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EXTINGUISHMENT OF ALKALI METAL FIRES

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ILLUSTRATIONS

ABSTRACT

The objective of this study was to establish the characteristics and methods of control of alkali metal fires. A review of present practices used in alkali metal fire control is presented. A section is also included on the physical and chemical properties of the alkali metals.

The effects of inert gas blanketing and oxygen partial pressure were evaluated. It was found that reduction of oxygen partial pressure was effective in inhibiting ignition and degree of combustion of lithium, sodium, NaK and potassium. Rubidium and cesium did not ignite, i.e., there was no emission of smoke or flame, but they completely oxidized even at lower oxygen partial pressures. Reduced oxygen partial pressure was also effective in inhibiting ignition of alkali metal jet streams.

A number of different salts, organic liquids, and polyurethane foam were evaluated with respect to alkali metal fire extinguishment. Met-L-X and TEC Powder were the most effective salts which were evaluated. The ratio of TEC Powder/alkali metal was 0.4 for 100 lb sodium fires and 0.2 for 500 lb sodium fires. Polyurethane foam was found to be effective on low temperature (1000°F) fires and was useful on alkali metal fires on or under insulation. Organic liquids were not particularly effective on alkali metal fires and in most cases the secondary organic fire was more severe than the alkali metal fire.

A section is presented on a typical alkali metal system which might be used to generate electrical power in space. The major fire hazards during the various phases of charging, injection into orbit and in-flight operations are outlined. Fire control procedures for each of the phases are outlined.

This technical documentary report has been reviewed and is approved.

BLACKWELL C. DUNNAM, Chief
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TABLE OF CONTENTS

Page

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

ILLUSTRATIONS

TABLES

TABLES (Continued)

I. INTRODUCTION

The advent of aerospace flight has resulted in increased temperature requirements for fluids used as heat transfer media, working fluids, hydraulic fluids and lubricants. The alkali metals have been selected as the most promising fluids since they exhibit the following physical characteristics:

1. Long liquidus range - 354°F (179°C) to 2403°F (1317°C) for lithium.
2. Relatively low melting points - 83°F (28.5°C) for cesium to 354°F (179°C) for lithium; NaK-78 melts at 10°F (-12.3°C)*.
3. High boiling points - 1270°F (688°C) for rubidium to 2403°F (1317°C) for lithium.
4. High transfer coefficients - 6400 Btu/hr-ft^2-°F/ft for sodium.
5. High temperature stability.
6. Non-corrosive when pure.

Lithium and sodium are being considered as heat transfer media for nuclear reactors and solar heat sources. Potassium, rubidium and cesium are being investigated as potential working fluids for turbines. The feasibility of ion engines using cesium has been demonstrated and cesium is being used in thermionic converters and other thermoelectric devices. A number of low melting binary, ternary and quaternary alkali metals are being considered as lubricants and hydraulic fluids.

Alkali metals, particularly sodium, have been used in industry for many years as heat transfer media and reaction media. These metals are extremely reactive with atmospheric gases, water, many organic materials, and a number of materials of construction, thus system design and formulation of operational procedures with

*A multicomponent alkali metal alloy with a freezing point of -94°F (-70°C) has been developed recently.

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respect to safety are given particular consideration. Most systems are surrounded by some sort of metal shielding to protect both personnel and equipment in the event of an alkali metal leak. A drip pan of sufficient size to contain all of the alkali metal in a system is usually positioned beneath the system. Water lines and drains are generally excluded from the immediate vicinity of the system. Handling techniques and fire extinguishment and control procedures have evolved from this experience with land-based systems.

In space, alkali metal ignition characteristics and fire control procedures might differ from those on earth. It may not be possible to extensively shield the system because of the wieght penalty imposed. A drip pan would be of limited value if the craft is not subjected to an artifical gravitational field; leaking alkali metal could migrate to any spatial location in the absence of a gravitational field. In certain cases, the compartment atmosphere may be pure oxygen at some reduced pressure; this could enhance combustion of the alkali metal. Conversely, it may be possible to operate a system in a compartment exhausted to the vacuum of space; in this case, combustion of the alkali metal would be eliminated.

Historically, three methods are used to control or extinguish fires:

1. Remove fuel
2. Remove oxidizer
3. Remove heat

Recently, a fourth technique has come into being - disruption of the chain reaction in the combustion zone by removal of free radicals produced in the flame. With fires resulting from the combustion of wood, paper, flammable organic liquids and gases, and electrical fires, these procedures can be used. A natural gas fire can be quelled by shutting off the fuel supply. Oxygen can be excluded from the area by use of CO_2 or foam. Heat is generally removed by applying a volatile heat absorbing material such as water or bromochloromethane to the fire. Alkali metal bicarbonates are being used to supply ions which will react with free radicals to inhibit flame propogation. The three primary methods of fire extinguishment can be adapted to alkali metal fires, although the procedures differ somewhat from those normally used for ABC fires.

Removal of fuel with respect to alkali metal fires is normally accomplished by lowering the cover gas pressure on the system to reduce the leakage rate, valving-off or freezing the leaking section, or draining the alkali metal into a sump tank. This procedure controls the severity and magnitude of an alkali metal fire but does not eliminate combustion of the metal which has escaped from a system. Two procedures are used to exclude oxygen from an alkali metal fire - (1) inert gas blanketing and (2) smothering with a non-reactive material such as an alkali metal chloride or graphite. Heat has been removed by plunging a cold iron bar into the burning melt, but this method is not generally amenable to an actual alkali metal fire.

II. SCOPE OF PROGRAM

The purpose of the study described in this report was to investigate agents and techniques for extinguishment and control of fires resulting from leakage of high temperature and high pressure alkali metals under normal atmospheric and reduced atmospheric environments. The program was subdivided into seven major phases of investigation:

Phase I - Review of Current Practices for Extinguishment and Control of Alkali Metal Fires

Phase II - Review of Physical and Chemical Properties of Alkali Metals With Respect to Fire Control and Extinguishment

Phase III - Effects of Inert Gas Blanketing and Oxygen Partial Pressures on Alkali Metal Fires

Phave IV - Extinguishment of Alkali Metal Fires Using Inorganic Salts and Salt Mixtures

Phave V - Extinguishment of Alkali Metal Fires Using Inorganic Salt Foams

Phave VI - Characterization of Alkali Metal Jet Stream Ignition at Various Pressure Conditions

Phave VII - Extinguishment of Large Scale Fires

Phases I and II consisted of a literature review to determine present practices used in alkali metal fire control and extinguishment and the effects of chemical and physical characteristics of the alkali metal on these controls. The following items were of particular importance:

1. Techniques and procedures used in alkali metal fire fighting.
2. Extinguishants used on alkali metal fires.
3. Methods of containing or confining leaking metal.
4. Post fire clean-up procedures.
5. Survey of conditions under which fires can occur and evaluation of how these conditions will affect fire control.
6. Flame temperatures of the alkali metals.
7. Compatibility of burning alkali metals with various materials of construction.
8. Toxicity problems.

In addition to the literature review, an industrial survey was made to determine alkali metal fire control procedures which are used at various sites throughout the country.

The effects of inert gas blanketing and oxygen partial pressures on alkali metal fires were evaluated in Phase III. This was performed in a combustion chamber where the atmosphere was varied from normal atmospheric composition to 90% Ar-10% air.

The use of inorganic salts and salt mixtures was evaluated in Phase IV. Data were collected on the rate of extinguishment and the quantity of extinguishant required as a function of fire size.

The original objective of Phase V was to evaluate the use of inorganic salt foams as alkali metal fire control media. Unfortunately, foams are generally water based and hence are not compatible with alkali metals. Organic foams were evaluated and showed some degree of promise.

Characteristics of alkali metal jet stream ignition were evaluated in Phase VI. This work was performed in the chamber used in the Phase III study.

Extinguishment of large scale fires ranging from 100 to 500 pounds of metal was evaluated in Phase VII. The results indicated that data collected on a 10 lb fire could be extrapolated to larger fires.

III. REVIEW OF CURRENT ALKALI METAL FIRE CONTROL PRACTICES (PHASE I)

The literature was reviewed to determine current practices for extinguishment and control of alkali metal fires. As would be expected, the information is scanty on alkali metal fires, but wood fires, hydrocarbon fires and the like are described more extensively. Fire Research Abstracts and Reviews(1) which was first published in 1958 deals extensively with the characteristics and techniques of extinguishing wood and flammable liquid fires. It is evident from these journals that fire research is advancing rapidly.

The results of the literature survey are summarized in Appendix I and Appendix II. The data presented in Appendix I relates to non-alkali metal fires and includes a discussion of combustion under zero gravity conditions.

Appendix II summarizes the current practices of alkali metal fire control and extinguishment. Results of a survey of a number of sites using alkali metals are also included in this appendix. Review of these practices led to the following conclusions:

1. Proper system design, construction and operation are essential for safe handling of alkali metals.
    a. System must be shielded to protect personnel and equipment.
    b. Drip pans must be provided to contain and leaking metal.
    c. Sump tanks must be provided to aid in removal of fuel from fire.
    d. Systems must not be located in areas which contain materials which react with the alkali metals.
2. Protective equipment must be worn to protect personnel from injury and provide maximum fire fighting efficiency.
    a. Head protection - hard hat
    b. Face protection - face shield
    c. Eye protection - side shield goggles

d. Hand protection - chrome leather gloves

e. Body protection - loose fitting coveralls or clothing or chrome leather aprons

f. Foot protection - leather safety shoes

g. Respiratory protection - respirator or self contained breathing apparatus depending upon the severity and nature of the fire

3. Extinguishants and techniques will depend upon the type of alkali metal and size of the fire.

   a. Extinguishant should be applied gently in the form of a thick, smothering layer

      i - Shovel or scoop application is suitable for small scale, well contained fires.

      ii - Pressurized extinguisher application is recommended for large fires.

   b. Extinguishing agents used will be dictated by the nature of the fire.

      i - Lithium - graphite

      ii - Sodium - treated NaCl

      iii - Potassium - treated NaCl

      iv - NaK - treated NaCl

      v - Rubidium and Cesium - there is essentially no practical background on fire fighting of these metals. It is assumed the NaCl will work well on these as on sodium and potassium fires.

4. Proper disposal of a fire residue will minimize hazards.

   a. Residues should be cleaned up as soon as they have cooled.

   b. NaK and cesium are particularly troublesome since they are liquid at room temperature.

c. Residues of potassium, rubidium and cesium fires may contain superoxides which are excellent oxidizing agents and react explosively with a number of organic materials.

d. Complete combustion of the residue in a disposal area is recommended. Residues may also be destroyed by dumping into a water pit if proper precautions are observed.

IV. REVIEW OF PHYSICAL AND CHEMICAL PROPERTIES OF ALKALI METALS (PHASE II)

A. INTRODUCTION

Physical and chemical characteristics of combustibles must be considered in the development of fire fighting agents and techniques. Gaseous or vapor fires must be fought differently than combustible liquid fires. The boiling point and vapor pressure of a flammable liquid are important facets of fire characteristics. Flowing liquid fires are obviously more difficult to handle than stationary solid fires. Secondary reactions between extinguishant and the fire must be consider d and a knowledge of toxic properties is a necessity when the fire is to be fought by personnel at the fire site. The factors which should be evaluated in a study of alkali metal fire fighting techniques are:

1. Chemical and physical properties of the alkali metals - melting point, boiling point, heat of reaction, combustion products, solubility of combustion products, etc.

2. Chemical and physical properties of extinguishing agents - melting point, reactivity with alkali metals, stability at flame temperature and so on.

3. Toxic properties of both the metals and extinguishing agents.

B. PHYSICAL PROPERTIES OF THE ALKALI METALS

The physical properties of the alkali metals are listed in Table 1. All of the alkali metals have a metallic luster in the pure state and all are silver in color except cesium which has a

TABLE 1 - PHYSICAL PROPERTIES OF THE ALKALI METALS

	Lithium	Sodium	Potassium	Rubidium	Cesium
Atomic number	3	11	19	37	55
Atomic weight	6.940	22.991	39.10	85.48	132.91
Specific gravity	0.534	0.9721/	0.859	1.532	1.873
Specific heat(cal/gm/°C)	0.7951	0.292	0.173	0.0802	0.0482
Melting point (°C)	186	97.7	63.6	39.0	28.45
(°F)	357	208	146	102	83
Heat of fusion (cal/gm)	32.81	27.5	14.63	6.144	3.766
Heat of fusion (cal/gm atom)	228	632	572	525	501
Boiling point (°C)	1,336	892	774	696	670
(°F)	2,440	1,618	1,400	1,270	1,260
Heat of sublimation at 25°C(Kcal/gm atom)	36.44	25.95	21.52	20.50	18.83
Atomic radius in A°	1.56	1.86	2.23	2.43	2.62
Ionization potential (volts)	5.37	5.12	4.32	4.16	3.87
Oxidation potential at 77°F(25°C) (E volts)	3.02	2.71	2.92	2.99	3.02
Flame coloration	carmine	yellow	violet	bluish-red	blue
Solubility of O_2 at 500°F (250°C) (%)	0.012	0.006	~0.5	>1	>>3
Heat of formation ($\Delta H_f°$,Kcal)*	-142(Li_2O) -47.2(Li_3N)	-99.4	-86.4	-78.9	-75.9

*These values are based on the assumption that the monoxides are formed during combustion.

gold color. They are relatively soft and of such a consistency that they can be cut with a knife. Their melting points are relatively low, ranging from 83°F for cesium to 357°F for lithium. They exhibit excellent heat transfer properties, hence their use as coolants is of interest. When contained in a pure state, particularly free of oxygen, they are non-corrosive. The low melting points add to the complexity of alkali metal fires since they are liquids at the flame temperatures. This property also increases the reactivity of the alkali metals with many materials. In contact with water, the exothermic reaction raises the temperature, which causes the metal to melt, which increases the surface area for reaction. For this reason lithium, with its higher melting point, is less reactive than the other alkali metals.

Specific gravity of the alkali metals must be considered when a smothering salt is used as the extinguishant. If the salt has a higher specific gravity than the alkali metal,there is a tendency for the salt to sink exposing fresh metal and extinguishment cannot be obtained. Commercial preparations of NaCl (Sp.Gr. = 2.165) will sink in lithium (Sp. Gr. = 0.534) rendering this material unsuitable as a lithium fire extinguishant. The denser metals, such as rubidium and cesium should support a salt crust better than the lighter alkali metals. However, lack of oxide formation on the surface due to high oxygen solubilities in the heavier alkali metals can be detrimental since there is no oxide crust on which the extinguishant can be supported.

Specific heat should have some effect on the characteristics of alkali metal fires. However, the heat of combustion, 1600 cal/g for sodium, is high enough to minimize any cooling effect of the bulk of the metal.

Boiling points of the alkali metals are extremely high compared to boiling points of flammable organic fluids. Many liquids are flammable because of the high vapor concentration above the liquid surface with the vapors burning rather than the liquid itself. It is unlikely that the alkali metals burn by this mechanism although the boiling points of the metals are approached in burning quiescent pools. However, alkali metals can ignite at temperatures where the vapor pressure is negligible - in fact ignition will occur at a few degrees above the melting point.

C. CHEMICAL PROPERTIES OF THE ALKALI METALS

The alkali metals are all extremely chemically reactive, with the reactivity increasing with an increase in atomic weight. They are all strong reducing agents and readily form univalent positive ions. Alkali metals react with water with explosive violence. Although they ignite spontaneously in the atmosphere, it has been reported that they can be heated in an atmosphere of <u>dry</u> oxygen to their melting points without reaction. Lithium reacts with both oxygen and nitrogen in the atmosphere, forming Li_2O and Li_3N. Sodium reacts with atmospheric oxygen forming either Na_2O or Na_2O_2. The remaining metals, potassium, rubidium and cesium, react with oxygen to form superoxides of the form MO_2 or M_2O_4. (The superoxides are useful in self-contained breathing apparatus and are now being considered as oxygen supplies in life support systems in space vehicles.)

The alkali metals ignite spontaneously at temperatures slightly above their melting points. A significant temperature range for ignition temperatures exists since spontaneous ignition depends upon the humidity, character of the exposed surface, degree of dispersion and so on. During combustion, only small flames are visible but an intense light is radiated from the burning mass.

Alkali metals react exothermically with the halogens, emitting light. Hence, halogenated hydrocarbons such as CCl_4 cannot be used to extinguish alkali metal fires. The reaction of alkali metals with CCl_4 is nearly as violent as the reaction with water. In general, any of the alkali metals will reduce salts of alkali metals of a higher atomic weight. This factor must be considered in choosing a salt extinguishant since reduction of the salt can result in a fire of the alkali metal originally combined in the salt. For example, NaCl used on a lithium fire can result in a sodium fire.

Historically, CO_2 has not been used as an extinguishant for alkali metal fires. This is not to suggest that a violent reaction will occur, but secondary products which are formed can be hazardous. Formation of CO in closed environments could lead to asphyxiation of fire fighting personnel and it has been suggested that carbonyls, which are potentially explosive in nature can be formed.

D. <u>TOXICITY OF THE ALKALI METALS</u>

Because of their extreme reactivity, it is unlikely that the alkali metals will exist as free elements in the atmosphere. However, the oxides, hydroxides and carbonates can become airborne and pose inhalation hazards. The principal hazard seems to be the caustic effect which can damage lung tissue. Values for a lethal dose of 50% (LD-50) of the alkali metal chlorides on intraperitoneal administration in mice are(2)

Salt	LD-50 (mg-kg)
KCL	670
LiCl	1060
RbCl	1209
CsCl	1683
NaCl	3096

Cochran, et al$^{(3)}$ reported an LD-50 of 1200 to 1500 mg/kg for CsCl, CsBr, CsI and $CsNO_3$ and an LD-50 of 100 mg/kg for CsOH. The caustic effect is dramatically shown by these comparative values.

V. EFFECTS OF INERT GAS BLANKETING AND OXYGEN PARTIAL PRESSURE ON ALKALI METAL FIRES (PHASE III)

A. INTRODUCTION

The purpose of this phase of the study was to determine the effect of atmospheric conditions on the severity of an alkali metal fire. The effect of oxygen partial pressure at normal atmospheric pressure and the effects of reduced absolute pressure on fire characteristics were studied. The data should indicate the atmospheric conditions which can inhibit an alkali metal fire; it should also demonstrate the effect of venting the compartment of a high altitude craft. Table 2 shows the physical characteristics of the atmosphere up to 100,000 ft. Evaluation of combustion characteristics in pure oxygen atmospheres at reduced pressure was not a part of this study.

B. APPARATUS

The controlled atmosphere combustion chamber was constructed of 1/4 in. carbon steel plate and was approximately 3 ft x 3 ft x 3 ft. Figure 1 shows a schematic diagram of the combustion vessel and a photograph of the combustion chamber. Reinforcing bars on the outside of the chamber prevented collapse of the walls during reduced pressure operations. The chamber held a vacuum of 0.1 atmosphere for 4 days. The chamber was fitted with 4 view ports for observation and filming of the fires. Openings were provided for evacuation, sampling and adjustment of the chamber atmosphere. Access to the chamber was through a square 1 1/4 ft door.

TABLE 2 - PHYSICAL CHARACTERISTICS OF ATMOSPHERE UP TO 100,000 FT.

Altitude (ft)	Absolute Pressure (mm Hg)	Absolute Pressure (in. Hg)	Partial Pressure O_2 (mm Hg)	Ambient Temp. (°F)	Boiling Point at Pressure (°F) Li	Na	K	Rb	Cs
0	760	29.92	160	65	2430	1620	1400	1270	1260
10,000	523	20.58	110	2.4	2340	1530	1340	1200	1190
20,000	349	13.75	73	-15	2230	1480	1260	1140	1110
30,000	226	8.89	47	-38	2160	1410	1200	1070	1050
40,000	141	5.54	30	↑	2070	1340	1130	1010	990
50,000	87	3.42	18		1970	1270	1060	950	930
60,000	54	2.12	11		1840	1210	1010	900	870
70,000	33	1.31	6.9	-51	1800	1150	950	850	820
80,000	21	0.81	4.4		1750	1100	910	800	770
90,000	13	0.504	2.7		1680	1040	850	750	730
100,000	8	0.320	1.7	↓	1600	990	810	710	680

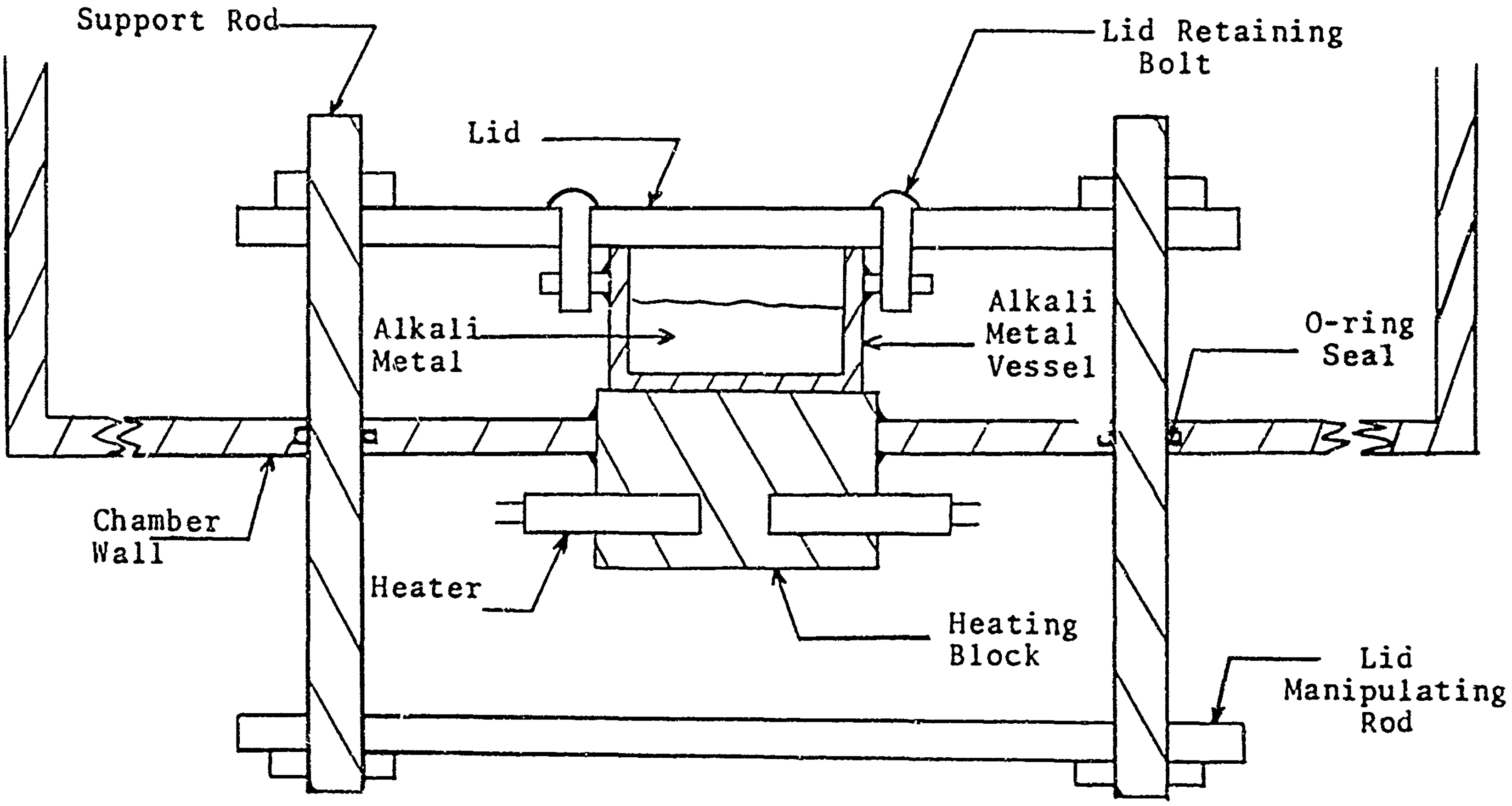


FIG 1a - DETAIL OF CONTROLLED ATMOSPHERE ALKALI METAL VESSEL

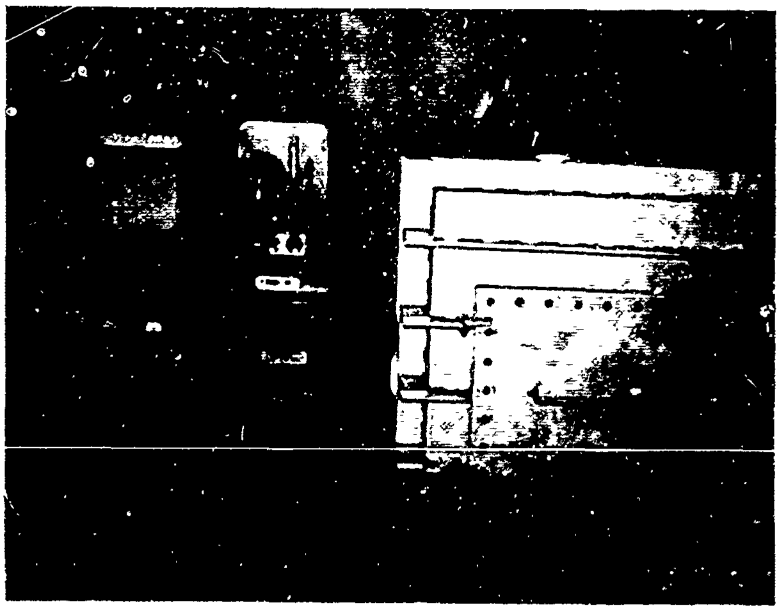


FIG 1b - CHAMBER FOR CONTROLLED ATMOSPHERE
ALKALI METAL FIRES

FIG 1 - APPARATUS FOR CONTROLLED ATMOSPHERE ALKALI METAL
COMBUSTION STUDIES

The alkali metal was contained in a 3 in. dia. x 3 in. deep combustion vessel. The vessel was fitted with a lid which was bolted in place after the vessel was filled with alkali metal. Heat was supplied to the vessel with four 275 watt Chromalox heaters positioned in a heating block located outside of the chamber. Temperatures were measured in the heating block, the alkali metal and ~1 in. above the alkali metal surface.

After the metal was charged to the combustion vessel, the vessel was placed in the chamber and connected to the manipulating rods which permitted removal of the lid after the chamber had been sealed, the atmosphere adjusted and the metal heated to temperature. After the combustion vessel had been secured in the chamber, the access door was bolted in place. The chamber atmosphere was adjusted by either pumping down to the desired absolute pressure or replacing the atmosphere with the desired oxygen-inert gas mixtures. Gas samples were transferred to the mass spectrometer for atmospheric composition analyses. The heaters were turned on and the combustion vessel was heated to the desired temperature. The lid was then removed from the vessel and the alkali metal ignited. The run was allowed to proceed until the fire extinguished itself or the melt was completely combusted.

C. RESULTS

Table 3 lists the results on the effects of inert gas blanketing and oxygen partial pressures. The weight of the various metals was varied, depending upon which metal was being used, so that the ratio of air to metal was 10 times that required for complete combustion. The alkali metal weights varied from 100g of sodium to 600g of cesium. Initially, an attempt was made to analyze the gas remaining after combustion, but the quantity of gas consumed was too small to allow reliable analyses. Each metal was exposed to air in the chamber at 1 atm (oxygen partial pressure = 0.2 atm) and 0.1 atm (O_2 pp = 0.02 atm) and to atmospheres containing 50% air-50% Ar (O_2 pp = 0.1 atm) and 10% air-90% Ar (O_2 pp = 0.02 atm). After the combustion ceased, the residues were removed from the chamber and analyzed for residual free metal.

Lithium exposed to normal atmospheric conditions did not ignite at 540°F. When the metal was heated to 600°F, it did ignite and gave a maximum flame temperature, as measured 1 in. above the combustion vessel, of 1420°F. At 0.1 atm and with 50% Ar and 90% Ar, lithium did not ignite even when heated to 800°F.

Sodium at 500°F ignited immediately when exposed to normal atmospheric composition, with 78% of the metal consumed in the fire. The maximum flame temperature was 1100°F. A repeat run under these conditions showed 82% combustion and a maximum flame

TABLE 3- EFFECTS OF INERT GAS BLANKETING AND O_2 PARTIAL PRESSURES

Run No.	Metal	Temp. (°F)	Metal Burned (%)	Absolute Pressure (atm)	Oxygen Partial (atm)	Maximum Flame Temp. (°F)	Remarks
1	Li	540	76	1	0.2	1420	No ignition; pot heated to 600°F and metal ignited.
2	Li	560	--	0.1	0.02	--	No Reaction; surface 20% black.
3	Li	500	--	$1^{(2)}$	0.1	--	No ignition.
4	Li	500	--	$1^{(2)}$	0.1	--	No ignition, metal stirred.
5	Li	550	--	$1^{(3)}$	0.02	--	Small wisps of smoke; no reaction.
6	Na	500	78	1	0.2	1100	Sample ignited upon removal of lid.
7	Na	500	82	1	0.2	1170	Sample ignited upon removal of lid.
8	Na	500-800	--	0.1	0.02	--	No ignition; occasional sparking.
9	Na	500	--(73)	$0.1(0.8)^{(4)}$	0.02	1180	No ignition; air admitted to chamber with ignition at 0.8 atm.
10	Na	500	53	$1^{(2)}$	0.1	1030	
11	Na	480	--	$1^{(3)}$	0.02	--	No ignition.
12	K	500	79	1	0.2	800	Sample ignited.
13	K	500	86	0.1	0.02	700	No fire: wisps of smoke; slow oxidation.
14	K	500	49	$1^{(2)}$	0.1	750	
15	K	550	46	$1^{(3)}$	0.02	350	Metal on side of vessel reacting.
16	Rb	500	100	1	0.2	670	Smoke but no flame.
17	Rb	520	96	0.1	0.02	--	No fire; sides of pot and surface of metal turned black.
18	Rb	500	$100^{(1)}$	$1^{(2)}$	0.1	500	No fire; heavy smoke reaction around upper edge of pot.
19	Rb	480	$100^{(1)}$	$1^{(3)}$	0.02	200	No fire but heavy smoke.
20	Cs	500	$100^{(1)}$	1	0.2	620	Smoke but no flame.
21	Cs	525	$100^{(1)}$	0.1	0.02	300	No fire; white oxide on surface; oxide turned black.
22	Cs	480	$100^{(1)}$	$1^{(2)}$	0.1	240	No fire; small amount of smoke coming from side of pot.
23	Cs	480	$100^{(1)}$	$1^{(3)}$	0.02	150	No fire but a small amount of smoke coming from sides.

(1) No evidence of free metal

(2) 50% air - 50% argon

(3) 10% air - 90% argon

(4) No ignition occurred at 0.1 atm so air was admitted to the chamber with ignition at 0.8 atm.

temperature of 1170°F. At 0.1 atm sodium did not ignite but did emit an occassional spark. Air was slowly admitted to the chamber and the metal ignited at 0.8 atm with 73% of the metal consumed. In the 50% air-50% Ar mixture, sodium ignited and 53% of the metal burned; the flame temperature was 1030°F. No ignition occurred in the 10% air-90% Ar mixture.

Potassium at 500°F ignited when exposed to air at normal atmosphere composition with 79% of the metal consumed and a maximum flame temperature of 800°F. At 0.1 atm, the metal did not ignite but it did slowly oxidize. The maximum temperature above the metal was 700°F; 86% of the metal was oxidized. Potassium did not ignite in the 50% Ar and 90% Ar atmospheres but again it slowly oxidized with 49% consumed in the 50% Ar atmosphere and 46% consumed in the 90% Ar atmosphere. The temperature above the metal rose to only 350°F under the latter condition.

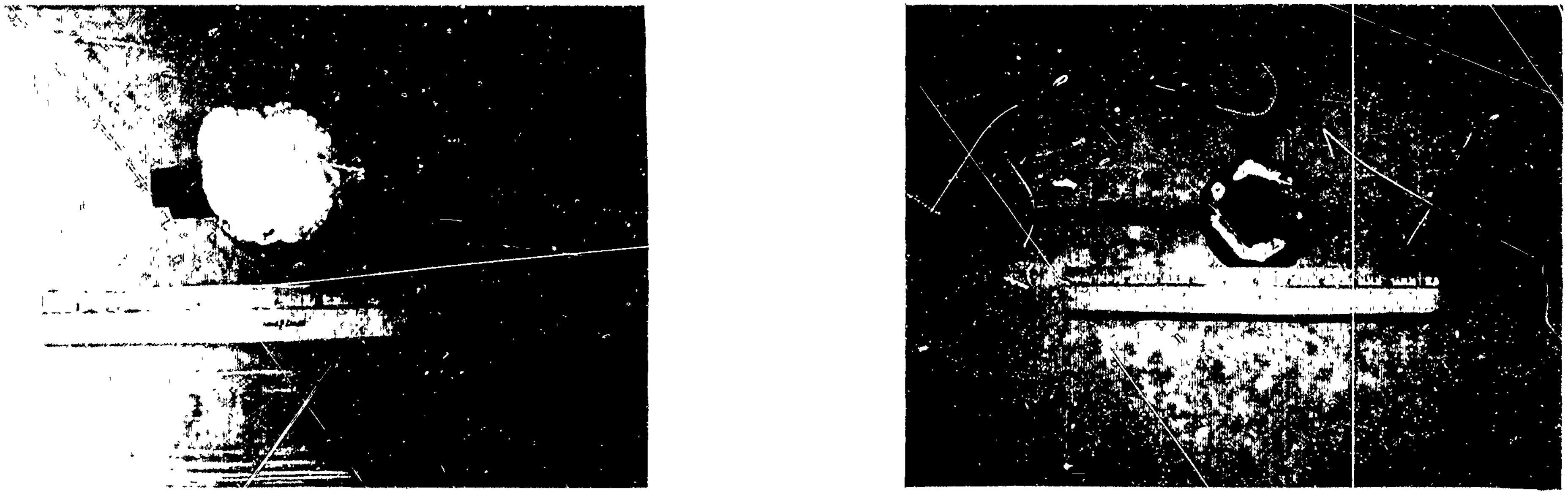
Rubidium at 500°F was completely consumed under all of the atmospheric conditions. However, the characteristic emission of light and dense oxide vapors normally associated with lithium, sodium and potassium fires were not evident with rubidium. Some smoke was given off, but no oxide was formed on the surface of the metal and there was no emission of light. The maximum temperature measured above the combustion vessel was 670°F. The residue after combustion was a dark brown to black mass and did not resemble a residue of lithium, sodium or potassium fires. Figure 2 shows a comparison of residues of the alkali metals.

Cesium behaved in a manner similar to rubidium. Little smoke and no emission of light was observed during oxidation of the metal. The metal was completely consumed and a maximum temperature of 620°F (under normal atmospheric conditions) was observed. With an atmosphere of 10% air-90% Ar, the metal was completely oxidized but the maximum temperature recorded above the combustion vessel was 150°F. Additional discussion of the oxidation characteristics of rubidium and cesium appears in the next section.

VI. EXTINGUISHMENT OF ALKALI METAL FIRES USING INORGANIC SALTS AND SALT MIXTURES (PHASE IV)

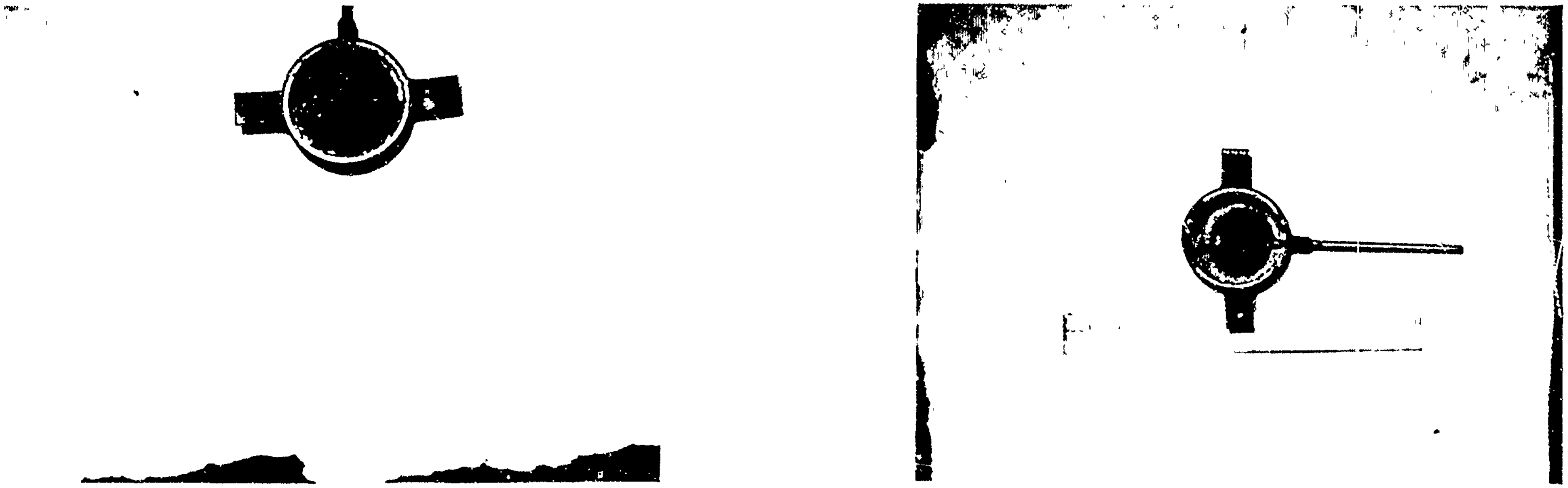
A. INTRODUCTION

The objective of this phase of the study was to evaluate various salts and salt mixtures as extinguishants for alkali metal fires. The effectiveness of these salts on potassium, rubidium and cesium fires was of particular interest since little data existed on the extinguishment of these alkali metal fires. Salts extinguish



Sodium

Potassium



Rubidium

Cesium

FIG 2 - FIRE RESIDUES

fires primarily by smothering the burning mass and excluding oxygen, although some cooling may be realized as a result of the heat absorbed during fusion of the salt. It is essential that these salts are absolutely dry and essentially non-reactive with the alkali metal. They must float on the liquid alkali metal or be suspended on the alkali metal oxide and must not be susceptible to burn-through.

It was recognized that a "standard fire" must be selected to compare the efficiencies of the various salts. Four combustion vessels with capacities of 0.1, 1.0, 10 and 100 pounds were fabricated and a number of preliminary tests were made to extinguish a standard fire size. Use of rubidium and cesium for the larger fires (over 1 lb) was not economically feasible. It was found that data generated with a 10 lb fire could be reliably extrapolated to larger fires although these extrapolations are more logically based on fire surface area rather than weight.

Prior to the experimental studies on this phase, Friedrich's(4) work on alkali metal fire extinguishment was reviewed. As a result of his work, several high boiling point organic liquids were evaluated in addition to the salts. Friedrich's work is summarized in Appendix III.

B. SELECTION OF SALTS TO BE USED ON ALKALI METAL FIRES

Salts to be used as extinguishants for alkali metal fires should exhibit certain characteristics. These characteristics include:

1. Non-reactive with the alkali metal
2. Melting points equal to or greater than the alkali metal flame temperature
3. Density less than the alkali metal density
4. Non-toxic

The ultimate salt would be one with a melting point equivalent to the flame temperature so that the salt in contact with the fire would fuse and form a "glass" crust over the metal. In this fashion, oxygen would be excluded from the fire.

It is also required that the salt be non-reactive with the alkali metal. A reactive salt could increase the temperature of the melt or, if explosively reactive, could spatter the alkali metal over a large area. One exception to this rule would be if the reaction products would form a fused coating over the raw metal.

A salt with a density less than the alkali metal is desirable since the salt would then float on the surface. Since the density of the alkali metals range from 0.534 gm/cm^3 for lithium to 1.873 gm/cm^3 for cesium, it is difficult to select a salt less dense than the alkali metals. Fortunately, the oxides of lithium, sodium, NaK and potassium form a coating on the metal surface thus minimizing this density requirement.

The desirability of non-toxic properties is obvious. This is particularly true in manned craft where dilution of the toxic vapors with large quantities of the ambient atmosphere is not feasible.

Table 4 lists a number of salts which were considered as potential candidates for alkali metal fire extinguishment. Table 5 lists a number of salt mixtures which were considered.

C. ESTABLISHMENT OF STANDARD FIRE

Four circular combustion pans were fabricated for this phase of the study. Typical configuration of these pans is shown in Figure 3. Characteristics of these pans are presented in Table 6. The pans were sized so that, when filled half way, they contained 0.1, 1.0, 10 or 100 lbs of metal. The surface to volume ratio was 0.65 to 0.69/1. By maintaining the same ratio in each pan, data from the various sized fires could be extrapolated either on the basis of surface exposed or weight of metal burning.

The pans were fabricated of 304 stainless steel and were instrumented with thermocouples to indicate the bulk metal temperature and the flame temperature. A typical run proceeded as follows:

1. Charge pan with alkali metal
2. Place lid on pan
3. Maintain metal under inert cover gas
4. Heat metal to 500°F
5. Remove lid
6. Allow fire to reach maximum flame temperature
7. Apply extinguishant
8. After fire was extinguished, rekindle and allow to burn to completion
9. Wash residue from pan with water.

Motion pictures were taken of all of the runs which were made and the research films are being submitted as part of the contractual agreements.

Initial efforts on debugging the equipment and establishing a standard fire were conducted with sodium metal. These results are presented in Table 7. Runs 1-307-1, 2-307-1 and 1-307-3 were made

TABLE 4 - SINGLE SALTS CONSIDERED FOR ALKALI METAL FIRE EXTINGUISHMENT

Extinguishant	M. P.(°C)	Specific Gravity	Reactivity(1)	Toxic Properties
Al_2O_3	2050	3.5	-	M
$Al_2(SO_4)_3$	770	2.71	-	H
$AlBr_3$	97.5	3.01	+	H
$AlCl_3$	190	2.44	+	H
B_2O_3	294	1.84	-	M
B_4C	-107	1.43	-	M
BN	3000 Subl.	2.20	-	M
BaO	1923	5.72	-	M
$BaCO_3$	1740	4.43	-	M
$BaBr_2$	847	4.78	+	M
$BaCl_2$	925	3.85	?	M
CaC_2O_4	d	2.2	+	M
$CaCO_3$	1339	2.71	-	S
CaF_2	1360	3.18	-	H
$CaBr_2$	765	3.35	+	H
$CaCl_2$	772	2.51	-	S
Cs_2CO_3	d610	--	+	U
Cs_2O	d360-400	4.36	+	U
$Cs_2C_2O_4$	--	--	+	H
CsF	684	3.58	-	H
CsBr	636	4.44	+	H
CsCl	646	3.97	-	U
CsI	621	4.51	+	H
$K_2C_2O_4$	d	2.127	+	H
K_2CO_3	891	2.428	-	H
K_2O	--	2.56	-	H
KBr	730	2.75	+	H
KCl	776	1.98	-	H
KI	723	3.13	+	H
K_2SO_4	588	2.66	-	H
KF	880	2.48	-	H
$Li_2C_2O_4$	d	2.121	+	H
Li_2CO_3	618	2.111	-	M
LiBr	547	3.464	+	H
LiCl	613	2.068	-	M
LiF	870	2.601	-	H
MgO	2800	3.58	-	M

TABLE 4 - Continued

Extinguishant	M. P.(°C)	Specific Gravity	Reactivity(1)	Toxic Properti
$Na_2C_2O_4$	?	2.34	+	H
Na_2CO_3	$-H_2O$ 850	2.25	-	M
Na_2SO_4	884	2.69	-	U
NaF	880-997	2.79	-	H
NaBr	755	3.20	+	H
NaCl	801	2.16	-	N
NaI	651	3.06	+	H
NH_4F	Subl.	1.31	+	H
NH_4Cl	Subl. 335	1.52	+	S
NH_4Br	Subl. 542	2.42	+	H
NH_4I	Subl. 551	2.51	+	M
Rb_2O	400	3.72	-	H
Rb_2CO_3	837	--	-	H
RbBr	682	3.35	+	H
RbCl	715	2.76	-	U
RbF	760	2.88	-	H
RbI	642	3.55	+	H
SiO_2	1710	2.32	+	M
SiC	2600 Subl.	3.21	-	S
$SrCO_3$	1497	3.70	-	S

(1) + indicates probable reaction; - no reaction

Toxicity Rating Code-Acute Inhalation Only

N - None
S - Slight
M - Moderate
H - High
U - Unknown

Oxalates - Corrosive, produces local irritation, dangerous fumes when heated (3).

Fluorides - Very toxic, acute effects due to HF (3).

Bromides - Toxic fumes when strongly heated; can produce depression, emanciation, psychoses, rashes (3).

Iodides - Toxic fumes of iodine when heated (3).

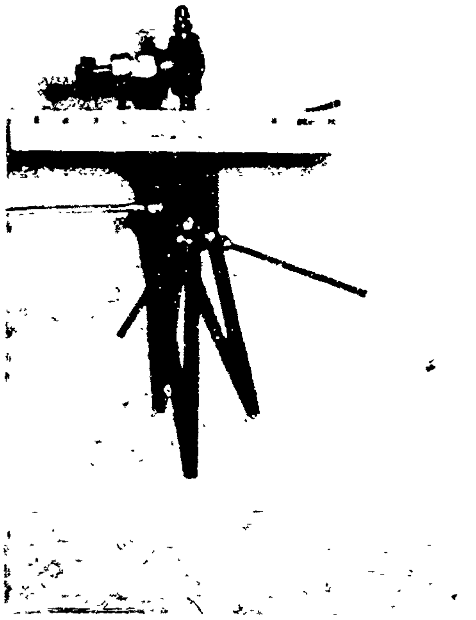
Chlorides - Vary widely, as NaCl has low toxicity and $COCl_2$ is very toxic. Can combine with H_2 to give toxic HCl fumes.

TABLE 5 - SALT MIXTURES

Salt Mixtures (Wt. %)	M. P. (°C)	Toxic Properties
43.87 NaCl - 56.13 $AlCl_3$	110	H
15.45 NaCl - 84.54 $CsCl_2$	490	U
71.79 NaCl - 28.21 LiCl	552	M
27.34 NaCl - 72.66 $MgCl_2$	450	M
50 LiCl - 50 KCl	287-323	M
33 LiCl - 33 KCl - 33 CsCl	425	M
50 LiCl - 50 KCl - 5 CsCl	287-323	U
50 LiCl - 50 KCl - 10 CsCl	287-323	U
57.02 LiCl - 42.98 KCl	443	M
2237 LiCl - 77.03 KCl	350	M
73 LiCl - 27 $BaCl_2$	510	M
62 LiCl - 38 $CaCl_2$	496	M
40 LiCl - 60 Li_2CO_3	506	M
79.42 LiCl - 20.58 $BaCl_2$	510	M
20 LiCl - 80 LiF	485	H
75 LiCl - 25 LiBr	520	H
12 LiBr - 88 LiF	453	H
26.77 LiF - 73.23 Li_2MoO_4	620	H
75 LiF - 25 Li_2CO_3	604	H
30.87 LiF - 69.13 KF	492	H
28.32 LiF - 71.68 NaF	652	H
5.17 LiF - 94.83 AlF_3	720	H
27.42 LiF - 72.58 KF	492	H
25.52 Li_2O - 74.48 B_2O_3	620	M
73 NaBr - 57 Na_2SO_4	625	H
22.49 NaBr - 77.51 CsBr	460	H
32 NaI - 68 CsI	435	H
6.5 NaCl- 93.5 CsF	615	H
40.75 NaF - 59.25 KF	710	H
47.76 $CuSO_4$ - 52.24 K_2SO_4	460	M
52.91 $CuSO_4$ - 47.09 Na_2SO_4	500	M

TABLE 5 - Continued

Salt Mixtures (Wt. %)	M. P. (^oC)	Toxic Properties
21.26 KCl - 78.74 $BaCl_2$	655	M
25.31 $(KPO_3)_2$ - 74.69 K_2SO_4	718	M
36.85 KCl - 63.15 $HgCl_2$	182	H
30 KBr - 70 K_2SO_4	660	H
45 K_2MoO_4 - 55 MoO_3	465	S
25 MoO_3 - 75 Na_2O	499	H
43 MoO_3 - 56.37 Na_2O	552	H
62.34 MoO_3 - 37.66 K_2O	470	H
70.17 Cs_2O - 29.83 MoO_3	460	U
75 $CdBr_2$ - 25 $ZrBr_2$	364	H



IG 3a - CONTAINER FOR 0.1 LB
ALKALI METAL FIRES

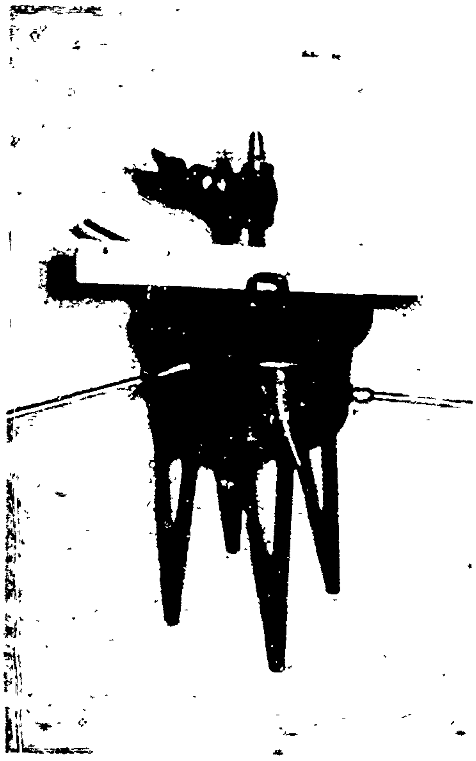


FIG 3b - CONTAINER FOR 1.0 LB
ALKALI METAL FIRES

FIG 3 - EXPERIMENTAL APPARATUS FOR ALKALI METAL
FIRE FIGHTING STUDIES

TABLE 6 - CHARACTERISTICS OF COMBUSTION PANS

Pan Dia. (in)	Cross Sectional Area (in^2)	Weight of Metal (lbs)$^{(1)}$	Volume of Metal (in^3)	Surface to Volume Ratio (S/V)
1.6	2	0.1	2.9	0.69
5	19.6	1.0	29	0.68
15.5	189	10	290	0.65
51	1950	100	2940	0.66

(1) Based on Na

TABLE 7 - SELECTED DATA ON ALKALI

Run No.	Metal	Temp. (°F)	R. H. (%)	Wind Vel. (ft/min)	Weight of Metal (lbs)	Time to Reach Max.Temp. (Min.)	Max. Temp. (°F)	Extinguishant
1-307-5	Na	500	46	400	10	37	1370	Met-L-X
2-307-5	Na	500	58	200	10	9	1160	Met-L-X
1-307-10	Na	500	60	250	100	27	1620	Met-L-X
3-307-13	Na	500	8	70	10	10	1000	Met-L-X
6-307-5	Li	500	55	0-30	1	7	2000+	Met-L-X
7-307-5	Li	500	60	0-5	1	8	2000+	Met-L-X
7-307-5	Li	500	40	0-20	1		2000+	ABC (Met-L-X)
6-307-8	Cs	500	32	170	0.1	6	620	Met-L-X
5-307-5	K	500	32	180	10	28	1000	Met-L-X
3-307-5	Na	500	54	200	10	13	1140	Purple K
4-307-5	Na	500	54	200	1	15	1160	Carbon Wool
9-307-9	Na	500	58	75	10	7	1280	Graphite
2-307-6	Na	500	40	40-100	10	10	1360	Na_3PO_4
5-307-8	Na	500	32	170	1	4	1130	Na_3PO_4
3-307-7	Na	500	40	40-100	10	5	1520	$Na_4P_2O_7$
7-307-8	Na	500	46	350-400	10	10	1290	$Ca_3(PO_4)_2$
8-307-9	Na	500	30	--	10	12	1320	$Ca_3(PO_4)_2$
3-307-7	Na	500	41	100	1	8	1140	NaF
3-307-7	Na	500	41	100	1	2	1260	NaCl
4-307-8	Na	500	42	170	1	4	1280	KF
4-307-8	Na	500	42	170	1	3	1080	KCl
3-307-7	Na	500	41	100	1	5	1180	LiI
3-307-7	Na	500	41	100	1	4	1230	LiCl
3-307-7	Na	500	41	100	1	2	1130	LiBr
4-307-8	Na	500	42	170	1	10	1240	KBr
7-307-8	Na	500	46	350-400	10	17	1520	Al_2O_3
7-307-8	Na	500	46	350-400	10	26	1410	$AlCl_3$
8-307-9	Na	500	30	--	10	15	1500	$CaSO_4$
9-307-9	Na	500	58	75	10	4	1310	B_2O_3
4-307-12	Na	500	28	0-60	10		1200	Lithium Fluoride
2-307-15	Na	500	-	60	10	5	1580	TIC Powder
	Na	500	-	60	10	5	1380	TIC Powder
	NaK	500	-	120	10	4	1220	TIC Powder
	K	500	-	100	10	5	1180	TIC Powder
	Li	500	-	250	10	8	2000	TIC Powder
2-307-10	Na	500	68	0-40	10		1020	Isopropyl Biphenyl & CO_2
3-307-10	Li	500	68	0-40	10		1420	Isopropyl Biphenyl & CO_2
2-307-11	Na	500	54	75	10	12	1020	Mineral oil
6-307-11	Na	500	48	500-600	10	15	1320	Tetrahydronapthalene
7-307-11	Na	500	48	500-600	10	8	1300	90% Tetrahydronapthalene 10% Bromochloromethane
8-307-11	Na	500	48	500-600	10	7	1250	90% Isopropyl Biphenyl 10% Bromochloromethane
1-307-12	Na	500	40	200	10	5	1280	80% Isopropyl Biphenyl 20% Bromochloromethane
2-307-12	Na	500	32	40-110	10	5	1180	80% Isopropyl Biphenyl 20% Bromochloromethane
1-307-13	Na	500	66	0-70	1	4	1160	80% Isopropyl Biphenyl 20% Bromochloromethane
3-307-12	Na	500	28	0-60	10		1150	Biphenyl
2-307-13	Na	500	40	345	0.1		800	Bromochloromethane
1-307-11	Na	500	42	0-5	10	12	950	Sodium Stearate
5-307-12	Na	500	58	80	10	5	1000	Sodium Stearate
3-307-13	Li	500	38	280	10	12	1600	Sodium Stearate

METAL FIRE EXTINGUISHANTS

Quantity of Extinguishant	Time to Extinguish (min.)	Method of Application	Comments
7#	1.25	Extinguisher	Fire extinguished, burns through in 2 min.
4#	0.8	Shovel	Fire extinguished, burns through in 2 min.
80#	3.5	Extinguisher	30# extinguisher insufficient, 150# unit extinguished fire.
2#	1	Shovel	Extinguished quickly, no burn through.
13#	---	Shovel	Extinguishant tends to sink.
3#	1	Shovel	Secondary sodium flames.
2#	---	Shovel	Violent reaction.
-	---	Shovel	Extinguishant sinks, but metal cools.
18#	1.75	Extinguisher	Extinguishes.
5#	---	Shovel	Some reaction, does not extinguish.
	---	Shovel	Carbon wool enhances combustion.
6#	1.25	Shovel	Covers well, but fire burns through in 2-3 minutes.
6#	0.25	Shovel	Extinguishes but later reignites.
2#	0.5	Extinguisher	Fire put out quickly, but burns through after 5 minutes.
6#	---	Shovel	Reaction.
-	---	Shovel	Reacts.
-	---	Shovel	Does not extinguish.
-	---	Shovel	Does not extinguish.
-	---	Shovel	Extinguishes, reignites
-	---	Shovel	Some reaction, does not extinguish.
-	---	Shovel	Extinguishes, but fire burns through in a few seconds.
-	---	Shovel	Extinguishes but fire burns through.
-	---	Shovel	Extinguishes but fire burns through.
-	---	Shovel	Initial flare up, does not extinguish.
-	---	Shovel	Reacts with burning metal.
-	---	Shovel	Does not extinguish.
-	---	Shovel	Reacts.
-	---	Shovel	Reacts.
-	---	Shovel	Reacts.
3#	1	Shovel	Extinguished very quickly, no burn through.
2#	0.5	Shovel	Extinguished; no burn through
2.5#	1.0	Extinguisher	Extinguished.
2.5#	0.5	Shovel	Extinguished.
3.0#	1.0	Shovel	Extinguished after oxide coating formed.
-	---	Shovel	Did not extinguish.
-	---	Tubing	Extinguished Na fire; secondary fire extinguished with CO_2.
-	---	Tubing	Did not extinguish.
12 liters	---	Tubing	Drop temp., but does not extinguish.
1 liter	---	Tubing	Does not extinguish.
1 liter	---	Tubing	Does not extinguish.
1 liter	---	Tubing	Does not extinguish.
1 liter	---	Tubing	Put out fire but sodium came to surface and reignited.
2 liters	---	Tubing	Put out fire but sodium came to surface and reignited.
1 liter	3	Tubing	Surface was flooded, fire extinguished.
2.2#	---	Shovel	Rapidly consumed, no effect on fire, small temperature drop.
0.5 liter	---	Tubing	Reacts.
2#	9	Shovel	Extinguished fire; secondary flash fire.
3#	5	Shovel	Extinguished but with flash secondary fire which died quickly.
6#	---	Shovel	Did not extinguish, molten Li came through crust.

with 0.1 lb charges of sodium in a 1.6 in. dia pan. The oxide which formed as a result of combustion rapidly formed a crust over the surface of the metal and the fire was self-extinguishing. The maximum flame temperatures were 780 to 950°F; when the surface crust was broken and the metal agitated, a flame temperature of 1480°F was attained.

Runs 2-307-2, 3-307-2 and 2-307-5 were made with 1 lb charges of sodium in a 5 in. dia pan. Although these fires were not self-extinguishing, the flame temperatures rose to only 1200-1420°F; it was predicted that the flame temperature should go as high as the boiling point of sodium (1600°F).

Runs 1-307-2 and 4-307-2 were made with 10 lb charges of sodium in a 15.5 in. dia pan. The flame temperatures were 1710°F and 1550°F, respectively. There were no signs of self-extinguishment with the 10 lb fires.

Run 1-307-10 was made with a 100 lb charge of sodium in a 51 in. dia pan. The flame temperature was 1620°F and time to reach the maximum temperature was 27 min; the 10 lb fires reached the maximum temperature in 6-14 min.

The criteria selected to determine whehter results with a certain size fire could be extrapolated to larger fires were:

1. That the fire would not be self-extinguishing.
2. That the flame temperatures would be similar.

On the basis of these results, it was felt that results from a 0.1 lb fire could not be extrapolated to larger fires since the fire could be self-extinguishing and the flame temperature could be 600-800°F lower than a large fire. The 1 lb fires were not self-extinguishing, but the flame temperatures were 300-400°F lower than the larger fires. Flame temperatures were the same for 10 and 100 lb fires, and there was no evidence of self extinguishment. Thus a 10 lb fire was selected as the standard fire size. Some of the later screening studies were made on 1 lb fires, but the primary objective of these fires was to establish whether there was a reaction between the extinguishant and the burning alkali metal.

D. CHARACTERISTICS OF OTHER ALKALI METAL FIRES

1. NaK Fires - A 1 lb NaK fire was ignited and the flame temperature reached 1040°F in 13 min. The crust formed on the NaK surface was similar to that formed on sodium fires, although initially there is a tendency for the resultant oxide to go into solution in the molten metal. A large scale fire (100 lb NaK)

resulted in a maximum flame temperature of $\sim$1450°F. On the basis of past experience, sodium and NaK fire characteristics are essentially identical except that NaK is liquid at room temperature. Therefore freezing does not serve to quell leakage of NaK from a system or inhibit the flow of metal across the surface onto which NaK has leaked.

2. Potassium Fires (K) - A 1 lb potassium fire was ignited at 500°F and the flame temperature reached a maximum of 1240°F in 11 min. Initially, no massive oxide film was formed on the surface, although there was visual evidence of oxide being formed and then going into solution in the potassium melt. The solubility of K_2O in potassium has been measured as 0.5% at 527°F. A surface oxide did form after $\sim$10 min of oxidation; this probably was a result of the melt being saturated with K_2O. Lack of oxide crust formation on the surface caused some concern with respect to fire extinguishment since the oxide crusts in sodium, lithium and NaK fires served to support the extinguishing salts.

3. Lithium Fires (Li) - A 1 lb lithium fire was ignited at 500°F and the flame temperature reached 1780°F in 6 min. The light emitted from a lithium fire is brighter than any of the other alkali metal fires and can best be described as a brilliant white. The oxide which was formed migrated up the inner wall of the vessel and down the outside wall bridging the space between the pan and the ground, a distance of $\sim$12 in. Free metal was drawn into the oxide by a wicking action and the oxide bridge ultimately acted as a siphon and drained metal from the pan. The oxides formed during sodium and NaK fires also wick up free metal and have a tendency to climb over the side of the containment vessel. Subsequent lithium fires demonstrated that the oxide will invariably migrate over the walls of the vessel. Lithium was the most corrosive of the alkali metals and the tops of the combustion pans where the oxide concentrations were the highest were generally corroded through the wall thickness (1/4 in.) in one fire.

4. Rubidium Fires (Rb) - A 0.1 lb rubidium fire was ignited at 500°F and reached a maximum temperature, above the melt, of 600°F in 8 min. The characteristics of this fire were completely contrary to all predictions made for rubidium fires. When the lid was removed from the 500°F melt, a reaction at the alkali metal-air interface was evident. However, the melt retained a mirror surface and there was no evidence of oxide crust formation or flame. Small wisps of smoke were emitted but these originated at the walls of the vessel where oxide particles were formed occasionally. The temperature of the melt rose to a maximum of 800°F and then slowly receded to ambient temperature. The resultant combustion products were a hard, solid black mass.

5. Cesium Fires (Cs) - Three cesium fires were ignited at 500°F - two 0.1 lb and one 1 lb fire. The vessels were heated to 500°F and the lids removed and, as with rubidium, the fires behaved differently from what was predicted. No visible flames were present and the maximum temperature was 880°F. Cesium pipetted from the vessel with a stainless steel tube and dropped through the air into the vessel ignited during descent but did not cause ignition in the vessel. To assure that a sufficient supply of oxygen was available, a stream of oxygen from an oxy-acetylene torch was directed onto the surface of the metal. Although there were no visible flames, the temperature of the melt rose to 1500°F at the surface. Comparison of the sodium and cesium fires indicates that the oxide formation on the surface aids in combustion. The oxide apparently acts as a wick, drawing the alkali metal to the surface and exposing a larger surface area and at the same time presenting a small heat sink compared to the bulk of the metal. The solubility of oxygen in cesium at the melting point is $\sim$3 wt % oxygen and at 1000°F it is reported that cesium and Cs_2O are miscible in all proportions. A review of the solubility of the oxide in the parent metal suggest burning characteristics of the metals are a function of oxide solubility:

Metal	Free Energy of Formation of Oxide at 1500°F (Kcal/gram-atom O_2)	Solubility of Oxide(wt%)
Li	-109	0.05 at 700°F
Na	- 63	0.04 at 700°F
NaK	-----	0.02 at 700°F
K	- 52	0.25 at 400°F
Rb	- 42	Unknown, probably high
Cs	- 32	3 at 80°F

If the wicking action of the oxide is an important mechanism in alkali metal combustion, these values suggest that lithium, sodium and NaK should burn easily, potassium less easily and rubidium and cesium with great difficulty. Results indicate such to be the case.

During oxidation the surface of the cesium metal retained a mirror finish and the color of the melt progressed from gold, to orange to brown to black. The residue from the cesium fires was a black solid melting at 700°F with an apparent density of 4.67 gm/cc. The melt contained corrosion products from the container wall. The residue reacted with water, releasing oxygen; quantitative measurements of the off-gases indicate the residue was primarily Cs_2O_4. A Kjehdahl analysis indicated no nitrogen in the sample.

Cesium metal was spilled across a metal surface and there was instantaneous ignition with emission of light and smoke. However, the combustion reaction was not self-sustaining although the exposed metal continued to oxidize. A similar spill was covered immediately with Ansul Met-L-X and further reaction was inhibited.

E. RESULTS OF EXTINGUISHMENT TESTS

Table 7 lists selected runs which were made with various alkali metal fire extinguishing agents. Figure 4 shows a typical procedure for these extinguishment studies. In all cases, the metal was preheated to 500°F, the lid was removed and the metal allowed to ignite spontaneously. Salts were added either from an extinguisher or with a shovel. Liquids were applied through tubing from pressurized containers. The time to extinguish is defined as that time required to completely cover the fire and eliminate all signs of flames.

The first tests were made with sodium using Ansul's Met-L-X both with an extinguisher and with a shovel. A 10 lb sodium fire was extinguished in 1.25 min with 7 lb of Met-L-X from an extinguisher. A similar fire was extinguished in 0.8 min with 4 lb of Met-L-X applied with a shovel. In both cases, the fire burned through the crust in about 2 min, but this was easily extinguished by additional application of the salt. Met-L-X was also applied to a 100 lb sodium fire; the fire was extinguished in 3.5 min with 80 lb of extinguishant. The weight and surface area were both a factor of 10 greater with the 100 lb fire compared to the 10 lb fire. Seven pounds of Met-L-X from a pressurized extinguisher were required to extinguish a 10 lb sodium fire and 80 lb were required to extinguish a 100 lb fire. The time required for extinguishment was 1.25 min for the 10 lb fire and 3.5 min for the 100 lb fire. Application with a shovel requires a smaller amount of extinguishant, 2-4 lb for a 10 lb fire.

Met-L-X was applied to a lithium fire with a shovel. The extinguishant tends to sink in lithium but the fire was extinguished. A secondary sodium fire ensues because of the reduction of NaCl with lithium. However, this fire is controlled with additional application of extinguishant. The first fire (6-307-5) was difficult

FIG 4a - HEATING Na TO 500°F

FIG 4b - IGNITION OF Na

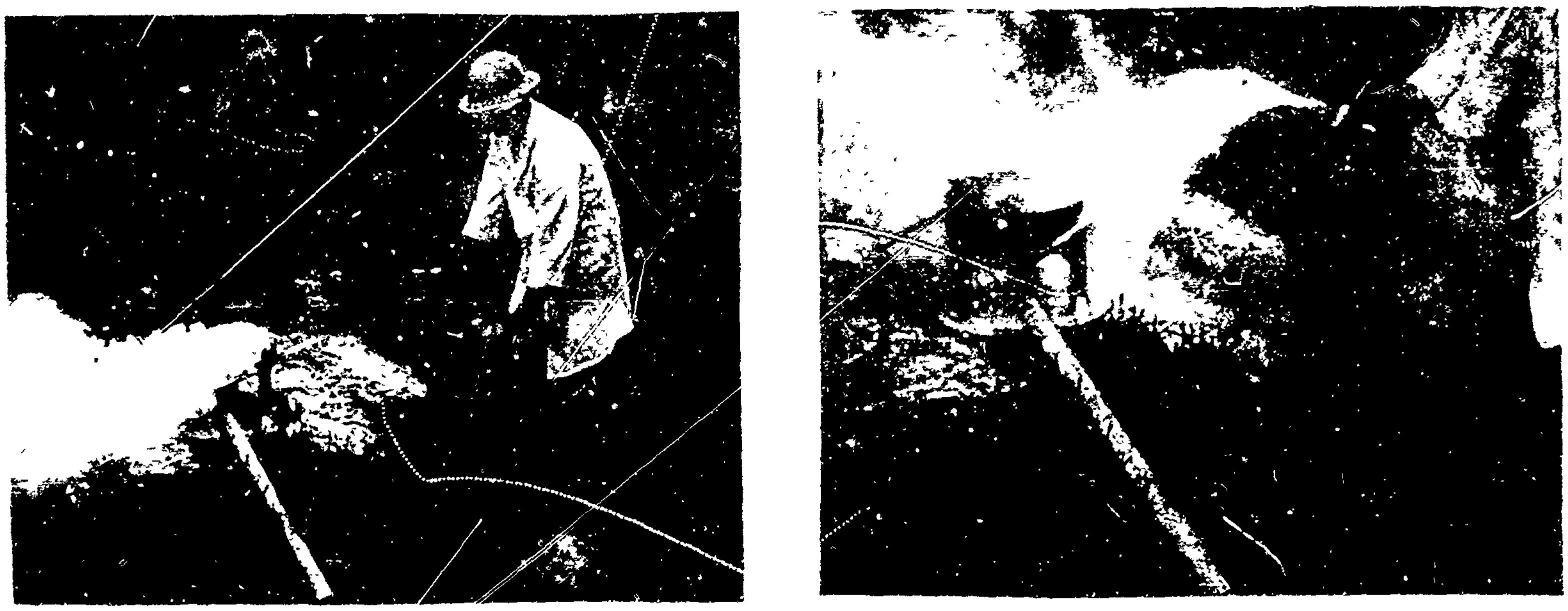


FIG 4c - BEGINNING OF EXTINGUISHMENT

FIG 4d - COMPLETION OF EXTINGUISHMENT

FIG 4 - EXTINGUISHMENT OF A 10 LB Na FIRE WITH ANSUL MET-L-X to extinguish because the oxide had migrated over the edge of the fire pan and this site served as a locus of reignition; 13 lb of extinguishant were required. The second fire was contained within the pan and only 3 lb of extinguishant were required.

A dry chemical marketed by Ansul Co., ABC Powder, for use on Class A, B and C fires reacted explosively with lithium and sodium. Subsequent application of Met-L-X extinguished the fire.

Met-L-X was applied to a 0.1 lb charge of cesium which had been heated to 500°F and exposed to the atmosphere. The extinguishant sank to the bottom of the fire pan since there was no oxide formed to support it. A small quantity of the hot cesium was poured onto a metal surface. When dispersed over this large surface area, the cesium did ignite. Met-L-X was applied and the fire was extinguished. Graphite was applied to a similar fire but did not extinguish the fire.

A 10 lb charge of potassium was heated to 500°F and exposed to the atmosphere. When the temperature reached a maximum of 1000°F, Met-L-X was applied although no oxide had formed on the surface. The extinguishant sank to the bottom of the pan. After 15 minutes, an oxide crust began to form on top of the potassium. Met-L-X was again added and the fire was extinguished but 18 lb of extinguishant was required. Graphite was added to a potassium fire under similar conditions and did not extinguish the fire. It appeared that there was some reaction between the potassium and graphite.

Purple K, a trade name for a $KHCO_3$-based powdered extinguishant, which has been used on natural gas and combustible organic fires with success was applied to a sodium fire. There was a reaction between the sodium and $KHCO_3$ and the fire was not extinguished.

ENT

Since graphite has been used to extinguish sodium fires, it was decided that carbon wool would be applied to a sodium fire. Powdered graphite extinguished a sodium fire, but burned through in $\sim$2 min. Additional graphite was added and the fire was extinguished. Carbon wool is made by carbonizing natural organic fibers and is essentially 100% carbon. The attractive feature of an extinguishant such as this is that it could be applied in layers on the fire surface or on insulation when a fire is located on the plumbing of a system. However, carbon wool was ineffective in extinguishing a sodium fire and in fact enhanced combustion since it acted as a wick and exposed a greater surface area of metal.

A number of inorganic salts were considered as potential alakli fire extinguishants. These were screened on 1 lb and 10 lb sodium fires and included Na_3PO_4, $Na_4P_2O_7$, $Ca_3(PO_4)_2$, NaF, NaCl, KF, KCl, LiF, LiCl, LiBr, KBr, Al_2O_3, $AlCl_3$, $CaSO_4$, B_2O_3 and TEC Powder. TEC Powder, a ternary eutectic compound, has been developed in England for extinguishment of zirconium, uranium and other reactive metal fires. The salts which showed the most promise were Na_3PO_4, NaCl, LiF, LiCl, KCl and TEC Powder. Of these most promising salts, NaCl, Na_3PO_4 and LiCl exhibited the greatest resistance to burn through. LiCl seemed to cover the fire and it extinguished it more rapidly than did NaCl or Na_3PO_4. However, the difference was not sufficiently great to justify the cost of LiCl versus NaCl.

When $Na_4P_2O_7$ was applied to the fire, an explosive reaction occurred. This was due to the oxygen available in the sodium pyrophosphate molecule. Potassium bromide reacted with the burning sodium probably by the reduction of KBr and formation of NaBr. Lithium bromide did not have any reaction with sodium, but it did not extinguish the fire. The $Ca_3(PO_4)_2$ exhibited slight reaction with the burning sodium and did not extinguish the fire. Aluminum oxide did not extinguish the sodium fire and $AlCl_3$ reacted explosively.

TEC Powder was used on a sodium fire. With a 10 lb sodium fire, 2 lb of the powder applied with a shovel extinguished the fire in 0.5 min and there was no burn through. With an extinguisher, a similar fire was extinguished in 1 min with 2.5 lb of the powder. The powder also is capable of extinguishing NaK fires, with 2.5 lb applied by shovel extinguishing the fire in 0.5 min; there was no burn through. When applied to a freshly ignited potassium fire with no oxide on the surface, the powder sank to the bottom of the fire pan and did not extinguish the fire. After $\sim$12 min, an oxide crust formed on the surface of the potassium fire; TEC Powder applied to this crust extinguished the fire. The powder was ineffective on lithium fires due to the excessively high temperature (2000+°F) which caused this powder to melt. The powder was also effective on 100 lb and 500 lb sodium fires; this will be discussed in a later section.

In light of Friedrick's work$^{(4)}$ with organic liquids on 100 gram alkali metal fires, it was decided that some of these fluids should be evaluated on larger fires. The procedure was to pressurize the vessel containing the liquid and to deliver the liquid to the fire surface through a 5/16" copper tube. Isopropyl biphenyl was used on a sodium fire which had reached a temperature of 1020°F. A layer of liquid $\sim$3 in. deep was applied to the burning surface. A secondary isopropyl biphenyl fire ensued but this was extinguished with CO_2. A second sodium fire reached 1420°F before the isopropyl biphenyl was applied. In this case, the fire was extinguished momentarily, but reignited. Application of CO_2 to the burning liquid did not prevent reignition of the alkali metal fires.

Mineral oil was applied to a 1020°F sodium fire. A total of 12 liters was added to the fire, but the fire was not extinguished.

Tetrahydronaphthalene was applied to 1320°F sodium fire. A secondary fire ensued and the alkali metal fire was not extinguished. Addition of 10% bromochloromethane was not effective in extinguishing the secondary tetrahydronaphthalene fire and the alkali metal fire continued to burn.

A mixture of 90% isopropyl biphenyl and 10% bromochloromethane was applied to a 1250°F sodium fire. The alkali metal fire was not extinguished and the secondary fire continued to burn until all of the isopropyl biphenyl was consumed. A mixture of 80% isopropyl biphenyl and 20% bromochloromethane momentarily extinguished an 1180°F sodium fire, but it reignited. The same composition used on an 1160°F sodium fire successfully extinguished the burning mass. Pure bromochloromethane reacted violently with an 800°F sodium fire.

Biphenyl was added to 1150°F sodium fire but was ineffective and rapidly consumed. Sodium stearate extinguished a 950°F sodium and a 1000°F sodium fire. Biphenyl was ineffective on a 1[illegible]0°F sodium fire and was rapidly and completely consumed when applied to a 1600°F lithium fire.

A number of fluoroalkyl esters have been formulated for the Air Force recently.(5) These are being considered as possible extinguishants for exotic propellant and/or metal, particularly magnesium fires. Three of these esters were evaluated on 10 lb sodium fires. The addition of 3 oz of fluoroalkyl sulfite ester to sodium reacted violently and blew all of the sodium from the pan. A similar reaction occurred when the fluoroalkyl phosphate ester was added to burning sodium. The fluoroalkyl borate ester did not react with the alkali metal, but the characteristic green flame of boron was observed in the secondary fire. A total of 3-3/4 lb was added but the alkali metal fire was not not extinguished. In fact, the addition of this material caused a temperature rise in the bulk alkali metal.

F. SUMMARY

The results from this phase of study indicated some promising extinguishants for alkali metal fires. Met-L-X efficiently extinguishes sodium, potassium and NaK deep pool fires. If Met-L-X is applied to a deep pool potassium fire before the oxides of potassium have formed on the surface, the extinguishant sinks to the bottom and is not effective. After the crust has formed, the extinguishant can be applied and it will extinguish the potassium fire. The weight ratio of extinguishant/alkali metal is 0.4/1 for shovel application and 0.72/1 by extinguisher application. With a 100 lb sodium fire, 80 lb of Met-L-X was required to extinguish the fire at a ratio of 0.8/1 or the same as with the 10 lb fire. The ratio for potassium extinguishant was 1.8/1.

Typical extinguishing times for quiescent burning pools of sodium were 1-2 min. In an actual alkali metal fire, the extinguishing time could be significantly longer since burning alkali metal may be dripping from a leak in the system or the metal may not be completely contained within the drip pan. In such cases, it is impossible to predict extinguishing times.

Deep pools of rubidium and cesium do not ignite, hence extinguishment is not required. When extinguishant is added to these oxidizing pools, it sinks to the bottom. Oxidation of deep pools of these metals are best controlled by smothering using a lid over the vessel where the metal is contained. When rubidium and cesium are spread over a large surface area, these metals do ignite and burn. This type of fire can be quelled by the addition of Met-L-X. Met-L-X was ineffective in controlling lithium fires. The NaCl was reduced and a sodium fire ensued. Graphite proved to be the best extinguishant for lithium fires.

Met-L-X has a tendency to burn through, however, reignition can be controlled by application of additional extinguishant. Burn through is preceeded by a darkening of the salt surface, hence additional application can be made before actual burn through occurs. TEC Powder was less susceptible to burn through.

TEC Powder proved effective on sodium, potassium and NaK pool fires as well as thin burning films of rubidium and cesium. The amount of TEC Powder required to extinguish these fires was slightly less than the amount of Met-L-X required with the ratio of extinguishant to sodium metal being 0.25/1.

Of the many salts that were evaluated, LiF seemed to be the most promising. The quantity required for extinguishment of 10 lb fires was approximately the same as Met-L-X or TEC Powder. LiF was resistant to burn through. One aspect which remained to be evaluated was the reliability of the data with respect to larger fires. This study is described in a later section.

Organic liquids showed some promise in extinguishing alkali metal fires but a secondary fire always ensued. Addition of bromochloromethane to the extinguishant reduced the possibility of a secondary fire, although it was not eliminated in all cases. It appears impractical to use an organic liquid on alkali metal fires since the secondary fire which may occur can be more severe than the alkali metal fire.

VII. INORGANIC SALT FOAMS

A. INTRODUCTION

The objective of this phase of study was to evaluate the use of inorganic salt foams as extinguishants for alkali metal fires. The advantages of a salt foam over a salt blanket are that less salt would be required for extinguishment and the foam would be self-supporting and therefore less susceptible to sinking in the alkali metal pool. A number of foam manufacturers were contacted for information on the generation of inorganic foams but these firms were familiar only with water based foams. These are stabilized with hydrolyzed protein but would not be suitable for use on alkali metal fires because of the violent reaction with water.

As an alternative to inorganic salt foams, it was decided that a polyurethane foam would be evaluated. It was recognized that these foams are susceptible to combustion, but additives are available which impart some fire retardant characteristics to the foam. Furthermore, since the foam is a good thermal insulater, it is possible for degradation to occur at the foam-alkali metal interface, with the formation of a charred carbon layer at the interface.

B. EXPERIMENTAL RESULTS

Initial tests were performed by preforming a solid mass of foam and placing the mass on the surface of a sodium fire. The foam did degrade at the interface but the fire was extinguished. However, the foam was somewhat susceptible to burn through. From a practical standpoint, it would be necessary to apply the foam in its semi-liquid form to the burning fire.

Some efforts were made at developing a suitable foam generating and applicating system. The system consisted of 2 containers (one for activator and one for resin), a solvent container, connecting plumbing and a mixing and applicating nozzle. Two major problems were encountered with this system. First, it was difficult to meter precisely the required quantities of the reactants and secondly, the nozzle did not provide complete mixing of the reactants. A number of modifications were made on the nozzle including injection of the reactants tangentially with the activator and resin inlets 180° apart, installation of a convoluted strip of metal in the nozzle and variation of nozzle size and geometry. It was concluded that design and fabrication of a suitable applicating system would be expensive and was not a part of the contract. Therefore, a commercially available foam system was purchased.* This unit was equipped with positive displacement proportioning pumps. The applicating nozzle was equipped with an air driven mixing motor which thoroughly mixed the reactants.

Initial tests with this system on sodium fires were promising. The foam was applied to 10 lb sodium fires and low temperature fires were selected for the initial tests. A sodium fire at 700°F was extinguished in 2 min with an application of 1 cu ft of foam. Burn through occurred at the edge of the pan in $\sim$2 min but this was quickly extinguished with additional application of foam.

At 1000°F surface temperature, the fire was more difficult to extinguish but the fire was finally brought under control in $\sim$4 min. Burn through occurred in $\sim$30 sec, but addition of fresh foam to these areas resulted in complete extinguishment of the fire. Potassium and NaK fires were also extinguished at 1000°F with essentially the same characteristics as the sodium fires. Rubidium and cesium in quiescent burning pools were also extinguished with the foam.

Lithium fires at 1000°F could not be extinguished with the foam and above 1000°F sodium, potassium and NaK fires could not be extinguished. Above 1000°F, the foam spray was degraded before it contacted the burning alkali metal surface. It appears that the polyurethane foam would be useful if application could be made before the maximum surface temperature of the fire is approached.

Foam was also sprayed on a simulated pipe leak. The apparatus consisted of 10 lb of sodium in a stainless steel vessel fitted with plumbing containing a leaking 1 in. flange. The plumbing was covered with 3 in. thick molded insulation as would be used on an operating system. The pot and plumbing were preheated to 700°F, pressurized to 10 psig and the valve to the leaking

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*MSA Regiseal

flange was opened. Sodium leaked through the flange and out through the joints in the insulation at a preselected leak rate of ~1 lb/hr. Foam was sprayed over the burning insulation and the pressure on the simulated system was released. There was initial burn through in ~2 min, but this was extinguished with additional foam. The foam is more easily applied to fires on insulation than is salt because of the inherent adhesive nature of the foam. However, if the surface temperature of the insulation is above ~400°F, the foam has a tendency to melt and drip off the insulation. In most alkali metal systems, the foam could be used on the type of fires described.

Attempts were made to incorporate inorganic salts in the foam but this proved impractical because of nozzle plugging. A liquid fire inhibitor was added to the foam that reduced the degree of combustion of the foam.

VIII. CHARACTERISTICS OF ALKALI METAL JET STREAM LEAKS AT VARIOUS PRESSURE CONDITIONS (PHASE VI)

A. INTRODUCTION

The purpose of this phase of the study was to determine ignition characteristics of alkali metal streams with respect to oxygen partial pressure and inert gas blanketing. The controlled atmosphere chamber was used for this study with alkali metal storage vessels situated outside of the chamber and entry to the chamber through 1/4 in. tubing. A catch pan was placed within the chamber to receive the alkali metal stream. Difficulties in capping the tubing until appropriate temperatures were attained were eliminated by maintaining a freeze seal at the end of the tubing until just prior to expulsion of metal.

With lithium, sodium and potassium, the metals were ejected through 1/4 in. tubing. Fine wires were placed over the end of the nozzle to break the 1/4 in. stream into four smaller streams. Rubidium and cesium were ejected through 1/8 in. tubing to conserve on the quantity of metal used. Efforts to measure changes in atmospheric composition were unsuccessful due to the large ratio of atmospheric volume to metal volume.

B. RESULTS OF TESTS

The results of the runs which were made are summarized in Table 8. Lithium was the first metal evaluated and was ejected into the chamber at 700°F through a 1/4 in. nozzle. There was

TABLE 8 - SUMMARY OF JET STREAM IGNITION RUNS

Run No.	Metal	Temperature (°F)	Absolute Pressure (atm.)	Nozzle Diameter (in.)	Remarks
1	Li	200	1	1/4	No ignition of stream or in catch pan.
2	Li	700	1	1/4	No ignition of stream or in catch pan.
3	Li	1250	1	1/4	No ignition of stream or in catch pan.
4	Na	780	1	1/4	Ignition of stream and fire in catch pan.
5	Na	780	0.1	1/4	No ignition of stream or in catch pan.
6	Na	780	0.1	1/4	No ignition of stream or in catch pan.
7	Na	780	1 (1)	1/4	No ignition of stream, but fire in catch pan.
8	Na	780	1 (2)	1/4	No ignition of stream or in catch pan.
9	K	700	1	1/4	Ignition of stream and fire in catch pan.
10	K	700	0.1	1/4	No ignition of stream, small fire in catch pan.
11	K	700	1 (1)	1/4	No ignition of stream or in catch pan.
12	K	700	1 (2)	1/4	No ignition of stream or in catch pan.
13	Rb	640	1	1/8	Ignition of stream and small fire in catch pan.
14	Rb	640	0.1	1/8	No ignition of stream but small fire in catch pan.
15	Rb	640	1 (1)	1/8	No ignition, spoils as metal hit pan.
16	Rb	640	1 (2)	1/8	No ignition in stream or in catch pan.
17	Cs	620	1	1/8	Ignition of stream but no sustained fire.
18	Cs	620	0.1	1/8	No ignition of stream or in catch pan.
19	Cs	620	1 (1)	1/8	No ignition of stream or in catch pan.
20	Cs	620	1 (2)	1/8	No ignition of stream or in catch pan.

(1) 50% Air-50% Argon

(2) 10% Air-90% Argon

no ignition of the stream and the metal did not ignite in the catch pan. A dark grey to black coating formed on the stream during ejection. A re-run under these conditions produced the same results so the supply vessel was heated to 1250°F. Again there was no ignition in either the stream or catch pan. The supply tank was disconnected from the chamber and transported to a building where larger quantities of lithium could be ejected into the atmosphere. About 10 lb of lithium at 1000°F were ejected into a pan under normal atmospheric conditions. The surface of the stream turned black during the run but there was no ignition of the stream. The metal in the catch pan did not immediately ignite but after standing for a few minutes burning nodules began to appear on the lithium surface.

The results indicate that a stream of lithium is not likely to ignite. This is probably due to a protective coating of oxides and nitrides which forms on the surface upon exposure to the atmosphere. However, when the stream hits a surface and is spread into a thin layer, ignition may occur. One of the factors which may promote ignition under these conditions is absorbed water vapor on the material on which the lithium is impinging.

Sodium at 780°F was ejected into the chamber through a 1/4 in. nozzle. Under normal atmospheric conditions, both the stream and the metal in the catch pan ignited. The fire in the catch pan was a sustained fire and much of the metal was consumed. At 0.1 atmosphere, there was no ignition in the stream or catch pan. This was also true in a 10% air-90% argon. In an atmosphere of 50% air-50% argon, there was no ignition of the stream but there was ignition and a sustained fire in the catch pan.

Potassium at 700°F was ejected into the chamber through a 1/4 in. nozzle. Under normal atmospheric conditions, the metal ignited both in the stream and in the pan. At 0.1 atmosphere, the stream did not ignite but the metal in the pan did ignite. No ignition of the stream occurred in a 50% air-50% argon or 10% air-90% argon.

Rubidium at 640°F was ejected into the chamber through a 1/8 in. nozzle. The metal ignited both in the stream and in the pan under normal atmospheric conditions. At 0.1 atmospheres, the stream did not ignite but there was a small fire in the catch pan; the fire in the catch pan was self-extinguishing. There was no ignition with 50% air-50% argon or 10% air-90% argon.

Cesium at 620°F was ejected into the chamber through a 1/8 in. nozzle. The stream of metal ignited under normal atmospheric conditions, but there was no sustained fire in the catch pan. The residue in the catch pan was a dark liquid characteristic of the residue from cesium exposed to air. There was no ignition of the stream or catch pan residue at 0.1 atmosphere, 50% air-50% argon or 10% air-90% argon.

TABLE 8 - SUMMARY OF JET STREAM IGNITION RUNS

IX. EXTINGUISHMENT OF LARGE SCALE FIRES (PHASE VII)

A. INTRODUCTION

The purpose of this phase of the study was to determine the reliability of the data generated with 10 lb fires and to demonstrate the feasibility of extinguishing large alkali metal fires. Sodium, potassium and NaK fires of 100 lb and 500 lb were extinguished with Met-L-X, TEC Powder, LiF and polyurethane foam. The materials represent the most promising extinguishants evaluated in Phase IV. All fires, except that on which polyurethane foam was used, were allowed to reach maximum temperature before the extinguishant was applied. The temperature of the fire on which polyurethane foam was used was to increase from 500°F, the temperature before the lid was removed, to 800°F before the foam was applied. The time required for this temperature rise was ~8 min. Approximately 30 min were required for fires to reach their maximum temperature.

B. TEST RESULTS

The results of the ten runs which were made are listed in Table 9. In the small scale fires, it was shown that the weight ratio of extinguishant to sodium metal was 0.72/1. This same ratio was found with the 100 lb sodium fire. With 500 lb sodium fires the ratio changed to 0.43/1 indicating that, on a unit weight basis, less extinguishant was required. Extinguishing times for the 100 lb and 500 lb fires (3-4 min) were longer than with the 10 lb fires (1-2 min) but did not increase in proportion to the weight of the burning metal. This was due to the more rapid application with the larger extinguishers (350 lb) compared with the smaller extinguishers (30 lb).

The ratio of TEC Powder/sodium metal was 0.4/1 on a 100 lb sodium fire and 0.2/1 on a 500 lb fire. Not only was less TEC Powder required than Met-L-X, but the extinguishing time was shorter. Both TEC Powder and Met-L-X exhibited some tendency for burn through, but these were quickly brought under control by application of additional extinguishant.

Lithium fluoride was the least effective of the salts used on large sodium fires. The ratio of LiF/sodium metal was 1.8/1. On the basis of these comparisons, LiF cannot be considered as an effective extinguishant.

Met-L-X and TEC Powder were applied to 500 lb NaK fires and gave ratios of 0.5/1 and 0.26/1, respectively. As was the case with the smaller fires, more extinguishant was required for NaK than for sodium fires and extinguishing times were slightly longer.

TABLE 9 - SUMMARY OF LARGE SCALE EXTINGUISHMENT STUDIES(1)

Alkali Metal	Weight (lbs)	Temp. (°F)	Extinguishant	Weight of Extinguishant (lbs)	Extinguishant-Metal Ratio	Remarks
Na	100	1280	Met-L-X	70	0.72	3 min to extinguish
Na	500	1350	Met-L-X	220	0.43	4.25 min to extinguish
Na	100	1300	TEC Powder	40	0.40	2.5 min to extinguish
Na	500	1400	TEC Powder	100	0.20	4.0 min to extinguish
Na	100	1450	LiF	175	1.80	8.0 min to extinguish
NaK	500	1280	Met-L-X	250	0.50	3.0 min to extinguish
NaK	500	1300	TEC Powder	130	0.26	5.0 min to extinguish
K	500	1200	Met-L-X	300	0.59	5.0 min to extinguish
K	500	1200	TEC	220	0.43	4.5 min to extinguish
Na	100	800	Polyurethane Foam	-	-	8.0 min to extinguish

(1) Salts applied from 350 lb pressurized extinguisher.

The ratio of Met-L-X and TEC Powder for 500 lb potassium fires was 0.59/1 and 0.43/1, respectively. It was necessary to allow the potassium fires to burn until an oxide crust formed on the surface. The crust then served as a support for the extinguishant.

Polyurethane foam was applied to a 100 lb sodium fire with temperature at 800°F. The fire was extinguished in 8 min. Frequent burn through and reignition occurred but this was controlled by application of additional foam.

The results indicate that large alkali metal fires can be extinguished with the application of salts. The ratio of salt to metal varies from 0.72/1 to 0.2/1 depending upon the size of the fire and the type of salt which is used. In practice, it is probably advisable to maintain an inventory of salt equivalent to the weight of metal contained within a system. Hopefully, emergency measures such as valving off a leaking reaction, reducing system pressure and the like, can be initiated to minimize loss of metal from the system. However, if a catastrophic rupture of the main system piping occurs, all of the metal could be ejected from the system before these emergency procedures could be instituted.

It would be desirable if optimum application rates could be established for these salts. However, it is essentially impossible to define an optimum rate; in spite of the amount of research which has been performed on non-alkali metal fires, the rate of application of water to a wood fire or halogenated hydrocarbons to flammable liquid fires has not been quantitized. Alkali metal fires which are generally more complex in nature than either wood or flammable liquid fires are more sensitive to the mode or technique of application. In general, the extinguishant should be applied to an alkali metal fire as rapidly as possible without disturbance of the salt crust.

X. CONCLUSIONS

A number of salts, organic liquids and an inorganic foam were evaluated as alkali metal fire extinguishants. TEC Powder, a ternary eutectic compound, was the most effective salt for sodium, potassium and NaK but economic consideration may dictate the continued use of Met-L-X which is also quite effective in extinguishing sodium, potassium and NaK fires. The extinguishant-alkali metal ratio ranged from 0.72/1 to 0.20/1 depending upon the salt which is used and the size of the fire. Extinguishing times of sodium fires as large as 500 lb were of the order of 4-5 min when the salt was applied from a 350 lb extinguisher. Both salts were effective in extinguishing rubidium and cesium spills but were ineffective on quiescent pools of rubidium and cesium. At low temperatures (< 700°F), polyurethane foam can be used on burning pools of rubidium and cesium. Because of the high temperature (2000°F+) and chemical reactivity of burning lithium, neither of the salts were effective. Graphite is recommended as the extinguishant for lithium fires.

Organic liquids proved somewhat effective on low temperature fires (< 1000°F). In all cases, a secondary liquid fire ensued, but these were controlled with application of CO_2 or bromochloromethane. In practice, the secondary organic liquid fire could be more severe and troublesome than the alkali metal fire, hence the use of organic liquids is not recommended.

Gas blanketing or reduction of oxygen partial pressure was effective in controlling lithium, sodium and potassium fires. At an oxygen partial pressure of 0.1 atm, lithium did not ignite. Sodium ignited in a 50% Ar-50% air atmosphere but less metal was consumed (53%) than when sodium was burned in a normal atmosphere (82%). In 90% Ar-10% air and in normal air at 0.1 atm, sodium did not ignite.

Potassium did not ignite when exposed to 0.1 atm, but slowly oxidized with 86% of the metal consumed. In atmospheres of 50% Ar-50% air and 90% Ar-10% air, potassium did not ignite but 46% and 49%, respectively, of the free metal was consumed by slow oxidation.

Rubidium and cesium in quiescent pools did not burn in the same manner as the other alkali metals, i.e., there was essentially no smoke, emission of light or formation of an oxide crust on the surface. However, when exposed to the normal atmosphere, 100% of the free metal was oxidized. And unlike the other alkali metals, the degree of oxidation could not be reduced by altering the atmosphere; 100% of the metal was oxidized in the 90% Ar-10% air atmosphere.

Variation of oxygen partial pressure was also effective in controlling ignition of jet streams of alkali metals. Streams of rubidium and cesium ignited in a normal atmosphere, but did not ignite in an atmosphere of 50% Ar-50% air or 90% Ar-10% air of 0.1 atm absolute pressure.

XI. RECOMMENDATIONS

A. INTRODUCTION

The results of this study coupled with past operating experience have led to the formulation of certain recommendations with respect to alkali metal fires. As an example, a typical alkali metal system has been chosen. It is recognized that there are obviously many other operational configurations which could have been selected such as alkali metals as hydraulic fluids, coolants and the like in high altitude aircraft, but the configuration selected represents a rather complete spectrum of conditions which might be encountered. As a basis for these recommendations, it is assumed that an alkali metal (sodium, potassium or NaK) cooled reactor is being used to generate electrical power on board a spacecraft. It is further assumed that the system will contain 500 lb of alkali metal at 1500°F. Table 10 presents the conditions which might exist and the procedures which should be employed.

B. SUPPLY CONTAINER

The alkali metal will be transported to the launch pad area in a supply container. This might be a container in which the supplier originally packaged the alkali metal, or a special container to which purified alkali metal has been charged. It is likely that some prepurification of the metal will be made prior to charging of the system. Prepurification procedures may entail hot trapping, cold trapping, filtration, distillation or any combination of these.

The supply containers will be large vessels containing from 200-500 lb of metal. These will be fabricated of stainless steel and will be equipped for heating the contained metal to 100-200°F above the melting point. Since the maximum operating temperature of these vessels will be 350-400°F, a catastrophic rupture of the vessel is improbable. Hence, the most likely accident and the maximum credible accident is valve and fitting leakage. Incidents such as these are controllable by valving off the leaking section, reducing pressure on the supply tank and in same cases freezing the leaking line. Although these procedures minimize the magnitude of leakage and fire, they do not extinguish the fire resulting from the metal which has leaked from the system.

The fire resulting from leakage from the container can be extinguished by application of Ansul's Met-L-X , TEC Powder or polyurethane foam. Although these three extinguishants are referenced throughout this section, the sodium chloride-based compound is probably the most likely choice based on cost, availability and past history. The quantity of extinguishant required will

TABLE 10 - TYPICAL ALKALI METAL FLOW SHEET

Operational Status	Supply Container(1)	Transfer From Container To System	Reactor on Pad	Abort	In Flight
Maximum Temp (°F)					
Sodium	350	400	Ambient to 350	--	1500
NaK	Ambient	Ambient	Ambient	--	1500
Potassium	300	350	Ambient to 300	--	1500
Most likely accident	Valve and fitting leakage	Leaking fittings or rupture of transfer line	Leaking fittings or valves	Catastrophic rupture	Catastrophic rupture
Maximum credible accident	Valve and fitting leakage	Rupture of transfer line	Catastrophic rupture	Catastrophic rupture	Catastrophic rupture
Fire Control Procedures					
Extinguishant	Met-L-X, TEC Powder or urethane foam	Met-L-X, TEC Powder or urethane foam	Met-L-X, TEC Powder or urethane foam plus inert gas blanketing	No control	Inert gas blanketing or venting to vacuum or space
Quantity	Equivalent of alkali metal contents	Equivalent of alkali metal contents	Equivalent of alkali metal contents	--	

(1) This might be the container provided by the supplier of the alkali metal, or an on-site vessel which has been used to collect prepurified alkali metal.

probably be small since the amount of alkali metal released from the container should be small. However, since a larger quantity of extinguishant will be required during transfer, the extinguishant will be on site while the alkali metal is contained within the supply vessel and the quantity which should be available should equal the weight of the metal contained in the supply vessel.

C. TRANSFER FROM CONTAINER TO SYSTEM

The bulk temperature of the alkali metal supply during transfer procedures will be ~ 350°F (for sodium) in the supply container. Connecting piping will be at least at this temperature and perhaps as much as 50°F higher. The most likely accident during transfer is the development of leaks in fittings or valves. These can be controlled in the same fashion described for supply containers where the leaking section is valved off, pressure on the supply container is reduced and extinguishant is applied to the metal which has leaked from the system.

The maximum credible accident during transfer would be a catastrophic rupture of the connecting plumbing. If the rupture occurs at a position where a valve is located between the supply tank and rupture, the severity of the fire can be controlled by closing the valve. If the rupture should occur between the supply tank and the valve, it is likely that all of the metal will be ejected from the system. In this case, a severe fire will follow and must be controlled by application of Met-L-X, TEC Powder or polyurethane foam. It has not been established whether the reactor would be charged before or after installation in the vehicle. It would be advisable to charge the reactor before installation since the length of connecting plumbing could be held to a minimum and the possibility of damage to the vehicle would be minimized.

D. REACTOR ON PAD

Prior to launch, the reactor will have been installed in the vehicle and will probably not undergo start up until orbit is attained, the purpose of this procedure being to reduce radiation hazards to the site. The temperature of the alkali metal then can vary from ambient temperature, if there are provisions to melt the alkali metal after orbit is attained, to 350°F if the metal must be molten prior to attaining orbit.

Again the most likely incident is leaking fittings or valves. If this occurs, while the vehicle is being readied for flight, extinguishants can be applied if the reactor compartment is readily accessible. Otherwise inert gas blanketing is the best method of controlling the fire. The maximum credible accident could be rupture of the primary piping of the alkali metal system. This would most likely occur during rocket ignition and lift off where vibrational and gravitational forces are greatest. Even if the craft were manned, it would be impossible for manual application of extinguishant. Automatic delivery of extinguishant to the fires is a possibility, but the weight penalty imposed due to extinguishant, extinguishant delivery system and pressurizing equipment would probably rule out the feasibility of such a system. Inert gas blanketing then would appear to be the only reasonable means of alkali metal fire control and extinguishment.

E. ABORT

If the vehicle suffers an abort during lift-off or while attaining orbit, catastrophic rupture of the main alkali metal plumbing is likely to occur. In this case, there seems to be little that can be done to extinguish or control the alkali metal fire which will follow. It should be noted that the fuel and oxidizer explosion and/or fire which would follow an abort would be infinietely greater than the alkali metal fire. Interaction between alkali metal and either fuel or oxidizer has been considered. There would be no reaction between some of the hydrocarbon fuels and the alkali metal, since sodium and NaK can be stored under mineral oil or kerosene. The severity of the reaction between the alkali metals and oxidizers or alcohol will depend upon the conditions which exist at the time of contact. In this study, an ampoule of NaK was immersed in liquid oxygen and the ampoule was broken. The only reaction which occurred was surface oxidation of the NaK; no fire resulted. Conversely, NaK was allowed to drip into liquid oxygen from a height of 15 ft. In this case, the NaK had ignited before contact with the liquid oxygen. There was severe spattering of the NaK when it contacted the liquid surface and the vessel in which the liquid oxygen was contained ignited and was completely consumed.

F. IN-FLIGHT

Under in-flight conditions, the most likely accident is fitting or valve leakage. If an artifical gravity has been imparted to the vehicle, the addition of Met-L-X or TEC Powder to the fire would be possible. Again, however, the weight penalty imposed by the salt which must be carried on board could be objectionable. Further, since the maximum credible accident would be catastrophic rupture of the primary alkali metal piping, inert gas blanketing would be required for extinguishment of the fire resulting from a maximum credible accident. It is recommended, then, that a low oxygen partial pressure in the reactor compartment be maintained (or that the compartment be vented to the vacuum of space) and that extinguishant not be carried on board.

APPENDIXES I THROUGH III

APPENDIX I

CHARACTERISTICS AND CONTROL OF NON-ALKALI METAL FIRES

A. INTRODUCTION

A proposed fire research program submitted by the Committee on Fire Research(6) lists the areas in which basic studies would contribute most significantly to understanding of fires. In summary these are:

1. Characteristics of convection of hot air and gases as affected by winds, topography, density, gradiants and turbulence.
2. Gas and flame emissivities as a function of frequency at high temperature.
3. Cooling, smothering and direct chemical kinetic action of flame suppressants.
4. Aerodynamic properties of burning bodies in motion.
5. Mechanism and thermochemistry of pyrolysis and oxidation of solid combustibles with emphasis on endothermic and exothermic reactions on solid phase, gas evolution and heat transfer from the surface and from burning gases.
6. Model laws for aerothermodynamic systems with respect to geometry, fuel type, radiation, heating rate and so on.
7. Fundamental studies of sprays including evaporation rates, distribution of droplet sizes, jet chracteristics and entrained air.

These suggestions are listed here since, although they apply basically to wood and hydrocarbon fires, many are applicable to alkali metal fires. To date most fire research has been guided by the empirical approach. The Committee on Fire Research suggests that the scientific disciplines including physics, chemistry, thermodynamics, fluid mechanics, chemical kinetics, heat transfer and so on be used to produce quantitative data on fires.

Some of the general statements made in Fire Research Abstracts and Reviews are listed here to establish the state of the art. Information relating specifically to alkali metal fires follows this listing.

B. DRY SALT EXTINGUISHING AGENTS

A review by Friedman and Levy(7) discusses the mechanisms of action of chemical agents for flame extinguishment. Two types of chemical agents are discussed - (1) covalent halides such as CCl_4, $CHCl_3$, CF_2Br_2, CH_2ClBr and the like and (2) inorganic salts such as $NaHCO_3$ and $KHCO_3$. The cogent point made is that these agents suppress fires by chemical action rather than by physical or mechanical interaction. This fact is verified in that the peak percentage of diluent (the percentage of diluent which will prevent a fuel-air mixture from burning) for a methane-air mixture is 38% N_2, 25% CO_2 but only 4.7% CH_3Br. This amount of CH_3Br is much too small to account for extinguishment by either cooling or smothering. The explanation advanced for this phenomenon is chemical inhibition by reaction with active species. Flame temperatures range from 1500 to 3000°C. At 2500°C water is dissociated into the active species H and OH; the same analogy holds for hydrocarbons with radicals such as CH_3 and C_2H_5 formed. With water, these species initiate chain reactions of the following type, with each reaction producing another reactive radical:

$$H + O_2 \longrightarrow OH + O$$

$$OH + H_2 \longrightarrow H_2O + H$$

$$O + H_2 \longrightarrow OH + H$$

Covalent halides are believed to break these chain reactions and thus act as extinguishants. Bromides and iodides are more efficient than chlorides and fluorides.

Rosser et al(8) present the following process as the flame extinguishing mechanism of the covalent halides:

$$OH + HBr \longrightarrow HOH + Br$$

$$Br + RH \longrightarrow HBr + R$$

HBr is formed by decomposition of the covalent bromide and subsequent reaction of the free Br with active H species. The net result is to replace the OH by a less reactive species Br or H. This theory also explains why the bromide and iodides are more effective than chlorides or fluorides since the H-Cl and H-F bonds are so strong that the first reaction is too slow to have any effect on the overall reactions occuring in the fire.

Commercial dry salt extinguishing agents are usually carbonate or bicarbonate salts. It was originally thought that the extinguishing capabilities of these salts were due to release of CO_2 as a smothering agent. However, recent studies show that the salts are essentially unchanged and salts which do not evolve CO_2 are as effective as the carbonates and bicarbonates. Hence, the extinguishing capabilities are attributed to chemical rather than physical mechanisms. When different solids of the same particle size are compared, tremendous differences in extinguishing capabilities are exhibited. However, some mechanical effect may be present, since the smaller the particle size, the more effective is the salt.

Neill(9) reports that an increasing extinguishing effect is evident with increasing atomic number of the alkali metals. Superior fire fighting qualities are evident for $KHCO_3$ compared to $NaHCO_3$.

C. EFFECT OF ATMOSPHERE ON COMBUSTION

Klein(10) has presented data on the effect of aircraft cabin atmosphere up to 25,000 feet on burning times, which might provide a correlation with alkali metal fires under various atmospheric conditions. Cotton cloth burning time decreases as the proportion of oxygen increases, regardless of the partial pressure of nitrogen; the same was true with helium instead of nitrogen. No atmospheric composition up to 25,000 feet will prevent silicone rubber, glass or Dacron braid insulation from burning. Ignition temperatures of hydraulic fluids increased as cabin pressure decreased with both pure oxygen and air. Conclusions are that a minimum oxygen content with maximum inert gas content provides an optimum atmosphere for a space vehicle.

Zehr(11) reported on a study of combustion intensity of wood dust and air mixtures with varying oxygen content. The following results are listed:

Oxygen Content (%)	Maximum Pressures (atm)	Calculated Pressures (atm)
21	4.1-4.3	10.7
19	3.9-4.1	--
17	3.5-3.7	--
15	2.9-3.1	8.3
13	1.6-1.8	--
11	No ignition	6.4

D. COMBUSTION UNDER ZERO GRAVITY CONDITIONS

A discussion of combustion under zero gravity conditions would seem warranted before alkali metal fires are discussed. Gerstein(12) suggests that two questions are principally involved:

1. Preparation of combustible mixtures where gaseous and liquid flammable material are involved.

2. The actual combustion process of all flammable materials present within the spacecraft.

In the absence of gravitational effects and forced convection, flammable vapor is spread only by diffusion. He estimates that mixing rates will be lower under zero gravity than under normal gravity conditions. He indicates however that if the spill is in motion a random distribution of flammable sources is expected and the formation of flammable mixtures would be more likely.

Experimental combustion studies have been made under normal gravity conditions, while theoretical studies have neglected gravitational effects and reasonable agreement exists between the two. Hence, the thesis is advanced that gravitational effects play a minor role in the combustion process. However, validity of this conclusion is subject to question.

Free fall studies of single burning drops show that:

1. The dimensions of the flame boundary and hot air zone become higher and narrower as acceleration increases because natural convection becomes stronger.

2. Burning rates increase as acceleration increases. Burning rates can be expressed in the form of:

$$D_o^2 - D^2 = kt$$

where:

D = drop diameter at time t
D_o = initial drop diameter
k = evaporation constant

The value of k roughly doubles in going from a zero gravity to the normal value for gravity.

Empriical equations which include natural convection effects have gravity appearing as a term raised to a fractional exponent:

$$\frac{\overset{o}{m}dc}{k} = 45B^{3/4} \left(\frac{gd^3}{\alpha}\right)^{1/4}$$

where:

$\overset{o}{m}$ = burning rate per unit surface area
d = sphere diameter
c = specific heat
k = thermal conductivity
B = transfer number, a function of fuel properties
g = acceleration due to gravity
α = thermal diffusivity

Since it is obvious that the burning rate is not zero when gravity is zero, Gerstein suggests the following equation would be more suitable,

$$\overset{o}{m}(g) = m_o[1 + f(g)]$$

with $f(g)$ small compared to unity. It is also suggested that flammability limits would be narrower under zero gravity conditions.

APPENDIX II

PRESENT PRACTICES OF ALKALI METAL FIRE EXTINGUISHMENT

A. INTRODUCTION

Extinguishment of alkali metal fires is discussed in the Liquid Metals Handbook.(13) Need for ventilation of alkali metal operating areas is stressed. Without proper ventilation, fire fighting personnel are handicapped by the dense clouds of alkali metal oxide smoke which limit visibility and cause throat, lung and eye irritation. A self-contained breathing apparatus is suggested if oxygen levels can be low, otherwise a respirator is sufficient. An advantage of the self-contained breathing apparatus is protection afforded to the facial skin and eyes.

It is reported that sodium and NaK will ignite spontaneously in air at temperatures above 115°C (239°F) with flame temperatures of 1500-1600°F. Ignition is dependent upon surface area, degree of dispersion and humidity. Combustion of sodium is not self-sustaining in an atmosphere of less than 5% oxygen. Dry alkali metal chlorides, graphite or soda ash act successfully as smothering agents. Water, carbon tetrachloride, carbon dioxide and sodium bicarbonate must never be used as alkali metal fire extinguishants; water and carbon tetrachloride react with explosive violence with alkali metals! It cannot be overstressed that the extinguishing agents must be of a completely anhydrous nature. Commercially prepared extinguishing agents, such as Met-L-X dry powder distributed by Ansul Chemical Company, are treated to prevent moisture pick-up and maintain the extinguishing agent in free flowing form. Pyrene G-1 powder distributed by Pyrene Manufacturing Company is a graphite-base material treated to prevent moisture pick-up. These extinguishants should be stored in covered buckets or drums, or in extinguishers.

Extinguishing agents can be applied either from extinguishers, or with scoops or shovels. Pressured extinguishers are available in 20, 30 and 350 pound sizes and fan spray type nozzles should be used to spread the salt and minimize disturbance of the burning alkali metal pool. Shovel or scoop application is usually preferred over extinguisher application. However for large fires, extinguisher application is advised. The choice must remain with the fire fighting personnel at the site. Technique of application of the extinguishing agent is an important aspect of fire fighting. Extinguishing agents must be applied carefully to prevent splashing and must completely cover the alkali metal surface. The salt fuses to form a crust over the alkali metal and serves to exclude oxygen; breakthrough of this crust must be avoided since the fire will rekindle if the alkali metal has not cooled to below the ignition temperature.

Alkali metal fires are not particularly hazardous unless burning metal contacts the skin, but secondary hazards must be avoided. Provisions must be made to prevent alkali metal contact with water, organics, combustibles and concrete floors. Temperatures of burning alkali metals are high enough to cause spalling of concrete which will add to the overall hazard.

Proper design of equipment will reduce hazards to personnel and equipment. Construction techniques and leak testing minimize the possibility of alkali metal leaks. A sump tank provides a means of rapidly draining the system and "removing fuel from the fire", gravity flow to the sump tank is advisable. A drip pan aids immeasurably in containing leaking alkali metal, aiding in fire control and preventing contact of burning metal with concrete. Grating over the drip pan will limit convection of oxygen to the fire and can provide a support for extinguishant. Drip pans should be of sufficient size to contain the volume of metal housed in a system.

No insulation is known which is impervious to molten alkali metals but the following are suitable for use:

1. High density refractory minerals fiber felts
2. High density mineral wool or glass fiber, either felted or in molded block form
3. Low density (not exceeding six lb per cu ft) mineral wool or glass fiber felts
4. Asbestos with low water of crystallization, such as felted or molded amosite
5. Molded aerogel insulation
6. Eighty-five percent magnesia insulation
7. Molded diatomaceous earth insulation (1900°F type)
8. Molded calcium silicate insulation
9. Stainless steel wool
10. Metal foil enclosures filled with any of the above materials.

Some of these materials, specifically high density mineral fiber felts, molded aerogel, molded diatomaceous earth and high temperature molded amosite, have displayed resistance to flow of liquid sodium. This characteristic can aid in fighting fires occurring in vertical pipes.

Clean-up is a facet of fire fighting which cannot be neglected. Alkali metal fires will result in a residue containing unburned metal, hydroxides, oxides, carbonates and fire extinguishing medium. It must be remembered that the reaction products are deliquescent and contact of these hydrated salts with free alkali metal can result in a fire or, under proper circumstances, an explosion. Hence, clean-up immediately following a fire cannot be overemphasized. The mass should be shovelled into a dry metal container equipped with a lid. The material should be transported to the disposal area and burned in an open pan with frequent stirring to assure complete combustion. Following the combustion process, the area should be thoroughly flushed with water.

Handling of NaK residues is more hazardous than the handling of sodium residues since the NaK remains liquid at room temperature. The same can be said for cesium residues.

B. SAFETY EQUIPMENT AND FIRST AID PROCEDURES

Proper safety equipment will protect personnel from injury and provide greater efficiency in fire fighting. The following equipment is considered the minimum requirement for fire fighting:

Eye protection - Non-flammable face shields along with safety goggles

Head protection - Safety or "hard" hat

Foot protection - Leather safety shoes

Body protection - Loose fitting, flame-proof clothing such as coveralls or loose jacket and trousers

Hand protection - Chrome leather gauntlet gloves

Respiratory protection - Respirator or self-contained breathing apparatus.

In the event of a spill of burning alkali metal on the clothing or skin of personnel, one of the two following procedures is recommended in the literature:

1. Remove clothing if covered with burning alkali metal and flood subject with water as quickly as possible, followed by neutralization with 3% acetic acid.

2. Flood with mineral oil and remove alkali metal particles by scraping or with tweezers.

Both techniques have their advantages and disadvantages and the choice must rest with personnel performing first aid treatment. Water rapidly and completely removes alkali metals and caustic from the skin, but scattering of the metal may result. Mineral oil is used to exclude air from the alkali metal, but can in itself ignite, and it tends to seal the caustic to the skin, causing chemical burns. In both cases, the treatment should be followed by neutralization with 3% acetic acid. Do not use acetic acid in the eyes, but flush with water or mineral oil and follow with 5% boric acid treatment.

A word on fighting radioactive alkali metal fires seems warranted since these metals will be used as reactor coolants. In general, radioactive fires should be fought in the same manner as non-radioactive fires, keeping in mind the radiation exposure and ingestion hazard to which fire fighting personnel are subjected. Protective equipment should include a self contained breathing apparatus rather than a respirator to eliminate the ingestion hazard.

Thorley and Raine(14) discuss safe handling of alkali metals. Health hazards are listed as:

1. Flesh burns from contact with metal or caustic residues
2. Eye, nose, throat and lung damage from inhalation of alkali metal oxide smoke.

Four points are listed to ensure maximum safety during handling:

1. Shield all apparatus
2. Incorporate dump vessels in the system
3. Use inert cover gas to prevent in-leakage of atmospheric gases and to aid in dumping
4. Install drip trays under the apparatus.

Soda ash (anhydrous) and zirconium carbonate are recommended as extinguishants with application from a CO_2 pressurized extinguisher. Sprinklers or scoops may also be used; scoops are particularly useful in forming salt dykes around molten alkali metals. The authors recommend that alkali metal burns be covered with liquid paraffin and that water never be used on alkali metal spills on the skin.

C. EXPERIMENTAL STUDIES WITH DRY POWDER EXTINGUISHANTS

Zeratsky(15) discusses dry powder extinguishing agents for alkali metal fires. G-1 powder is the trade name of a product of the Pyr-Fyter Company and is composed of granular graphite to which is added phosphorous-containing compounds. The product decomposes to phosphorous compounds which blanket the fire and graphite which cools the alkali metal to below the ignition point. It can be applied with shovel or scoop but cannot be discharged from an extinguisher.

Met-L-X , manufactured by Ansul Chemical Company, is a sodium chloride base with additives to render it free flowing (tricalcium phosphate) and cause heat caking (metal stearates). A thermo-plastic material is added to bind the sodium chloride particles into a solid mass under fire conditions.

Both G-1 and Met-L-X are non-combustible and secondary fires do not result. They are generally non-toxic and their use will not increase the intensity of a fire. Both are treated to maintain the extinguishant in an anhydrous condition.

Pan fires and spill fires of sodium are easily extinguished with Met-L-X or G-1. Because of its ability to adhere to molten sodium, Met-L-X can be used on sprayed or spilled sodium on vertical surfaces.

Either extinguishant can be used on potassium or NaK fires, but since the specific gravity of the molten metals is less than that of G-1 or Met-L-X, the powders tend to sink. A perforated plate located near the liquid metal surface has been used to support the crust formed with these extinguishants.

G-1 is suitable for both lithium spill fires and lithium fires in depth. Met-L-X is not recommended for lithium fires of depth since it sinks and lithium reacts with the salt to produce LiCl and sodium metal. Thin layer lithium spill fires can be fought with Met-L-X since the salt cannot sink; the resultant sodium fire is more easily extinguished than a lithium fire. Lith-X, a graphite-base powder, has been developed by Ansul Chemical Company for lithium fires.

Lith-X is also used on triethylaluminum fires where it extinguishes only by absorption of the liquid. Met-L-Kyl, a bicarbonate base with an activated absorbant, has also been developed for triethylaluminum fires. Water and foams reacted explosively, CO_2 was ineffective and dry chemical and chlorobromomethane extinguished but permitted reignition of triethylaluminum fires. About 7-10 pounds of Lith-X or Met-L-Kyl are required per pound of triethylaluminum.

Other metal fires are discussed with the following recommendations:

Magnesium - Fires in dry or oily chips, turnings or castings can be extinguished with either agent

Uranium - Both agents are effective

Titanium - G-1 is more effective than Met-L-X which cannot form a crust at combustion temperatures

Zirconium - Fires with chips or turnings coated with oil-water coolant can be extinguished with either agent. Fires involving moist chips or turnings are only controlled.

Blackmer(16) has reported on the hazards associated with NaK, suggesting removal of fuel (to a dump tank) as the best fire fighting technique. Fire hazards in aircraft could be reduced by packing all voids with vermiculite or some other lightweight, fire proof insulation.

Kumpitsch(17) describes a NaK disposal facility for test equipment. It consists essentially of an 8 foot deep water tank with remote control devices for immersing containers in the reservoir. Although the reaction is violent, no oxide fumes are formed and the technique is considered superior to spraying with water. Andrews and King(18) describe underwater disposal of molten sodium. Sodium at 350°F was discharged under 10 feet of water at a rate of 90 lbs/min with little oxide smoke and no hydrogen fires. Later work by King and Milich(19) demonstrated the necessity of efficiently dispersing the metal upon discharge. A nozzle producing high shear forces was used as the dispersing mechanism.

Little(20) has reported on the use of powders for extinguishing sodium or NaK fires. Rock dust ($CaCO_3$), soda ash and potassium chloride powders were applied to sodium and NaK fires. Pressurized extinguishers were used on 50 pound fires and shovel application was used for 5 pound fires. With nitrogen as a propellant the weight ratio of $CaCO_3$ to metal was 3.4/1 for 5 pound fires and 5.8/1 for 50 pound fires; air as a propellant increased the ratio to 7.2/1 for 50 pound fires. Results are summarized in Table 11.

TABLE 11- RESULTS OF POWDER EXTINGUISHANTS ON Na AND NaK FIRES

Metal	Quantity (lbs)	Dust Used	Means of Distributing	Extinguishing Time (min)	Quantity of Dust Used (lbs)	Re-ignition	Hazardous Disposal
Alloy*	5	$CaCO_3$	Ansul(CO_2)**	1	17	no	no
Alloy*	5	$CaCO_3$	Shovel	2	17	no	no
Alloy*	5	$NaCO_3$	Ansul(CO_2)**	1	17	yes	yes
Alloy*	5	$NaCO_3$	Shovel	2	17	yes	yes
Na	50	KCl	Rock Duster (air)**	10	420	yes	yes
Na	50	$CaCO_3$	Rock Duster (air)**	9.8	360	no	no
Na	50	$CaCO_3$	Rock Duster (N_2)**	6.7	240	no	no

* 66 wt % K - 34 wt % Na

**Dust propelling agent used

D. EFFECT OF OXYGEN PRESSURE ON ALKALI METAL

Mangold and Tidball(21) have reported on the effect of oxygen partial pressure on sodium fires. Results indicate that combustion of sodium cannot be sustained below 5% oxygen (temperature of leaking sodium = 850°F). Table 12 shows the results of this study. Analysis of the residue from one of the fires showed 25% Na_2O_2. Cooling the surface on which the molten sodium was placed minimized the quantity of sodium which burned.

E. TYPICAL ALKALI METAL FIRE FIGHTING PROCEDURES

Alkali metal fire fighting procedures used at Oak Ridge National Laboratory (ORNL) are outlined in two documents.(22,23) The following procedures are recommended for combating alkali metal fires:

1. Reduce pressure in system.
2. Turn in the fire alarm.
3. Isolate the system electrically.
4. Remove heat source.
5. Actuate emergency ventilation system.
6. Put on protective clothing as required.
7. Wear gas masks or other specified protective equipment as necessary.
8. Use graphite on fire, applied by shovel or pressurized extinguisher. Met-L-X may be used on sodium, potassium or NaK fires.
9. Take all possible measures to confine the metal by forming dykes with graphite, catching in metal pans, or control with insulating blankets or metal shields.
10. Leave insulation around leaking portion of rig in place.
11. If the fire is confined, other equipment is not being damaged, and fumes are being adequately removed, the fire may be allowed to burn itself out without the necessity for applying an extinguishing agent.

TABLE 12- SODIUM COMBUSTION UNDER REDUCED OXYGEN PARTIAL PRESSURE

Weight of Na (lbs)	O_2 Concentration Before Burning(%)	Vol % After Burning	Weight of Na(1) Burned (lbs)
47	2.75	2.62	1.3
32	9.69	8.43	12.5
43.5	13.44	12.17	12.6
41.5	20.28	14.87	53.6(2)
37.5	6.97	6.31	6.5
45	11.92	9.76	21.4

(1) Calculated from vol % O_2 assuming combustion product is Na_2O

(2) Calculated Na burned higher than the original charge due to Na_2O_2

ORNL recommends graphite powder in cases where more than one inflammable metal is being handled. If a single inflammable metal is being handled the following recommendations are made.

Lithium - Graphite

Sodium - Met-L-X, Graphite, Pyrene G-1, Soda Ash, Calcium Carbonate

Potassium - Same as for sodium

NaK - Same as for sodium

Exposure of the metals to moist air can result in generation of hydrogen. After a fire, covers should be replaced on drums as soon as possible and smoking should be restricted in areas where handling is in progress.

Mineral oil flushing is recommended in cases where there has been contact of burning alkali metal with the skin.

A short discussion of system clean-out procedures is presented since proper clean-out techniques will minimize the proability of a fire. Correct draining procedures cannot be overemphasized since they will reduce the quantity of metal available for reaction and provide greater assurance of drainage of narrow passages. Draining should be performed at the highest practical temperature to minimize drainage film thickness. Inert gas coverage is necessary during this procedure.

Following drainage, the residual alkali metal can be removed in a number of ways. Dry steam reacts slowly with alkali metals. The hydrogen produced may ignite upon leaving the equipment but no explosions will occur within the system since steam displaces any oxygen which may be present. Moist steam can also be used if there are no obstructed passages. Water reacts explosively with sodium with approximately 1/10 the force of TNT, thus contact of condensed water with sodium in a closed system must be avoided. Water can be used to clean lithium systems if the water flowrate is sufficiently high to maintain the equipment at or near ambient temperature.

Equipment may also be cleaned with alcohols (the higher alcohols react more slowly with sodium). Care must be taken since hydrogen and heat are released during reacting and the alcohols themselves are flammable.

Molten sodium hydroxide may also prove suitable for removal of residual sodium. Regardless of the cleaning technique used, water is always used as a final rinse.

Procedures for alkali metal fire fighting at Los Alamos Scientific Laboratory are described by Stout.(24) Prompt action is vital with Na_2CO_3, NaCl or graphite recommended for sodium and potassium fires. Graphite is recommended for lithium fires since free sodium is liberated from Na_2CO_3 and NaCl when used on lithium fires. Zirconium silicate and lithium chloride are also suggested for lithium fires. Steel covers on drip pans with holes giving a maximum open area of about 25% will result in self extinguishment.

Little(25) has reported on the action of NaK and sodium on various protective equipment. Cotton cloth gloves, chrome leather gloves and aprons, MSA Nu-Look goggles, laminated bakelite hats and face shields with acetate windows were subjected to streams of sodium and NaK at 150, 350 and 500°C. Chrome leather and laminated bakelite were the only material to give 100% protection at 500°C. Rubber gloves, face shields and goggles protect against NaK to 150°C and sodium to 350°C while cotton cloth is good only at room temperatures.

Materials were subjected to a 1/16 in. diameter stream of lithium at 1100°F and 60 psig for 30 seconds.(26) The materials were positioned 6 feet from the orifice and were sprayed with 7 lbs of lithium. The following results were listed:

Chrome leather - charred and glowed almost instantly, shrunk but some remained as coke.

Chamois leather - disappeared quickly and completely.

Greylite - disappeared quickly and completely.

1/8 in. thick plexiglass - disappeared quickly and completely.

1/2 in. thick plexiglass - ignited and eventually burned out after jet removed.

G.E. multilayer protective cloth metal - disappeared.

1/8 in. thick steel backing plate - severe buckling, no penetration, bright cherry red spot 18 in. diameter with almost white hot center spot.

F. INDUSTRIAL SURVEY ON FIRE FIGHTING TECHNIQUES

In addition to the literature survey, an industrial survey was made to determine the most up-to-date techniques used by various companies. Specific information which was requested was "fire fighting manuals and other literature on procedures used in alkali metal fire fighting." The information obtained is summarized below.

Organization A uses soda ash as an extinguishing agent. The largest fire encountered was a 5 lb container of sodium which ruptured during melting and the dispersed sodium started multiple fires. These were quickly brought under control with soda ash applied by an operator wearing a gas mask.

Organization B has had several spills with rubidium, cesium and NaK followed in some cases by small fires. During transfer of NaK from a shipping container, NaK poured out of the one of the lines and into a wooden shipping box. The box was broken open and NaK ran onto an asphalt tile floor. Met-L-X from an extinguisher was applied to the box while calcium carbonate was shoveled onto the NaK on the floor. Both fires were rapidly brought under control. During clean-up of the residue, the crust was disturbed and the NaK reignited. Again calcium carbonate was used to bring the NaK fire under control. This residue was reacted with 80% isopropyl alcohol-20% water.

Organization C used Met-L-X on NaK fires and powdered graphite on lithium fires. Lith-X is also on hand but has never been used.

Organization D recommends smothering with a lid if the metal is contained in a tank. Open sodium fires are extinguished with Na_2CO_3.

APPENDIX III

SUMMARY OF FRIEDRICH'S WORK ON ALKALI METAL FIRES

Friedrich's$^{(5)}$ study of extinguishing agents for alkali metal fires has suggested some possibilities. He considered three possible effects from extinguishing agents:

1. Smothering effect
2. Cooling effect
    a. Removal of heat by endothermic reaction
    b. Removal of heat by absorption
3. Chemical effect

The third effect is analogous to the extinguishing mechanism of dry chemical on flammable liquid or gaseous fires. Friedrich reasons that since the alkali metals can be heated to their boiling points in an atmosphere of dry oxygen yet ignite at their melting points in normally moist atmosphere, traces of water must play an important part in the oxidation mechanism. A comparison is made between CO and oxygen which react slowly under anhydrous conditions but rapidly in the presence of traces of water:

$CO+OH \longrightarrow CO_2+H$/(Starting Reaction)/$Na+OH \longrightarrow 1/2Na_2O_2+H$
$H+O_2+M \longrightarrow HO_2+M$/(M=foreign molecule or wall)/$H+O_2+M \longrightarrow HO_2+M$
$CO+HO_2 \longrightarrow CO_2+OH$/(Chain branching)/$Na+HO_2 \longrightarrow 1/2Na_2O_2+OH$

Both OH and HO_2 radicals have been observed spectroscopically. The HO_2 radical is readily broken down by contact with salts by the following reaction

$$HO_2+e \longrightarrow 1/2H_2O+3/4O_2+e$$

The validity of this theory of extinguishment of alkali metal fires is, of course, open to question but is worth consideration.

Results of Friedrich's work on lithium, sodium and potassium fires of the 1, 10 and 100 gram size are presented in Tables 13 to 22. The intensity of the reaction is qualitatively rated, using a scale in which 0 indicates no visible reaction while a rating of 4 indicates a full strength reaction (strong increase in flames; even explosion)

TABLE 13- EXTINGUISHMENT WITH PULVERIZED SUBSTANCES (60 μ MEAN MESH SIZE) AGAINST Li FIRE (1 g)

Extinguishant	Reaction Severity	Burning Li Not Completely Covered With Extinguishant	Perfectly Covered With Extinguishant*
$Li_2C_2O_4$	4	Flames increase-strong smoke develops	It burns further
$Na_2C_2O_4$	4	"	It does not burn further
$K_2C_2O_4$	4	"	"
Li_2CO_3	2	Little increase of flame	"
Na_2CO_3	3	Dazzling sparks, yellow	"
K_2CO_3	4	Dazzling sparks,pale-violet	"
NH_4F	4	Flames increase-strong smoke develops	It burns further
NH_4Cl	4	"	"
NH_4Br	4	"	"
NH_4I	4	"	"
LiF**	0	LiF melts in part	It burns no further
LiCl**	0	LiCl melts in part	"
LiBr**	1	LiBr melts in part	"
NaF	2	Dazzling sparks; yellow smoke develops	"
NaCl	4	"	"
NaBr	4	"	"
NaI	2	NaI melts in part-weak I_2 separation	"
$SrCO_3$	3	Increasing flames under emission of red light; dazzling sparks; smoke	"

TABLE 13- EXTINGUISHMENT WITH PULVERIZED SUBSTANCES - Continued

Extinguishant	Reaction Severity	Burning Li Not Completely Covered With Extinguishant	Perfectly Covered With Extinguishant
$BaCO_3$	3	Increasing flames under emission of yellow, bright light; smoke develops	It burns no further
BaO	3	Increasing flames, BaO melts in part	"
CaO	1	Insignificant increase of flames	It burns further
CaF_2*	0	CaF_2 melts in part	It does not burn further
SiC_2 *	0	----	"
Graphite*	0	----	"
Talcum	2	Trivial increase in flames, smoke generated	It burns no further
Concrete or Pumice Powder	4	Strong increase in flames	"
B_4C	4	Pointed flames build up; smoke generated	It burns further
BN	2	Increasing flames; smoke generated under emission of yellow light	It burns no further
Vermiculite	4	Strong increase in flaming; emission of sparks	It burns further
KF	2	Dazzling sparks; pale-violet	It burns no further
KCl	4	Strong dazzling sparks; pale-violet strong smoke develops	"
KBr	3	"	"
KI	1	KI melts in part, weak iodine (extraction or separation)	"

TABLE 13 - EXTINGUISHMENT WITH PULVERIZED SUBSTANCES - Continued

Extinguishant	Reaction Severity	Burning Li Not Completely Covered With Extinguishant	Perfectly Covered With Extinguishant
Na_2SO_4	4	Violent spattering with burning Li	It burns further
K_2SO_4	4	"	"
MgO	3	Increasing flames under emission of bright yellow light	It burns no further
Al_2O_3	2	"	"
SiO_2	3	Increasing flames under emission of yellow light, smoke generated	"
B_2O_3	3	Increasing flames under emission of yellow light, smoke generated, B_2O_3 melts in part	"
TiO_2	4	Explosive reaction; dazzling sparks	"
$CaCO_3$	2	Weakly increasing flames under emission of bright yellow light; smoke generated	"

* The perfect covering would be about 5 to 10 fold quantity of pulverized substance excess in reference to the alkali metal quantity used, in order to extinguish the fire.

** Indicates most promising materials.

TABLE 14- EXTINGUISHMENT WITH PULVERIZED SUBSTANCES (60 μ MEAN MESH SIZE) AGAINST Na FIRE (1 g)

Extinguishant	Reaction Severity	Burning Na Not Completely Covered With Extinguishant	Perfectly Covered With Extinguishant*
$Li_2C_2O_4$	2	Flame-up; smoke generated	It burns no further
$Na_2C_2O_4$	1	Weak flame-up	"
$K_2C_2O_4$	1	"	"
Li_2CO_3	2	Flame-up; smoke developed	"
Na_2CO_3**	0	--	"
K_2CO_3	2	K_2CO_3 melts a little; weak sparking; partial flame-up; smoke generated	"
NH_4F	4	Strong increased flaming; smoke develops	It burns further
NH_4Cl	4	--	"
NH_4Br	4	--	"
NH_4I	4	--	"
LiF	1	Weak flame-up, LiF melts in part	It burns no further
LiCl	1	Weak flame-up, LiCl melts in part	"
LiBr	2	Weak flame-up; LiBr melts in part	"
NaF	1	Weak flame-up; NaF melts in part	"
NaCl**	0	---	"
NaBr	2	Weak flame-up	"
NaI	1	NaI melts in part, weak I_2 (precipitate or separation)	"
KF	1	Weak flame-up	"

TABLE 14- EXTINGUISHMENT WITH PULVERIZED SUBSTANCES - Continued

Extinguishant	Reaction Severity	Burning Na Not Completely Covered With Extinguishant	Perfectly Covered With Extinguishant
KCl**	0	--	It burns no further
KBr	2	Smoke generated; weak flame-up	It burns no longer
KI	1	KI melts in part, weak I_2 (separation or precipitation)	"
Na_2SO_4	1	Na_2SO_4 melts in part	"
K_2SO_4	4	Severe spattering of Na	It burns further
MgO	2	Weak increase in flaming; smoke develops	It burns no further
Al_2O_3	4	Sparking; flame-up and smoke develops	"
SiO_2	2	Flame-up and smoke generated	"
B_2O_3	4	Explosion; B_2O_3 melts in part	"
TiO_2	4	Explosion; smoke generated	"
$CaCO_3$	2	Weak flame-up; smoke generated	"
$SrCO_3$	2	--	"
$BaCO_3$	3	Flame up; smoke develops	"
BaO	4	Dazzling sparks; pointed flames build up; smoke developes	"
CaO	1	Weak flame-up; CaO melts in part	"
CaF_2**	0	--	"
SiC_2**	0	--	"
Graphite*	0	--	"

TABLE 14 - EXTINGUISHMENT WITH PULVERIZED SUBSTANCES - Continued

Extinguishant	Reaction Severity	Burning Na Not Completely Covered With Extinguishant	Perfectly Covered With Extinguishant
Talcum	3	Dazzling sparks; flames increase	It burns no further
Pumice Powder	4	Dazzling sparks; flames increase; pointed flames build up; smoke develops	"
B_4C	4	Pointed flames build up; smoke generated	It burns further
BN	3	Flames increase; dazzling sparks	It burns no further
Vermiculite	4	Flames increase; dazzling sparks	It burns further

* At complete covering would be approximately 5-10 fold quantity of pulverized substance excess in reference to the quantity of alkali metal used, in order to extinguish the fire.

** Indicates most promising materials.

TABLE 15 - EXTINGUISHMENT WITH PULVERIZED SUBSTANCES
(60 μ MEAN MESH SIZE) AGAINST K FIRE (1 g)

Extinguishant	Reaction Severity	Burning K Not Completely Covered With Extinguishant	Perfectly Covered With Extinguishant*
LiC_2O_4	3	Flames increase; smoke develops	It burns no further
$Na_2C_2O_4$	2	"	"
$K_2C_2O_4$	1	Weak increase in flaming; weak development of smoke	"
Li_2CO_3	2	Flame-up; weak flame increase; smoke generated	"
Na_2CO_3	1	Weak flame-up; Na_2CO_3 melt in part	"
K_2CO_3	1	K_2CO_3 melts in part; weak flame increase	"
NH_4F	4	Strong increase in flames	It burns further
NH_4Cl	4	"	"
NH_4Br	4	"	"
NH_4I	4	"	"
LiF	1	Weak increase in flames; LiF melts in part	It burns no further
LiCl	2	Weak increase in flames; LiCl melts in part	"
LiBr	3	Very strong increase in flames; LiBr melts in part	"
NaF**	0	NaF melts in part	"
NaCl	1	Weak flame-up; NaCl melts in part	"
NaBr	3	Dazzling sparks; NaBr melts in part	"
NaI	1	NaI melts in part; trivial I_2 (separation or precipitation)	"

TABLE 15 - EXTINGUISHMENT WITH PULVERIZED SUBSTANCES - Continued

Extinguishant	Reaction Severity	Burning K Not Completely Covered With Extinguishant	Perfectly Covered With Extinguishant
KF	1	Weak flame-up	It burns no further
KCl**	0	"	"
KBr	2	Flame-up; KBr melts in part	"
KI	0	KI melts in part; trivial I_2 (separation or precipitation)	"
Na_2SO_4**	0	Na_2SO_4 melts in part	"
K_2SO_4**	0	K_2SO_4 melts in part	"
MgO	2	Flame-up and smoke develops	"
Al_2O_3	3	Strong flame increase	"
SiO_2	1	Weak flame-up; weak smoke generated	"
B_2O_3	4	Explosion;dazzling sparks; strong smoke develops; B_2O_3 melts in part	"
TiO_2	4	Pointed flames build up; strong smoke generation	"
$CaCO_3$	1	Weak flame increase and smoke develops	"
$SrCO_3$	2	Flames increase and smoke develops	"
BaO	3	Pointed flames build up; smoke generated; BaO melts in part	"
CaO	2	Weak flame increase	"
CaF_2	1	Negligible flame increase	"
SiC_2**	0	--	"

TABLE 15 - EXTINGUISHMENT WITH PULVERIZED SUBSTANCES - Continued

Extinguishant	Reaction Severity	Burning K Not Completely Covered With Extinguishant	Perfectly Covered With Extinguishant
Graphite	1	Trivial flame increase and smoke develops	It burns no further
Talcum	3	Increased flaming and smoke develops	"
Pumice Powder	3	"	"
B_4C	3	Dazzling sparks	It burns further
BN	3	Flames increase	"
Vermiculite	4	Strong increase flaming; dazzling sparks	"

* The perfect covering would be about 5 to 10 fold quantity of pulverized substance excess in reference to the alkali metal quantity used, in order to extinguish the fire.

** Indicates most promising materials.

TABLE 16- AMOUNTS IN GRAMS OF POWDERY, SOLID SUBSTANCES ($60\ \mu$ AVERAGE GRANULE SIZE) USED AGAINST FIRES OF LITHIUM, SODIUM, AND POTASSIUM (10- and 100-g. SAMPLES)

	Lithium		Sodium		Potassium	
Extinguishant	10 g.	100 g.	10 g.	100 g.	10 g.	100 g.
Graphite	39	430	21	250	19	220
KF	51	710	36	280	32	265
SiC_2	78	---	48	---	39	---

TABLE 17- EXTINGUISHING RESULTS OF LIQUIDS AGAINST Li, Na, and K FIRES (1g)

Fluid Extinguishant	Flash Point (°C)	Extinguishant Used in cc(Flowrate 2 cm^3/sec)			Remarks
		Li	Na	K	
spindle oil	225	N.E.*	8.6	6.4	With Li secondary burning
" + 20% CB**		8.0	5.8	4.3	Smoke generated
paraffin oil	213	N.E.	4.9	2.5	With Li secondary burning
" + 20% CB		5.0	2.9	4.9	Strong smoke developed
silicon oil AK250	315	N.E.	7.3	12.5	With Li secondary burning; weak smoke developed
" + 20% CB		6.3	5.7	10.0	Strong smoke developed
didecylphthalate	216	N.E.	9.2	8.5	With Li secondary burning
" + 20% CB		7.5	6.5	5.3	Strong smoke developed
bis-2 ehtylhexylphthalate	190	N.E.	12.2	10.3	With Li secondary burning
" + 20% CB		10.0	5.9	4.3	Strong smoke developed
diethylphthalate	156	N.E.	N.E.	N.E.	Secondary burning
" + 20% CB		16.5	13.5	10.4	Strong smoke generated
dibutylphthalate	170	N.E.	N.E.	N.E.	Secondary burning
" + 20% CB		12.2	8.0	6.8	Strong smoke generated
dimethylphthalate	132	N.E.N	N.E.	N.E.	Secondary burning
" + 20% CB		9.4	7.5	5.8	Strong smoke developed
butylbenzylphthalate	190	N.E.	N.E.	N.E.	Secondary burning
" + 20% CB		9.8	8.2	6.2	Strong smoke developed
dimethylglycolphthalate	174	N.E.	23.0	18.8	With Li secondary burning
" + 20% CB		6.5	4.5	3.8	Strong smoke developed
butylglycolphthalate	185	N.E.	30.0	28.2	With Li secondary burning
" + 20% CB		7.5	7.2	6.7	Strong smoke generated
dioctylphthalate	204	N.E.	13.3	12.7	With Li secondary burning
" + 20% CB		6.0	5.2	4.9	Strong smoke developed
dinonylphthalate	210	N.E.	13.0	12.5	With Li secondary burning
" + 20% CB		4.6	4.0	3.8	Strong smoke generated
octylstearate	205	11.6	9.4	7.5	Saponification
" + 20% CB		5.6	4.8	4.5	Saponification; smoke developed

TABLE 17 - EXTINGUISHING RESULTS OF LIQUIDS AGAINST Li, Na, and K FIRES (1g) (Continued)

Fluid Extinguishant	Flash Point (°C)	Extinguishant Used in cc (Flowrate 2 cm^3/sec)			Remarks
		Li	Na	K	
dibenzyltoluene	180	16.5	8.3	6.8	---
" + 20% CB		4.2	4.0	2.5	Smoke generated
benzylbutyladipate	185	N.E.	39.0	32.5	Strong smoke developed
" + 20% CB		8.2	6.3	10.1	
benzyloctyladipate	214	13.7	10.7	8.5	---
" + 20% CB		5.8	3.3	4.8	Strong smoke developed
diphenylxylenylphosphate	240	N.E.	7.9	8.2	With Li secondary burning; strong smoke developed.
" + 20% CB		5.0	2.1	6.3	---
trichloroethylphosphate	232	15.6	13.2	12.1	Smoke generated
" + 20% CB		N.E.	N.E.	N.E.	Stronger secondary burning
tricresylphosphate	235	21.5	12.5	8.5	Strong smoke developed
" + 20% CB		4.8	3.1	3.6	Strong smoke and soot developed
dioctylsebacate	213	10.1	9.2	8.5	---
" + 20% CB		3.2	6.1	11.9	Strong smoke generated
dibutylsebacate		N.E.	21.0	18.3	With Li secondary burning
" + 20% CB		7.0	5.5	16.5	Strong smoke developed
diglycol	124	N.E.	N.E.	N.E.	Secondary burning and alcoholate formation
" + 20% CB		"	"	"	More violent burning
triglycol	177	"	"	"	Secondary burning and alcoholate formation
" + 20% CB		"	"	"	More violent secondary burning
ethyltriglycol	122	"	"	"	Secondary burning and alcoholate formation
" + 20% CB		"	"	"	Secondary burning
butyltriglycol	135	"	"	"	Secondary burning and alcoholate formation
" + 20% CB		"	"	"	More violent secondary burning

TABLE 17 - EXTINGUISHING RESULTS OF LIQUIDS AGAINST Li, Na, AND K FIRES (1g) (Continued)

Fluid Extinguishant	Flash Point (°C)	Extinguishant Used in cc(Flowrate 2 cm^3/sec)			Remarks
		Li	Na	K	
castor oil	229	8.6	4.9	4.0	Saponification
" + 20% CB		4.5	3.0	8.3	Strong smoke developed; saponification
sunflower oil	230	12.5	8.0	6.9	Saponification
" + 20% CB		4.0	3.2	3.4	Smoke generated, saponification
linseed oil	205	17.5	9.8	22.2	Saponification
" + 20% CB		3.2	6.6	12.9	Extreme strong smoke generation;saponification
olive oil	225	8.2	8.0	10.2	Saponification
" + 20% CB		4.1	3.4	10.5	Strong smoke developed; saponification
peanut oil	282	6.2	6.9	6.3	Saponification
" + 20% CB		2.1	5.1	10.3	Strong smoke developed; saponification
cod-liver oil	230	12.5	6.7	5.6	Saponification
" + 20% CB		3.1	12.8	11.1	Saponification; strong smoke developed
neat's-foot oil	243	8.5	6.2	5.3	Saponification
" + 20% CB		3.5	2.3	10.4	Saponification; strong smoke developed
bone oil	232	6.5	5.5	3.5	Saponification
" + 20%		3.0	4.1	12.9	Strong smoke generated; saponification

*N. E. - Not Extinguished

**CB - Chlorobromoethane

TABLE 18 - EXTINGUISHING RESULTS OF LIQUIDS AGAINST 10 g FIRES Li, Na AND K

Liquid Extinguishant	Extinguishant Used in cm^3 (Flowrate 6 cm^3/sec)			Remarks
	Li	Na	K	
Dibenzyltoluene	N.E.	N.E.	80	With Li and Na secondary fire
" + 20% CB	30	14	7.5	Smoke generated
Spindle oil	N.E.	N.E.	N.E.	Secondary fire
" + 20% CB	49	17	35	Smoke developed
Octylsterate	N.E.	N.E.	N.E.	Secondary fire; saponification
" + 20% CB	55	23	N.E.	Smoke generated; with K saponification
Sunflower oil	N.E.	45	76	With Li secondary fire, saponification
" + 20% CB	26	8	72	Smoke developed; saponification especially strong with K

TABLE 19 - RESULTS USING FLOWRATE OF 20 cm^3/sec

Dibenzyltoluene	450	125	62	-----
Spindle oil	N.E.	N.E.	N.E.	Saponification
Octylstearate	225	175	520	" ; especially strong with K
Sunflower oil	200	76	42	Saponification

TABLE 20 - RESULTS USING FLOWRATE OF 60 cm^3/sec

Dibenzyltoluene	165	37	25	-----
Spindle oil	N.E.	255	170	With Li secondary fire
Octylstearate	150	75	375	Saponification; especially strong with K
Sunflower oil	65	62	36	Saponification

*N.E. - Not Extinguished

TABLE 21 - EXTINGUISHING RESULTS OF LIQUIDS AGAINST 100 g FIRES OF Li, Na AND K

Liquid Extinguishant	Extinguishant Used in cm^3 (Flowrate 60 cm^3/sec)			Remarks
	Li	Na	K	
Dibenzyltoluene	N.E.*	N.E.	805	With Li and Na secondary burning
Spindle oil	N.E.	N.E.	N.E.	Secondary burning
Sunflower oil	1125	475	665	Saponification;especially strong with K

TABLE 22 - RESULTS USING FLOWRATE OF 120 cm^3/sec

Liquid Extinguishant	Li	Na	K	Remarks
Dibenzyltoluene	N.E.	1085	670	With Li secondary burning
" + 20% CB**	175	153	140	Smoke developed
Spindle oil	N.E.	N.E.	N.E.	Secondary burning
" + 20% CB	155	137	112	Strong smoke generated
Sunflower oil	715	355	565	Saponification; especially strong with K

*N.E. - Not Extinguished **CB - Chorobromoethane

The 1 g fires were used as screening tests and only those solids which exhibited no reaction were used on 10 and 100 g fires. Silicon carbide did not show any reaction but was not suitable as an extinguishant since it penetrated the liquid metal and did not form a cohesive bond. Calcium fluoride which showed no reaction on 1 g fires exhibited slight reaction in the larger fires. Graphite worked well on all fires.

Liquid extinguishants, with high ignition points as the basic criterion of selection, were also evaluated. Extinguishing mechanisms were attributed to cooling, smothering, charring and/or saponification. Secondary fires occurred frequently but the addition of a halogenated hydrocarbon inhibited secondary dires.

Friedrich concluded that dibenzyltoluene and sunflower oil proved best suited as extinguishants for up to 100 g of alkali metal. Calcium fluoride or graphite were the best powders tested. Friedrich concluded that liquids are best suited for quiescent pools of burning metals while powders are best suited for spills which are not contained.

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