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A PRIMER FOR THE SAFE USE OF LIQUID ALKALI METALS

Frank A. Anderson

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A PRIMER FOR THE SAFE USE OF LIQUID ALKALI METALS

Frank A. Anderson

JANUARY 1967

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Frank A. Anderson

PREFACE

The increasing interest in and use of the so-called "liquid metals," especially in nuclear energy applications, has resulted in the gradual development during the past 25 years of a considerable body of knowledge dealing with the characteristics of these materials and the techniques for their safe handling. To make pertinent bits of this information available to the engineers, scientists, and technicians who are concerned with the use of liquid metals, this primer has been prepared. Primary emphasis is placed on providing a background of information that will give the newcomer a sound, meaningful, and working insight into this field of interest, or, in simple words, to give him a "feel" for the subject. The primer is actually what the name suggests. It is not intended to be a chemical treatise or a detailed design or instruction booklet.

INTRODUCTION

The 100-plus elements that make up all matter may be loosely divided into two groups, the metals and the nonmetals. Most of the metals are solids at or near normal room temperatures, have a silvery appearance (gold and copper are well-known exceptions), and are conductors of electricity. Although mercury is the best known liquid metal, several other metals also exist in the liquid state at or near room temperatures. Examples, with their melting points, are cesium (83°F), gallium (86°F), and rubidium (102°F). Other metals that have relatively low melting points include potassium (146°F), sodium (208°F), indium (311°F), and lithium (354°F). Mixtures, or alloys, of sodium and potassium, usually designated by the combined chemical symbols NaK (pronounced "nack"), may have melting points as low as 10°F. A multicomponent alloy (sodium-potassium-cesium) has been developed recently that is reported to have a melting point of -110°F.[1]

Five of these liquid or near-liquid elements have similar chemical properties and are known as the alkali metals: cesium (Cs), rubidium (Rb), potassium (K), sodium (Na), and lithium (Li). These metals, plus their many low-melting-point alloys such as NaK, are now often referred to loosely as the "liquid metals." It is these metals and alloys that are of basic interest to us in this primer.

The steady growth of interest in the alkali metals during the past two decades is due almost solely to the pressing needs of the nation's nuclear energy and aerospace programs. In particular, the requirement for high-temperature coolants has focused attention on several interesting characteristics of the alkali metals: (a) their long liquidus range (see Table 1), (b) their low vapor pressure at high temperatures, (c) their stability (since they are elements), (d) their low specific gravity, (e) their excellent heat-transfer characteristics, and (f) their compatibility, when free of impurities, with many of the "solid" metals and their alloys.

Table 1. Selected Physical Properties of the Alkali Metals

Metal	Cesium	Rubidium	Potassium	Sodium	Lithium
Melting point, °F	83	102	146	308	354
Boiling point, °F	1260	1270	1400	1618	2440
Liquidus range, °F	1177	1168	1254	1410	2086
Specific gravity	1.873	1.532	0.859	0.972	0.534

As is usually the case in most matters, a price must be paid to gain the advantages of the alkali metals. These metals have several undesirable properties that must always be borne in mind and given major consideration by the equipment designer and the user. The alkali metals are extremely reactive (cesium is considered the most chemically active of all the metals), reacting readily with oxygen, water, carbon dioxide, many organic materials, and a number of materials of construction. These chemical characteristics obviously impose stringent, even severe, limitations on the use and handling of the alkali metals and their alloys. Despite these limitations, however, experience has shown that the alkali metals can

be used profitably and safely. A sound, basic understanding of the nature of these metals and a healthy respect for their properties--based on understanding and not fear--will help prepare newcomers to this field to design sound, safe equipment and to handle liquid metals with efficiency and safety.

Succeeding portions of this primer are devoted to brief discussions of the important characteristics of the alkali metals, to general suggestions concerning basic design features of liquid metal facilities, and to recommendations for the safe handling and use of these metals. Suggestions and recommendations reflect the general status of the art, not specific procedures or practices followed by certain research institutes, universities, governmental agencies, or industrial establishments. For specific recommendations pertaining to the various Oak Ridge facilities of the U. S. Atomic Energy Commission, the reader is urged to read the Alkali Metals Safety Guide, Report No. Y-811, Supplemental Issue of May 15, 1961.[2]

PROPERTIES OF THE ALKALI METALS

Only those properties of the alkali metals and their alloys that are of general concern and importance in the design of liquid metal facilities and in the use and handling of liquid metals are covered in this section of the primer.

Physical Properties

The alkali metals have many physical properties in common. They all have a silvery color in the free, unoxidized state (cesium is an exception, having a gold color), are good conductors of electricity and heat, have low specific gravities (or densities) for metals (see Table 1), have low melting and high boiling points (see Table 1), and are soft and easily worked in the solid state.

Color

Pure samples of alkali metals should have a clean metallic luster and silvery color (with the exception of cesium). If this is not the case, the metal is either oxidized (see section on Chemical Properties) or is otherwise contaminated.

Electrical Conductivity

The electrical conductivity of the alkali metals is good and may be used to advantage (a) by employing electromagnetic meters to determine the rates of flow of the molten metals through pipelines, (b) by employing electromagnetic pumps to pump molten alkali metals, and (c) by utilizing electrically operated liquid level devices to sense the level of liquid metals in storage tanks and surge pots.

Thermal Conductivity

The alkali metals, like most metals, are good conductors of heat--a property that accounts for many of the uses of these substances. Sodium has a thermal conductivity comparable to nickel and almost twice that of potassium. Both of these metals have conductivities that are considerably higher than that of their various NaK alloys. NaK is peculiar in that its conductivity does not vary greatly with temperature. Sodium and potassium show a marked decrease in thermal conductivity with increasing temperatures.

Specific Gravity

The light weight (low specific gravity or density) of the liquid alkali metals has the advantage of reducing the total weight of liquid metal systems and also makes it easy to transfer liquid metals by pressurizing (with an inert gas such as nitrogen, helium, or argon) or "blowing." The light weight also means that lithium, sodium, and potassium will tend to float on water, on most aqueous solutions, and on some organic liquids. It is important that this fact be considered when plans are formulated for fighting alkali metals fires. A smothering agent, for instance, to be effective in quenching such a fire, should either float on, or be capable of forming a product that will float on, the molten metal.

Boiling Point

The high boiling points of the liquid alkali metals, in comparison to the boiling points of organic liquids, mean that the vapor pressures of these materials will be low at most temperatures of current interest. Even at temperatures as high as 1800°F, for example, almost 200°F above

its normal boiling point, sodium has a vapor pressure less than 3 atmospheres. Most liquid alkali metal systems, therefore, are low pressure systems, an obvious advantage in design.

Melting Point

As low as the melting points of the liquid alkali metals are, they are above normal room temperatures (with the exception of cesium and some NaK alloys). This means that freezing of the metal will occur if temperatures in liquid alkali metal systems drop too low, and plugging of the system or parts thereof will eventually take place. This possibility must especially be guarded against in instrument lines and in other system branches in which flow does not normally occur. At the same time, an advantage exists in that "freeze-seal" techniques can be used as necessary to seal off or to block liquid metal systems.

Softness

The solid alkali metals are soft enough so that they can be cut with relative ease with a knife. This softness, combined with the low melting points of the metals, is advantageous when disassembling equipment that has been incompletely drained.

Chemical Properties

Because of the similar electronic structure of the atoms of the alkali metals, each atom having one electron in its outer shell or orbit, the chemical properties of these metals are very similar. In general, differences in the chemical properties from one alkali metal to the next represent gradual transitions rather than abrupt changes. Thus, specific knowledge of the chemistry of any one alkali metal provides general knowledge of the chemistry of all these metals. One highly important property characterizes the alkali metals--their extreme reactivity. The alkali atoms lose their single outer electrons readily. In other words, they are easily oxidized and thus are good reducing agents.

Reactions with Oxygen

If M represents an atom of any alkali metal, the following simplified equation may be used to show one typical reaction of the metal with oxygen:

$$2M + 1/2\ O_2 \rightarrow M_2O + \text{Heat} \qquad (1)$$

Depending on the particular alkali metal involved and other factors such as the temperature and whether or not the oxygen is dry or moist, the reaction may proceed slowly and almost imperceptably or rapidly and brilliantly. Sodium, for instance, reacts readily with the oxygen of the air at room temperature to form a thick coating of the white oxide but will not ignite spontaneously until its temperature is about 115°C (239°F), or about 30°F above its melting point. Liquid NaK formulations, on the other hand, may ignite spontaneously in the atmosphere at room temperatures. The heat released by the reaction of a solid alkali metal can raise the temperature of the body and ultimately melt it. As the temperature rises, the reaction increases in speed until finally the metal ignites and begins to burn, producing large volumes of a thick, white smoke, composed of the oxide (M_2O) combustion product. Not all of the oxide is carried away as smoke, however; much of it remains behind at the combustion site. Because no flammable vapors are produced, as is the case when wood, coal, oil, and other organic materials burn, the burning alkali metal does not produce typical combustion flames. Flames, if there are any, are small, and may not be readily visible. A brilliant light may be emitted from intense "hot spots," which are the combustion sites or areas. In the case of sodium, the hot spot of burning metal is a brilliant yellow. Once a mass of sodium has ignited, for example, the temperature of the liquid pool of metal will build up gradually and may reach as high as the boiling point (1618°F). Rubidium and cesium, the less well-known and less used alkali metals, apparently do not behave entirely like sodium on combustion.[3] According to Rogers and Everson[3] "...burning characteristics of the metals (alkali) are a function of (their) oxide solubility...."

Although the voluminous white smoke produced from the burning alkali metal looks threatening, there is no danger of explosion from the burning metal itself. The white smoke, however, is dangerous, because the hot oxide particles are very reactive and will readily combine with moisture in the air, or on the skin, or from any other source.

$$M_2O + H_2O \rightarrow 2MOH \qquad (2)$$

The alkali hydroxide, MOH, is a strong caustic that will "burn" skin, eyes, and other tissue. Lung tissue can be severely damaged by this and other caustic material. Obviously, therefore, personnel who are fighting an alkali metal fire or who are in the vicinity of a fire should minimize exposure to the smoke. Nature has provided a protective mechanism in that the fumes normally cause discomfort to eyes, skin, and nose well before overexposure or excessive concentrations occur. However, protective clothing and breathing apparatus should be used by personnel who fight these fires unless the fires are very small and not likely to spread.

Both alkali oxides (M_2O) and hydroxides (MOH) are powerful corrosives and will attack tissue, clothing, and many materials of construction. Because these substances are readily soluble in water, washing affected areas with large volumes of water is immediately beneficial. Large volumes of water must be used to keep the concentration of the resulting hydroxide solution so low that the solution will not cause trouble.

Although the alkali metals will ignite spontaneously when heated in the atmosphere, it has been reported that they can be heated to their melting points in an atmosphere of dry oxygen without reaction. Once the metal is molten, spontaneous ignition soon follows in most instances. Ignition may occur over a significant temperature range, depending on the specific metal involved, the humidity of the surrounding atmosphere, the nature of the surface, the amount of material present and its degree of dispersion, and the oxygen concentration of the surrounding atmosphere. Sodium, for example, will not burn in an atmosphere containing less than about 5% oxygen, although it may continue to react and to produce some smoke. Excluding oxygen, therefore, is the basis for one method of fighting alkali metal, as well as other, fires.

Although the chemical properties of the alkali metals are similar, as previously stated, there are differences that should be recognized. Whereas

sodium reacts with oxygen of the air to form the oxide, Na_2O, potassium reacts to form the peroxide:

$$2K + O_2 \rightarrow K_2O_2 \qquad (3)$$

This peroxide, under certain circumstances, can react explosively with organic material. As a general safety precaution, thus, it is good practice to keep the alkali metals away from organic materials.

Reaction with Water

The alkali metals react violently with water, usually with an accompanying explosion caused by the secondary reaction of the liberated hydrogen with the oxygen of the air.

$$2M + 2H_2O \rightarrow 2MOH + H_2 + \text{Heat} \qquad (4)$$

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (5)$$

The heat liberated by reaction (4) is sufficient to cause reaction (5) to occur. When explosion occurs, the unreacted metal is usually scattered over a wide area, where it can cause further trouble. In view of the foregoing, it is a cardinal rule when handling the alkali metals to keep them completely isolated from water or aqueous solutions. This means, too, when fighting alkali metal fires that water or water solution fire extinguishing agents such as the soda-acid-foam types must never be used.

It is interesting to note that investigators at Mine Safety Appliances Company, Callery, Pennsylvania,[4] have shown that sodium can be disposed of safely under water by forcing the molten metal (at 350°F) through an "open end" annulus at Reynold's numbers over 45,000 provided a minimum water depth of 10 ft. is used.

Reaction with Steam

Although water and steam are identical so far as chemical composition is concerned, steam does not necessarily react with the alkali metals with the same physical effect as does water. The hydrogen resulting from the

reaction is often sufficiently diluted so that the danger of an explosive reaction with oxygen from the air is greatly minimized. Dry steam (steam free of condensed water), therefore, is extensively used to clean apparatus or piping containing sodium. The steam not only dilutes the by-product hydrogen but also helps to exclude oxygen from the reaction site and to dissipate the heat of the reaction. To increase further the safety of this operation, an inert diluant gas such as nitrogen or argon might be mixed with the steam. It goes without saying, however, that the steam cleaning of apparatus, especially when restricted passages are involved, must always be carried out with the exercise of due precautions, for even though no chemical explosion might occur, by-product hydrogen might accumulate and build up enough pressure to fracture explosively the unit being cleaned.

Reaction with Carbon Dioxide

The reactions of the alkali metals and carbon dioxide are complex but probably can be simply and adequately summarized as follows:

$$2M + CO_2 \rightarrow M_2O + CO \qquad (6)$$

$$M_2O + CO_2 \rightarrow M_2CO_3 \qquad (7)$$

Principally because of reaction (6), it is not advisable to use carbon dioxide as an extinguishant on alkali metal fires. Reaction (6) produces not only the highly caustic oxide, M_2O, but also poisonous carbon monoxide, CO. The formation and accumulation of CO in a laboratory or in a closed environment raises the possibility of asphyxiation of operating or fire-fighting personnel who might be trying to extinguish an alkali metal fire with CO_2.

Reaction with Carbon Tetrachloride

The reaction of the alkali metals with carbon tetrachloride (CCl_4) and other halogenated hydrocarbon (i.e., trichloroethylene) is characterized as being of explosive violence. Consequently, it is considered sound design practice to isolate completely the alkali metals from these materials. Furthermore, there is the possibility that deadly phosgene

gas can form when CCl_4 is used on an alkali metal fire. Thus, carbon tetrachloride or the familiar Pyrene-type of fire extinguishants are forbidden for use on alkali metal fires.

Reactions with Alcohols

The alkali metals will react with alcohols in basically the same manner as they react with water, but the reaction proceeds more slowly.

$$M + ROH \rightarrow ROM + 1/2\ H_2 \qquad (8)$$

("R" represents an organic radical such as CH_3 (methyl), C_2H_5 (ethyl), C_3H_7 (propyl), C_4H_9 (butyl), etc.) By using a large volume of alcohol with a small amount of metal, the reaction can be controlled to provide a safe means for the disposal of waste alkali metals. Care must be taken, of course, because both hydrogen and heat are produced by the reaction; and the alcohols themselves are flammable. In general, the rate of the reaction decreases as the molecular weight of the alcohol increases. Thus, for instance, the reaction will be markedly slower with butyl alcohol (butanol-C_4H_9OH) than with ethyl alcohol (ethanol-C_2H_5OH). Because the chemical activity of the alkali metals increases with increasing atomic weight, it is advisable, when disposing of waste alkali metals, to use the higher weight alcohols with the higher weight metals. It is also known that NaK alloys react more vigorously with a given alcohol than does sodium. If therefore a given amount of a certain alcohol is known to give a smooth, safe reaction with sodium, it would be advisable to use a greater amount of a heavier (i.e., higher molecular weight) alcohol for reaction with NaK.

Since the alcohol-alkali metal reaction is controllable, alcohols are often used to free intricate apparatus or equipment from alkali metals. Precautions should be taken to make certain that the hydrogen released by the reaction does not accumulate and build up a potentially dangerous pressure. The ROM compounds, or alcoholates, formed by the alcohol-alkali metal reaction are not considered as corrosive as the alkali hydroxides (ROH). Thus they are not as dangerous to handle. They are corrosive, however, and should be handled with respect and care,

as should all chemicals. If splashed on the skin and clothing, they should be washed off immediately.

Inertness to Noble Gases and Nitrogen

The alkali metals, reactive as they are, will not react with nitrogen (see comment about lithium that follows) or with any of the elements collectively known as the "noble gases"--helium (He), neon (Ne), argon (A), krypton (Kr), and xenon (Xe). Hence, the readily available and inexpensive nitrogen gas and the two most readily available and least expensive noble gases, helium and argon, are often used as "cover" gases to exclude oxygen from the alkali metals. At the higher temperatures, helium and argon are most commonly used since nitrogen may react with the solid, metallic components of a system to form nitrides that alter the physical properties of the system piping, tanks, and other components. At high temperatures nitrogen will also react with lithium to form lithium nitride, thus introducing a contaminant in a liquid lithium system.

DESIGN OF LIQUID ALKALI METAL EXPERIMENTAL FACILITIES

The design considerations and recommendations made herein are based on experiences gained from the design and operation of liquid alkali metal facilities by numerous investigators over the past 20 years or more. Reasonable adherence to the suggestions that follow should result in the design of facilities that are safe to use and easy to operate.

Experimental Apparatus

In general, the comments that follow apply to laboratory bench-scale apparatus and larger, pilot-plant facilities.

Driptrays

Use driptrays under all apparatus and equipment. If leakage or equipment failure should occur, the tray will confine the molten alkali metal to the experimental area and make fire fighting easier. The protection so afforded concrete floors will help to prevent explosive spalling of the concrete. Spalling of concrete in direct contact with burning alkali metals could send showers of the molten metal over operating and fire-fighting personnel and over adjacent areas, thus enhancing the possibility

of damage resulting from a fire. Although driptrays are extremely useful, it should be noted that the oxides formed during an alkali metal fire may migrate over the walls of a tray. This oxide possesses a "wicking" action that can draw liquid metal over the edge of the tray and thus drain metal from the tray. (For further information, see reference 3.)

Perforated flooring for driptrays having a maximum open area of about 25 per cent have been shown to be effective in limiting the access of air to burning alkali metal, thus serving to extinguish the fire.

Driptrays are also useful in helping to confine fire-fighting chemicals and thus to improve their effectiveness.

Shields

Use metal shields that are fitted inside the lip of the driptray around all liquid metal containing apparatus and equipment. If leakage or failure does occur, the shields will minimize the danger to operating personnel from the spraying liquid metal and will help to confine the metal to the driptrays.

Hoods

Locate experimental and test apparatus under a hood when possible. Hoods can prevent the spread of the irritating white oxide particles from an alkali metal fire. The copious clouds of smoke may be dense enough to limit vision in the area of an alkali metal fire and to hinder operation of equipment, providing first aid, and fighting the fire. However, the hood must not discharge into an area where the oxide smoke could cause more trouble than if it were confined to the general area of the fire. High ceilings and overhead forced ventilation can serve as an adequate substitute for hoods.

Drain Tanks

Include dump, sump, or drain tanks at a low point in the liquid metal system. In an emergency, it will often be possible to dump much of the liquid metal in an apparatus or system, thus minimizing the spill and, consequently, minimizing fires and the problem of cleanup after a fire. Drain tanks should be large enough to hold more than the entire volume of liquid metal in a system. The design of the system should be such that it will drain completely by gravity. The pressure of a cover gas (see next

section) may be of use in draining a system more rapidly than can be achieved by gravity alone. However, one may have to forego this advantage and release or decrease the pressure in the event of an emergency to cut down the loss of molten metal through system leaks.

Cover Gas

Use an inert cover gas in the liquid metal system. By using an inert gas such as nitrogen, helium, or argon under pressure in the liquid metal system, several advantages will be gained: (a) pressure will be available to help dump the liquid metal in the event of an emergency, and (b) the inleakage of air to the system will be minimized. Minimizing the oxygen in a liquid alkali metal system will reduce the amount of alkali metal oxide formed and help to keep the system clean. These oxides have a limited solubility that is markedly temperature dependent--the solubility decreasing with decreasing temperatures. Troublesome deposits of oxides, therefore, will accumulate in the cold portions of a liquid metal system and may lead to plugging of lines. Every possible precaution should be taken to minimize oxide formation for a second reason: The oxides contribute to corrosive attack on many materials of construction, thus inviting trouble and lessening the life expectancy of the liquid metal system. Because nitrogen will react with hot lithium to form lithium nitride, thus introducing an impurity into a lithium system, nitrogen is not recommended as a cover gas for lithium.

Cold Traps

Include a "cold trap" in the liquid metal system. As pointed out in the preceding section, alkali metal oxides show decreasing solubilities with decreasing temperatures. This property can be used to advantage to help keep liquid alkali metals clean by the installation of "cold traps" or "cold fingers." The cold trap is normally a tank containing a mesh packing, through which the liquid metal is pumped and cooled. Precipitated oxides are retained on the packing. Cold fingers are nothing more than small vessels on stubs of piping that are incorporated in the colder portion of the liquid alkali metal system. By keeping the cold finger markedly colder than any other part of the system, alkali oxides will gradually accumulate by diffusion in the trap, thus helping to keep the

system clean and free of troublesome deposits. Cold trap design is an art rather than a science and should be learned from experimenters who have had successful experience with the operation of these devices. It must be remembered that whether planned or not, the coldest point in any alkali metal system will automatically function as a cold trap.

Air and Water Lines

Do not use air or water lines in conjunction with piping handling liquid metals without serious consideration of the safety aspects involved. When designing and installing liquid metals systems, never make it possible--directly or indirectly through cross connections--to introduce air or water into any piping through which liquid metals will flow. In preceding sections of this primer, the danger involved in mixing air and water with alkali metals has been pointed out repeatedly.

Storage Facilities

It is a good rule to assume that all chemicals are dangerous in one way or another and that thought and care must be given to their safe use, handling, and storage. In view of the reactive nature of the alkali metals, it should be evident that special consideration must be given to the specific problem of the storage of the alkali metals. The bibliography of this primer contains several references to articles on this subject.

Commercial-grade alkali metals are normally received from the producer in the form of bricks, which are stacked in airtight metal containers having readily removable covers. High purity alkali metals and alloys (NaK) are usually shipped in metal containers equipped with valves, so that the liquid can be forced from the container by inert gas pressure.

Containers should always be stored on cement blocks or platforms (do not use wooden supports) above the floor level to facilitate visual inspection of the container for leakage and to prevent liquid spills of any kind on the floor from coming into contact with the containers. The storage area should not contain a sprinkler system and should not have water lines passing through it. It is important also that the area be kept free of other materials that might react with spilled or leaking alkali metal or that, if a fire started, would require the use of

extinguishants that might react with the alkali metals. All organic materials, including wooden shipping containers and boxes and paper, should be kept out of the storage room. It is highly recommended that the room or area in which alkali metals are stored be used for this purpose only.

The storage area should be posted with signs (including "No Smoking") indicating the nature of the stored material and warning against the use of water or other fire extinguishants that will react with the alkali metals. A supply of the proper type of fire extinguishing material should be nearby. If these materials are capable of absorbing moisture, provision must be made to keep them dry. The storage area must be kept dry and should be well ventilated to keep the humidity at a minimum and to remove the heavy oxide fumes if a fire should start.

HANDLING OF ALKALI METALS

Alkali metals can be handled safely and with a minimum of danger if they are given the consideration that they deserve and require. It is the responsibility of the individual who is directly concerned with the handling and use of alkali metals to acquire a sound, basic understanding of the nature of these useful--and reactive--materials, so that he may approach the problem of handling them with confidence. The key to the safe use of all materials is to "<u>know them</u>."

It is not within the scope of this primer to provide step-by-step directions for handling alkali metals under specific conditions. Instead, suggestions and recommendations are advanced which, upon study, will provide the reader with information--based on the chemical and physical properties of the alkali metals--to enable him to develop the all-important "feel" for this problem. With this "feel," or background of stored information, the reader will be in a position, with experience, to develop his own safe procedures or directions for handling specific problems involving the alkali metals.

It is recommended strongly that at least two persons be involved in any situation where alkali metals are being handled or used. This excellent safety precaution cannot afford to be relaxed. If one person should panic

or become incapacitated in the event of an accident, the second person can be available to take over or to provide help. This second person is also available, if necessary, to start fire fighting, to help shut down equipment, to turn in an alarm, or to provide any other assistance that might be needed.

Protective Clothing

Before anyone becomes involved in a problem dealing with the handling of the alkali metals, the type and the location of the available protective clothing and equipment should be determined. Protection should be available for the head, face, eyes, hands, body, feet, as well as for the breathing passages and the lungs. Remember that ordinary cotton or synthetic fiber clothing offers little or no protection against the liquid alkali metals except at room temperature. According to information released by the Mine Safety Appliances Company,[5] chrome leather gloves and aprons and laminated Bakelite hats offer 100% protection against 500°C (932°F) sodium and NaK. Rubber gloves, face shields with acetate windows and MSA Nu-Looks goggles protect against 150°C (302°F) NaK and 350°C (662°F) sodium. MSA chipping goggles and MSA welding goggles show excellent resistance. It is unreasonable to expect this clothing to withstand prolonged or severe exposure to molten or burning alkali metals. For instance, no protective clothing or equipment currently available can withstand the effect of a 1/16-in.-diam stream of lithium at 600°C (1100°F) and 60 lb per in.^{2} (Ref. 3). Specific information on protective clothing is found in TRG Report 25C, "Guidance in the Safe Handling of Alkali Metals," published in 1961 by the United Kingdom Atomic Energy Authority[6] and in the report prepared by Rodgers and Everson.[3]

General Safety Precautions

The following general safety precautions should be observed at all times when handling the alkali metals.

1. Do not smoke. Make certain also that there are no open flames of any kind in the area.

2. Make certain that an adequate supply of fire controlling and extinguishing material is on hand to deal with any spillage or fire.

3. Make certain that all equipment, including tools, to be used during the handling operation is absolutely dry. The use of nonsparking tools in opening alkali metal drums is strongly recommended since hydrogen can accumulate in the drums and cause explosion and fire. If moisture from the air were trapped in the container from a previous opening, it would have reacted with the alkali metal to produce hydrogen. Although it may appear unlikely that a dangerous amount of hydrogen will be formed in this manner, it should be assumed that this could happen.

4. If a "hissing" sound is heard when an alkali metal container is opened, hydrogen gas may be present in a dangerous amount. Proper ventilation in the area will help to disperse the hydrogen and will lessen the danger of an explosion.

5. Handle solid alkali metals only with tongs or with nonporous, washable gloves.

6. Transfer all molten alkali metals at the lowest possible temperature and pressure to minimize the possibility of fire or the effect of an accident.

7. Always use an inert cover gas when transferring molten alkali metals.

8. Be prepared to remove promptly any spilled alkali metals or residues from alkali metal fires.

9. Replace drum covers immediately after removing alkali metal bricks to minimize the introduction of oxygen and moisture. By replacing the drum covers, the possibility of a future accident will be lessened and contamination of the metal (by the formation of oxides, hydroxides, and carbonates) kept to a minimum.

Elimination and Disposal of Residual and Waste Alkali Metals

Sooner or later the investigator working with NaK or an alkali metal will face an important problem: How do I eliminate or dispose of waste or residual material? Suggestions for dealing with this eventuality are presented herewith.

If a waste disposal officer is a member of your organization, waste disposal plans should first be discussed with him, particularly if sizable amounts of waste are involved. If a special waste disposal facility exists, it is probable that skilled personnel will assume the responsibility for disposing of accumulated waste metal. The waste disposal suggestions that follow, thus, deal primarily with the problem of collecting and disposing of small amounts of waste alkali metals.

1. In the case of a spill, shovel the liquid material into a dry, metal container equipped with a lid and replace the lid promptly. This procedure may be followed even if the metal is burning. With the lid in place, oxygen will be excluded; and the fire will go out. If preferred, a suitable fire extinguishant (possibly powdered graphite or Met-L-X Powder) can first be shoveled or sprayed on the spill before the metal is put into the disposal container. A layer of the extinguishant may also be added to the container before the spilled or waste metal is dumped therein.

2. Small amounts of waste or residual metal in small sections of piping or tubing or in small pieces of apparatus can be eliminated by placing the unit in a container of alcohol of the proper kind (see Section "Reactions with Alcohols" p. 10). When the reaction between the alkali metal and the alcohol is over (make certain no unreacted alkali metal remains in the liquid), dispose of the resulting solution through a laboratory sink drain. Flushing of the sink with a large amount of water is then advisable.

3. When NaK or other liquid metals are drained from a sizable piece of equipment, residual metal may remain throughout the equipment due to poor drainage, low spots, or crevices. In cases such as this, a suitable alcohol (see Section "Reactions with Alcohols" p. 10) may be circulated through the system to remove the alkali metal, making certain that the system is kept open so that the by-product hydrogen is allowed to escape safely.

Dry steam may also be used effectively to clean apparatus. The apparatus should first be heated (trace heating is entirely suitable) to above 100°C to prevent condensation of steam. Care should be taken to make certain that no air enters the system with the dry steam. In an air-free atmosphere, the steam-alkali metal reaction will proceed smoothly without

danger of an explosion. A final flush with water is normally permissible after other cleaning techniques have been applied. If the mixture leaving the apparatus being cleaned contains the strongly caustic alkali hydroxide formed by the reaction, the mixture should not be discharged indiscriminately.

Fighting Alkali Metal Fires

If a person handling or using an alkali metal always remembers that a fire might occur--but that the fire can be handled safely if he knows the ground rules--he will always be psychologically prepared if a fire should break out. He should remember that flames, if any, may be practically invisible, that large quantities of white, opaque smoke will be produced, but that the burning metal cannot, of itself, explode. An alkali metal fire, as such, is not particularly hazardous (all fires, of course, present a hazard) but secondary effects--the caustic alkali oxide cloud of smoke and reactions with nearby materials--may be.

In his excellent article "Extinguishing Sodium-Potassium Alloy Fires," Lee[7] points out that, as with regular fires, three ingredients are necessary before it is possible to have a fire: fuel, heat, and oxygen. Removal of any one of the three ingredients will extinguish the fire.

Under ordinary conditions, if a fire develops, first remove the alkali metal fuel. Although this removal will not extinguish the fire, it will limit the size of the fire. If only a small amount of metal is involved, the simplest and safest procedure <u>may be</u> to do nothing--simply allow the metal to burn and keep a safe distance away from the smoke. Under certain conditions, it may be advisable to leave the scene of the fire temporarily to turn in a fire alarm.

When larger amounts of alkali metal, several pounds or more, are burning, a standard procedure for handling the fire should be put into

operation. This means that no one should handle or use alkali metals without first developing, or becoming familiar with, an emergency procedure that is applicable to his particular situation.

Heat is the second ingredient necessary for a fire. Although "cooling" a fire will lessen its intensity, or even extinguish it, this is not always easy to accomplish. Since this procedure is normally not applicable to alkali metal fires, it will not be discussed here.

Oxygen is the third ingredient necessary for an alkali metal fire. If oxygen is excluded, the fire promptly dies out; for, in every sense of the word, it suffocates. Actually, a nonflammable, nontoxic, and nonreactive liquid having a high latent heat and producing a heavy (high molecular weight) vapor would be an ideal fire fighting material. If such a liquid were sprayed on a fire, vaporization would absorb the heat, thereby cooling the fire and helping to extinguish it. Furthermore, as the heavy vapor formed, it would blanket the fire and exclude oxygen, thus extinguishing the fire. Unfortunately, no such ideal fire fighting liquid exists. Fire fighting materials that are used, therefore, have limitations that make them suitable only for rather specific purposes. It is not too surprising, consequently, that the well-known fire extinguishants such as carbon dioxide, carbon tetrachloride, and water are not suitable for use on alkali metal fires. A review of the chemistry of the alkali metals presented in the section on "Chemical Properties," p. 5 will show why these materials should <u>never</u> be used to combat alkali metal fires.

Several fire fighting materials that are recommended for use on alkali metal fires are discussed briefly below:

1. <u>Soda Ash (anhydrous Na_2CO_3)</u>. Only the anhydrous and completely moisture-free material is suitable for use. This substance can be sprinkled or shovelled on the fire or sprayed on from an extinguisher, using CO_2 pressure. The powder blankets the fire and tends to prevent the reaction of the carrier gas (CO_2) with the metal. Soda ash is often used on sodium fires and is generally accepted as being suitable for use on potassium and NaK fires. A General Electric safety manual[8] states

that "Soda ash is not recommended as an extinguishing agent for lithium since it reacts violently on contact."

2. Zirconium Carbonate. (See general comments under "Soda Ash"). This material has been used effectively on alkali metal fires. It is expensive, though, in comparison to soda ash and does not appear to have specific advantages that make its use compelling.

3. Powdered Graphite. This is an excellent blanketing agent and has been widely used in fighting alkali metal and NaK fires. Care should be taken to distribute the graphite powder smoothly over the burning metal and to avoid dumping it on the fire. Dumping might cause splattering of the burning metal and might also result in the mass of graphite sinking through the burning metal, thus failing to provide the desired blanketing effect. Rodgers and Everson[3] report that graphite is the best among many extinguishants tested on lithium fires. The action of graphite on a liquid metal fire is apparently dual. By blanketing the surface, the powder excludes air, thus suffocating the fire. Also, since it is a respectable conductor of heat, the graphite probably cools the burning metal somewhat and thus helps to extinguish the fire.

4. Met-L-X. This fire fighting material is a dry, free-flowing, impregnated sodium chloride (distributed by Ansul Chemical Company), which is available in pressurized extinguishers. When Met-L-X is sprayed on an alkali metal fire, it forms a crust that excludes oxygen from the fire--thus extinguishing it. It is usually considered advisable to intermittently sprinkle the Met-L-X lightly on the burning surface. This procedure will hasten the formation of the crust. Met-L-X is not combustible and thus will not cause secondary fires when it is used on liquid metal fires. Because of its ability to adhere to molten sodium, Met-L-X is particularly suitable for use on sodium fires on walls and piping. It is advisable to clean thoroughly the high-temperature equipment in the area where Met-L-X has been used to avoid corrosion problems in subsequent operation.

5. Pyrene G-1 Powder. This material is a graphite-base extinguishant produced by the Fyr-Fyter Company. It may be applied from tubes, or, if it is available in bulk form, may be sprinkled from shovels. Since it is not combustible, secondary fires will not result from its application to a burning alkali metal.

Details concerning the performance of various materials tested for their ability to extinguish burning alkali metals and NaK may be found in the report prepared by Rodgers and Everson,[3] pp. 36-37. An excellent analysis of fire extinguishants is made by Gracie and Droher[9] in Chapter V of their exhaustive report entitled "A Study of Sodium Fires."

First Aid

Personnel handling or using alkali metals should know the basic rules of first aid, so that effective action can be taken and help administered should an accident occur. An amply supplied first aid cabinet or locker located nearby in a readily accessible area is basic to providing aid. Minimum first aid material should include tongs or tweezers, some kind of a scraper or spatula, swabs, bandages, and a container of mineral oil. Tongs are useful in picking chunks of metal from clothing or skin. A scraper or swab is useful in scraping alkali metal from clothing and skin. Mineral oil can be used to cover a cleaned area to exclude air and moisture from residual material.

If an accident occurs and someone is splashed with molten alkali metal that is not burning, the metal should be scraped from the skin as rapidly as possible. Should the metal have come in contact with normal work clothing, the clothing should be removed promptly, the alkali metal in contact with the skin swiftly scraped off, and the affected areas flooded with mineral oil. Any detectable bits of alkali metal should be removed promptly with the tweezers or by swabbing. The accident victim should then be removed to a hospital or infirmary for observation by trained medical personnel and for any further treatment that is necessary.

If a person has been sprayed with burning alkali metal, the same general procedure as outlined above may be followed or an alternate procedure used. This alternate procedure calls for immediate removal of all clothing and massive amounts of alkali metal, flooding of the affected areas with large amounts of water (small amounts will probably do more harm than good), and neutralizing with a 3% acetic acid solution. According to the Liquid Metals Handbook,[10] considerable controversy exists concerning the best procedure to be followed in giving first aid to a person splashed with burning liquid metal.

It is suggested, therefore, that the reader determine what the recommended procedure is at his laboratory or installation and that he act accordingly in the event of an emergency.

Although prompt first air treatment is always in order, it is a necessity in the case of an eye burn. If goggles did not provide protection and an eye is burned, it should be flooded immediately with large amounts of low pressure water for about 15 minutes. The eye should then be treated with a 5% solution of boric acid to neutralize any caustic that may still remain. Subsequent treatment by medical personnel is always recommended even though no apparent damage may have been suffered.

SUMMARY

The liquid alkali metals are valuable but are very reactive and potentially dangerous materials. With a sound understanding of, and an appreciation for, their characteristic physical properties and chemical nature, they can be used profitably and with safety. It is the responsibility of the individual who needs to handle and to use the alkali metals and their alloys to acquaint himself with the pertinent information concerning these materials so that he can proceed with their use with confidence.

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