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Survey Of Suppression Of Sodium Fires In Liquid Metal Fast Breeder Reactors

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Survey Of Suppression Of Sodium Fires In Liquid Metal Fast Breeder Reactors

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ABSTRACT

A survey was made of protection and suppression technologies relative to liquid sodium fires at selected sites. These technologies will find application in the Liquid Metal Fast Breeder Reactor (LMFBR) program.

Based on this survey, a series of conclusions and recommendations are given. Dry type powder agents will only be of use on relatively small sodium fires. Large fires will be extinguished by inerting the chamber or collecting pans where the sodium leak occurs.

Liquid sodium fire suppression methods must be incorporated into the initial design of an LMFBR. There exists a need for close coordination of liquid sodium fire technology and guidelines for fire fighting personnel.

Suggestions are made for a number of technical development programs. An extensive search for new suppression agents is not recommended although carbon microspheres should be submitted for approval.

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I

INTRODUCTION

Under subcontract to E(49-1)-3737 Factory Mutual Research Corporation (FMRC) was requested to evaluate carbon microspheres as a fire suppression material for alkali metals with respect to potential application in ERDA's Liquid Metal Fast Breeder Reactor program (LMFBR). Shortly after the program started the scope was broadened to include a review of the general problem of alkali metal fires.

Information for the conclusions and recommendations of this report was obtained from personal interviews at selected facilities combined with discussions with Factory Mutual personnel. The facilities visited were 1) Oak Ridge Y-12 Plant; 2) Experimental Breeder Reactor II, Idaho Falls, Idaho; 3) Fast Flux Test Facility. Richland, Washington; 4) Rocketdyne, Santa Susana Facility, Canoga Park, California; 5) Argonne National Laboratory, Argonne, Illinois. Following each trip, reviews were held with the contract monitor at ERDA's Germantown, Md. facility. A complete list of facilities visited and personnel interviewed is included in Appendix A.

This document does not attempt to present a detailed technical review of liquid sodium technology as applied to LMFBR's. The purpose of the report is to present a series of recommendations which can serve as a guide for future installations. Principal attention was given to the secondary liquid sodium heat transfer system. The primary system was not covered, since this is intimately connected with the reactor construction and operation which was beyond the scope of this work. Likewise, the interface between the secondary sodium and water (steam generation) system was not covered because the primary concern in this program was liquid sodium fires in air. It should not be inferred that the primary system and sodium/water (steam) interface are of no concern. They should be the subjects of separate studies. The isolation of the secondary system is somewhat artificial, since the failure of any major component of a LMFBR will have an effect on the overall system operation and safety.

The conclusions and recommendations of this study are highly subjective, due to the fact that there have been very few accidents - too few to establish any statistical trends or experience. Most liquid sodium accidents have occurred in test facilities where equipment has a relatively short expected lifetime. Such equipment is operated on a non-routine basis by highly skilled and motivated technical personnel who regard occasional leaks or spills as more or less "part of the game".

The forthcoming Fast Flux Test Facility, Clinch River Project and subsequent generations of LMFBR's are at least one order of magnitude larger than current operations (EBR II). Consequently, it is difficult to extrapolate liquid sodium fire experience to the future large facilities. An economically viable LMFBR will use liquid sodium inventories and circulation rates at a scale larger than any current chemical process in the United States.

II

SUMMARY AND CONCLUSIONS OF SURVEY

Liquid sodium is the preferred heat transfer medium for use in Liquid Metal Fast Breeder Reactors (LMFBR's). The choice is based on 1) wide liquid range (melting point:208°F, boiling point:1618°F); 2) high thermal and electrical conductivity; 3) relatively low viscosity; and 4) high temperature compatibility with stainless steel in a dry, oxygen-free environment.

The sodium-potassium (NaK) alloy has been considered but, for large-scale use, has yielded to liquid sodium. NaK, being a liquid at ambient temperatures, presents a serious cleanup problem in the advent of a spill. It is equivalent to trying to pick up a pool of mercury. Furthermore, the superoxide of potassium, K_2O_4, reacts explosively with many materials.

In contrast to its desirable heat transfer properties, liquid sodium is very reactive chemically and represents a potential fire hazard.

2.1 COMBUSTION OF LIQUID SODIUM

Sodium reacts directly with oxygen in the atmosphere:

$$Na + O_2 \text{ (air)} \rightarrow Na_2O \text{ and/or } Na_2O_2 \text{ (unbalanced)}$$
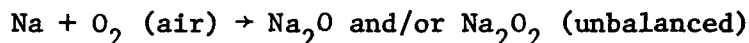
The oxidation proceeds slowly at ambient temperatures where it is evidenced by the tarnishing of an initially bright, silvery solid surface. At elevated temperatures (liquid sodium) the oxidation can be rapid enough to be termed a combustion.

The combustion of liquid sodium is accompanied by a bright yellow-orange incandescence at the liquid surface and the release of a dense, white smoke (sodium oxides). The temperature of the liquid can rise to the boiling point (1618°F) depending on heat losses from the liquid.

The fire is unlike that of a conventional combustible, e.g., liquid fuels, plastics, etc. In the case of sodium, usually there is little or no flame.

3

One merely observes an incandescent surface. Short flames are possible if the liquid temperature approaches the boiling point, but this rarely happens due to the high thermal conductivity of the liquid and existence of convective currents. The radiant heat flux from the burning surface is much less than from a conventional combustible. One can stand quite near a sizable sodium fire. Further, the heat of combustion of sodium (2.16 kcal/gm) is much lower than conventional materials (n-heptane $\approx$ 12.4 kcal/gm).

The conditions for ignition of sodium are subject to some uncertainty; it has been stated that sodium can be ignited at any temperature above the melting point. Other sources contacted in this study have given ignition temperatures as 300°F and 800°F. This disparity of opinion appears to depend upon the following factors:

1) Pool fires require a higher initial temperature for ignition than do small particles resulting from a spray or jet impinging on a surface.

2) It is reported that clean (unoxidized) sodium surfaces ignite more readily than do surfaces covered with oxides. Probably this is true in cases where heat losses are small (jets, sprays, etc.). However, in the case of pools of liquid sodium (where heat losses by conduction and convection are large), usually it is observed that ignition starts as specific points or areas on the surface and gradually spreads across the surface. This is particularly true when ignition is achieved by heating the pool from a low initial temperature (solid) through the melting point to ignition. In this case, it appears that ignition starts on particles of oxide crust floating on the liquid surface. The oxide acts as a wick removing the sodium from strong thermal contact with the massive underlying liquid. Wicking reduces the heat losses from the burning surface to the liquid pool.

Thus, quite different results may be expected between the situations where 1) preheated, clean liquid is injected into the atmosphere and 2) a pool is heated to the ignition point.

3) The ignition of liquid sodium is strongly dependent on the presence of water, either in the atmosphere or on surfaces where the liquid impinges. Water enhances the ignition.

Sodium will burn more violently on a concrete than on a steel surface. The heat from the burning sodium releases free water from the concrete.

Although the conditions for ignition of liquid sodium are variable and somewhat uncertain, it must be assumed that, under the high temperature conditions encountered in breeder reactor heat transfer loops, substantial quantities of liquid which leak to the atmosphere will ignite and will continue to burn until consumed or extinguishment methods are employed. Very small leaks (drips) probably will not ignite but represent the possibility of a serious failure if not detected because of the corrosive effect of sodium on stainless steel when in contact with the atmosphere. It has been claimed that small leaks are self sealing due to oxide formation; however, this will not eliminate the corrosion problem.

Some physical properties of sodium are presented in Appendix B.

2.2 SODIUM SMOKE

A dense white smoke accompanies burning sodium. The smoke consists of particles of sodium oxide. The total smoke mass can amount to one third of the total sodium burned, the remainder being a sodium oxide residue (ash). Frequently, the smoke density is so great as to completely obscure vision of the burning surface.

The smoke from a sodium fire will settle out on all surfaces. The smoke (sodium oxide) will react with water to form sodium hydroxide. Thus, any surface in the vicinity of a sodium fire may be expected to be coated with sodium hydroxide unless careful cleanup follows the fire. Smoke from a sodium fire can cause corrosion of stainless steel components.

Smoke from a sodium fire will form sodium hydroxide on contact with the moisture in the eyes, nose, throat and lungs. The result is extreme irritation and it is virtually impossible for a human to endure exposure to sodium smoke without protective equipment. Also, the smoke will form sodium hydroxide on contact with skin moisture and the result will be the same as contact with concentrated lye.

Protective clothing and breathing apparatus is required when fighting all but the smallest sodium fires.

2.3 OTHER CHEMICAL REACTIONS

Sodium will react with carbon dioxide, halogenated hydrocarbons (Halons) and many organic materials. Sodium is inert to saturated hydrocarbons and commonly is protected from the atmosphere by submersion under oil. Sodium will not react with nitrogen or argon which are commonly used inerting gases.

Sodium (solid or liquid) reacts with water to produce hydrogen:

$$Na + H_2O \rightarrow NaOH + 1/2H_2$$
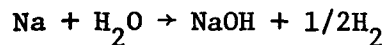
This reaction usually occurs explosively if oxygen is present due to the ignition of the hydrogen. If the concentration of water is small, the reaction proceeds slowly but large amounts of sodium hydroxide remain as a residue.

2.4 EXTINGUISHMENT OF SODIUM FIRES

It is apparent from previous discussion that most conventional extinguishment methods are useless for sodium fires. Water would be dangerous. The problem is compounded by dense smoke which causes reduced visibility, physiological problems for personnel and corrosive effects on equipment.

Currently, the only practical methods for extinguishing a liquid sodium fire are 1) dry powder agents and 2) inerting. These methods will be discussed separately.

2.4.1 Dry Powder Agents

Currently, the approved agents for sodium fires are Met-L-X and NaX. Met-L-X is basically sodium chloride while NaX is sodium carbonate. NaX was developed to eliminate the threat of chloride stress corrosion which would be expected from the use of Met-L-X on stainless steel components.

The Oak Ridge Y-12 plant has introduced a material called carbon microspheres for extinguishing metal fires. The material consists of small

spheroids of carbon and has been demonstrated to be effective on fires of sodium, potassium, lithium, magnesium, uranium and other metals. The carbon microspheres contain less chloride than NaX and appear to work well through conventional pressurized dry powder dispensing systems. The carbon microspheres are dust free, which eliminates a frequent objection to NaX. They show no tendency to cake or pick up water.

The current cost of carbon microspheres is about 6¢/lb as compared with 80-90¢/lb for NaX. Met-L-X costs about 60¢/lb. As yet, no approval has been obtained for the carbon microspheres.

Sand has been used for sodium fires but there is some controversy as to its effectiveness. It has been reported that sand can enhance a sodium fire. ANL reports no trouble with a carefully dried, high-silica sand ("Ottawa Sand"). It should be noted that sand will not flow through pressurized equipment and must be applied by shovel. Because of its tendency to pick up moisture and the uncertainty as to impurities in sand obtained from different sources, sand should be regarded as inferior to NaX or carbon microspheres.

ANL continues to use Met-L-X instead of NaX in cases where chloride corrosion is no problem because of concern of blocking of NaX in pressurized extinguishers.

All dry-type agents appear to work by smothering the burning surface: they reduce the availability of oxygen. Some merit has been claimed for Met-L-X in that the sodium chloride melts (1473°F) and coats the liquid sodium surface. This effect, if operable, would not be achieved with NaX, sand or carbon microspheres. There is no evidence of any chemical interactions which contribute to fire suppression.

Dry agents are applied to sodium fires manually (by shovel), through portable pressurized extinguishers, or by pressurized fixed systems (analogous to conventional water sprinklers). Very few fixed systems have been installed and, to date, none have been challenged by a sodium fire. The effectiveness of fixed systems is unproven.

Dry agents are only of value against pool fires, i.e., pools of burning
sodium on horizontal surfaces. The agents are ineffective against sprays,
jets or burning liquid running down vertical surfaces or cascading down through
pipe networks.

There is general consensus that dry agents can only be used effectively on
pool fires up to about 100 sq ft (10 ft x 10 ft) in area. One facility quoted
the maximum spill at 50 gal and noted that a 35-gal spill was extinguished
with difficulty.

In addition, there is general consensus that approximately 1 in. of agent
is required to effectively smother a sodium fire, whether the agent is Met-L-X
or carbon microspheres. For Met-L-X this corresponds to about 10 lb/sq ft
of burning surface. At present it is not clear how the agent thickness depends
on application rate, pool depth or pool temperature.

The statements relative to areas and agent thickness assume that the sodium
is burning in a metal pan, i.e., that there are no problems with water from con-
crete.

2.4.1.1 Personnel Considerations - Manual application of dry agents entails
serious questions of personnel protection. It may be expected that any sodium
fire in a closed area will generate sufficient smoke to seriously impair visi-
bility. Thus, it is entirely possible that fire fighting personnel will be
unable to determine the location or size of the fire. It is essential that
detection devices be available to perform the following duties:

    1) Detect and locate small leaks before a major fire occurs;

    2) Determine the magnitude and location of the fire;

    3) Indicate oxygen concentrations in the affected area.

It is essential that guidelines and regulations be established to determine,
in advance, whether personnel should even attempt to attack a liquid sodium
fire. We note the following possible hazards:

    1) Limited visibility may cause personnel to attempt to attack a fire
larger than their capability;

2) With limited visibility, personnel could actually walk into a burning pool or be showered by an elevated leak;

3) A sodium fire could cause a serious decrease in oxygen concentration. Ventilation may have been limited by design to minimize the exposure of equipment to sodium smoke in adjacent areas. Ventilation may also have been limited by design as a means of fire suppression, i.e., oxygen starvation.

4) Misjudgment of the size of a sodium fire could cause personnel to enter without proper protective dress and breathing equipment as well as under-capacity agent dispensers. The mere existence of agent dispensers could constitute a trap in that personnel could be encouraged in an emergency to tackle a fire beyond their capacity.

The foregoing comments are not intended to suggest that agents and dispensers should not be available or be used. We do suggest that their use be only under carefully specified conditions (which will vary from location-to-location in any given facility) and only by carefully trained people with proper protective equipment.

2.4.2 Extinguishment by Inerting

The term "inerting" is taken to mean the extinguishment of a sodium fire by oxygen starvation (agents really do the same thing). This may be accomplished by allowing the sodium to burn up the available oxygen or by flooding a chamber with an inert gas such as nitrogen or argon. In either case, a fairly tight enclosure would be required.

Extinguishment of sodium fires by inerting may take either or both of two forms: 1) localized oxygen starvation or 2) chamber oxygen starvation.

2.4.2.1 Local Oxygen Starvation - Because of the adverse reactions of liquid sodium in contact with concrete, it will be necessary that all areas where spills are expected be equipped with steel catch pans or troughs. If the expected spill is large enough, the entire room may be lined with steel. The volume of the steel containment should be about 1 1/2 times the maximum volume of expected spill.

An effective method for extinguishing sodium fires is to construct each catch pan with a metal baffle which contains holes or slots. The baffle is located several inches above the maximum liquid sodium level which is expected to accumulate in the pan. The holes or slots permit the molten sodium to flow into the catch pan but, at the same time, restrict the access of air to the burning metal. If properly designed, the heat losses through the bottom and sides of the pan are greater than the heat generated by combustion.

For the Clinch River Project it has been proposed that a slow stream of nitrogen be fed underneath the baffle and above the liquid sodium surface. The effectiveness of a nitrogen purge will be dependent on the systems used to detect sodium spills. It would be unreasonable to have a continuous nitrogen purge at all times in all baffled catch pans. This would create a dangerous respiratory personnel threat.

Catch pans do have the advantage of confining a spill to a fixed portion of a chamber. Thus, in some cases, dry agents might be used where they would be ineffective if the liquid sodium spreads out over the floor. There is merit in constructing the floor as a series of dyked compartments covered by perforated baffles. This could be done in addition to the use of special catch pans under specific suspected trouble spots.

The use of catch pans does not entirely remove the liquid sodium-concrete problem. Steam will be released underneath any heated catch pan in direct contact with concrete. An insulating layer would reduce the steam evolution, but would also reduce the cooling rate of the liquid sodium in the pan.

At this time it appears that more work is needed on the design and installation of catch pans as well as specification as to where and under what conditions they should be used.

2.4.2.2 <u>Chamber Oxygen Starvation</u> - For large sodium spills, the most effective method of fire suppression is to seal the entire affected chamber. This may be the only way to control large spills. Oxygen depletion in the sealed chamber will suppress the fire, but several conditions will be required:

1)   The liquid sodium must not come in contact with concrete.

2)   Temperatures of concrete surfaces must not be permitted to rise high enough to release substantial quantities of water.

3)   Pressure relief vents must be provided to prevent dangerous overpressure during the initial stages of combustion. Also, an inert gas purge probably will be needed to prevent the back flow of oxygen during cooling stages.

4)   Wherever possible, all piping and equipment which would be damaged by contact with liquid sodium should be located well above the floor.

5)   It would be desirable that each chamber be supplied with access which would not expose adjacent chambers to combustion products.

6)   The facility should be designed so that liquid sodium inventories can be shunted to storage tanks in the event of a major spill. This would reduce the fire load on the chamber where the spill occurred.

7)   Detection apparatus must be adequate to detect the occurrence and location of a spill and activate the various dump, seal and purging operations.

Chamber oxygen starvation contingencies can be used in addition to catch pans for lesser leaks. Even with major leaks, catch pans will facilitate cleanup.

It must be emphasized that chamber isolation is not a method of fire suppression which can be added after a facility has been constructed. Chamber isolation must be part of the initial design, construction and operation of the entire facility. In addition, cleanup procedures must be worked out in advance and should be part of the facility design.

III

RECOMMENDATIONS

1.   A program should be initiated to collect and coordinate all available information relative to sodium fire prevention and suppression. The goal of this program would be the establishment of guidelines for architectural and engineering personnel in the design, construction and operation of Liquid Metal Fast Breeder Reactors from the standpoint of fire safety.

2.   Qualified fire protection personnel should be involved throughout the design and construction stages of each LMFBR.

3.   It would be useful to establish a consulting group for each LMFBR project. This group would consist of personnel with direct hands-on experience in liquid sodium handling and fire technology. The group would assist design and construction units and, where deemed necessary, have authority to institute mandatory design or construction rules.

4.   There should be specific guidelines for operating personnel in handling sodium fires.

5.   It would be helpful to have more frequent meetings between personnel engaged in the development of liquid sodium technology as well as meetings between development and fire suppression personnel.

6.   The following areas of technical development are suggested:

    a)   Further investigation of the effects of large sodium spills on concrete including the effects of heat where the sodium does not directly contact the concrete.

    b)   Development of catch pans and baffle plates. Determination of dry powder requirements with baffled catch pans.

    c)   Study of the usefulness of fixed dry powder systems: 1) which kind of agent, 2) plugging, caking problems, 3) distribution pattern and coverage rates.

    d)   Determination of dry agent requirements as a function of coverage rate, pool depth and pool temperature.

e) Sufficient work should be done with carbon microspheres to obtain approval of this agent from a recognized testing laboratory.

f) Further study of the caustic corrosion of stainless steel with the goal of protecting stainless steel components against 1) liquid sodium leaks and 2) sodium combustion products.

7. Full-scale model tests are recommended including:

a) Determination of failure modes;

b) Effectiveness of catch pans;

c) Effectiveness of inerting;

d) Operation of detection devices; placement of detection devices;

e) Determination of degree of effectiveness of dry powder agents: only for small spills or also final stages of a large spill?

f) Smoke venting: 1) should it be done at all? 2) how to do it? 3) what is to be done with the smoke?;

g) Cleanup and removal of residues.

8. Study of detection methods and their application should be continued. Early detection of leaks represents the best method of extinguishing large fires (before they happen).

9. The expenditure of substantial monies on research for new agents is not recommended.

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APPENDIX A

FACILITIES VISITED AND PERSONNEL INTERVIEWED

A. <u>Oak Ridge Y-12 plant (28, 29 Oct 1975)</u>

Oak Ridge, Tenn.

J.M. Schreyer	Union Carbide
J.R. de Monbrun	"
C.R. Schmitt	"
J.M. Googin	"
J.W. McCormick	"
W.L. Richardson	"
R. Handler	ERDA
K. Leifheit	ERDA

B. <u>National Reactor Test Station (18 Nov 1975)</u>

Experimental Breeder Reactor II

Idaho Falls, Ida.

C.S. Abrams	Argonne
L. Witbeck	"
W. Stephens	"
E. Graham	"
C.R. Moore	ERDA

C. <u>Hanford Engineering Development Laboratory (20 Nov 1975)</u>

Fast Flux Test Facility

Richland, Wash.

R.K. Hilliard	Westinghouse
J.L. Ballif III	"
W.E. Taylor	"

D. <u>Rockwell International (21 Jan 1976)</u>

Rocketdyne Division

Liquid Metal Engineering Center (Santa Susana)

Canoga Park, Calif.

F.F. Couture

H.A. Morewitz

C.T. Nelson

R. Steele

R. Fenton

E. <u>Argonne National Laboratory (22 Jan 1976)</u>

Argonne, Ill.

F.O. Pancner

F.A. Smith

F. <u>Energy Research and Development Administration</u>

Germantown, Md.

6 Nov, 18 Dec 1975; 10 Feb 1976

D.E. Patterson

A. Weintraub

W. Maybee

P.J. Davis

G. <u>The Ansul Company</u>

Marinette, Wisc

J.F. Riley

Phone conversations on 31 Oct 1975, 12 Dec 1975, 15 Dec 1975

APPENDIX B

PHYSICAL PROPERTIES OF SODIUM

Atomic number	11
Atomic weight	22.991
Specific gravity	0.9721
Melting point (°C)	97.7
(°F)	208
Specific heat (cal/gm/°C)	0.292
Heat of fusion (cal/gm)	632
Boiling point (°C)	892
(°F)	1618
Heat of sublimation at 25°C (kcal/gm)	25.95
Heat of formation of monoxide (kcal)	-99.4 (Na_2O)