making metallic thorium in a reduction bomb, a mixer was being used to blend metallic calcium, dry zinc chloride, and dry thorium fluoride. After several revolutions of the mixer, the operator opened the mixer vent and, noting the dust and gas were escaping, decided to call his foreman. A second operator closed the vent, started the mixer, and soon heard a rumbling noise, followed by a sudden burst of flame covering a 45 degree angle and extending parallel to the floor for 12.19 m (40 ft). Of the eight persons injured by the blaze, two subsequently died. Reason for initiation of the reduction reaction in the blender is uncertain and unprecedented. It was subsequently found that the calcium used was particularly reactive.

Miscellaneous Incidents (Smith, 1956)

On June 16, 1954, employees of a high-energy-fuel laboratory were sampling 15 drums of "bag fines" magnesium powder, which were opened in a special room that had been purged with nitrogen until the oxygen content had dropped below 1 percent. During sampling of the fifth drum, the powder ignited suddenly. The flame shot out from the drum, immediately subsided, and the operators left the room after replacing the drum cover. From an external observation window, the employees noticed a gradual darkening of the drum's exterior, moving down to within 50.8 to 101.6 mm (2 to 4 in) of the drum bottom. The following day the drum was opened and contained a definite yellow coloration, which was presumed due to formation of magnesium nitride.

A massive block of metallic barium was cut into 19.05 mm (3/4 in) square pieces while submerged in kerosene. During attempts to remove residual kerosene with carbon tetrachloride (an operation that had been performed many times before without incident), a violent reaction dispersed glass fragments and burning barium over the immediate area. Similar explosions have also occurred when sodium, uranium, and zirconium were treated with carbon tetrachloride.

Trouble had been experienced in getting a Kroll process reduction of zirconium chloride, with magnesium to go to completion. When the furnace was opened up, a slate grey material was noted on the surface, which was thought to consist of zirconium, magnesium, and magnesium chloride. A sample of this material, roughly 6.36 mm (1/4 in) thick and 203.2mm (8 in) square, was removed for test and was totally inert when scratched with a file or hit with a hammer. A piece of the sample melted under an oxyacetylene flame but showed no pyrophoric properties. Samples were then placed in water and a slight evolution of gas was noted. The following day an attempt was made to further wash the samples in several changes of water. While under 127 mm (5 in) of water and without any prior evidence of reaction, an explosion occurred that shattered the laboratory bench, threw the technician against the wall, and blew out a window 7.62 m (25 ft) away. Portions of the water-washed sample blown to the floor ignited and "spit" when stepped upon. Small samples were subsequently tested and found to contain magnesium, zirconium, and 1 percent carbon.

Rocky Flats Plant Fire, 1969

On May 11, 1969, Rocky Flats Plant experienced the worst accident in plant history, a major fire in the 776-777 building, initially caused by pyrophoric plutonium scrap. One of the costliest industrial fires of all time—damages were estimated at between \$26 to \$50 million dollars—this accident was intensified and confounded by a number of operational errors.

The fire at 2:27 p.m. Sunday was reportedly caused by spontaneous ignition of a 1.5 kg (3.3 lb) briquette of plutonium alloy scrap contained in a metal can. This scrap was believed to have been oily and coated with residual CCl₄ (carbon tetrachloride). Once ignited, the fire spread through several hundred interconnected gloveboxes in the two connected buildings.

The fire started in the west end of the north line, progressed eastward, crossed over to the south line through the interconnecting boxes, and spread through the south line. The fire spread through the machining boxes at the east end of 776 and into the inspection boxes in 777. Damage was extensive. Both Benelex, a combustible neutron shielding material added to the gloveboxes, and the combustible Plexiglas glovebox windows contributed to rapid spread of the fire.

The main fire lasted about four hours, with minor flare-ups occurring through the next night. After futile attempts to control the fire with conventional procedures, the firemen finally resorted to the unorthodox procedure of applying water to bring the fire under control. This was the first time in history that water had been used to fight a plutonium fire. Despite attendant criticality dangers, the use of water was successful in controlling the fire.

The interiors of the two extremely large, high-bay buildings were grossly contaminated. An extensive, long-term cleanup effort was necessary for decontamination. Limited production was restarted about six months later in a temporary production line constructed in an adjacent building.

As damaging as the fire was, the water use prevented breaching of the outer walls and ceiling of 776 and 777, thus preventing a major release of plutonium to the environment. The small amount of plutonium released—almost entirely contained on plant site—was about 0.0002 curies. Slightly contaminated external areas were subsequently cleaned up.

Fortunately, the fire caused no direct deaths. However, one fireman received significant plutonium lung burdens, and other firemen and personnel incurred smaller radiation inhalations and exposures while fighting the fire and later cleaning up heavily contaminated areas.

Immediately prior to the fire, personnel levels were significantly cut with no real decrease in work load or production demands. Strict attention to plutonium chip handling no longer seemed to have been a top priority.

The many lessons learned from this 1969 fire include the following:

- Plutonium pyrophoricity is unpredictable as to when it may occur.
- Combustible materials such as Benelex and Plexiglas should be kept to a minimum in process buildings.
- Uncleaned and uncanned briquettes cannot be left unprotected and unattended on off-shifts.
- Buildings 776-777 were essentially one large room with interconnected glovebox trains with basically no fire breaks or fire walls. This setup allowed for rapid, large- area spread of fire and radioactive contamination.

These lessons learned from the 1969 fire led to a number of safety improvements including the following equipment modifications and procedural revisions prior to the decommissioning of the plant:

- A central, computerized alarm system has been installed.
- A sprinkler/water system has been put in place.
- Gloveboxes with inert atmospheres, heat detectors, and minimal Benelex and Plexiglas shielding are used.
- Water-filled double walls have been constructed.
- Firewater dams on doors are in place.
- Removal of flammable material from gloveboxes is done regularly.
- Briquettes are stored in metal containers with tight lids.
- Containers are placed on metal racks with heat detectors.
- Canning of briquettes is done in an inert atmosphere or vacuum for unattended (overnight or longer) storage.

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Vendor information: For air sensitive reagents see:

http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al134.pdf

For pyrophoric reagents see:

http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al164.pdf

Video: <https://www.youtube.com/watch?v=21iC4YEgOAs>

